Natural and engineered clays and clay minerals for the removal of poly- and perfluoroalkyl substances from water: State-of-the-art and future perspectives

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Natural and engineered clays and clay minerals for the removal of poly- and perfluoroalkyl substances from water: State-of-the-art and future perspectives

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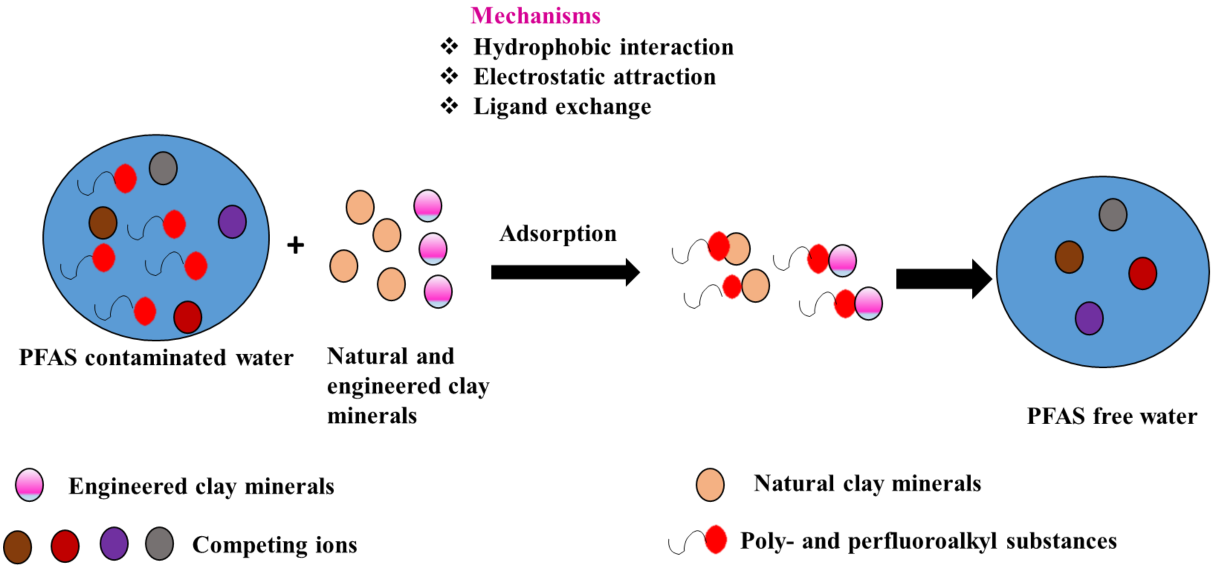
Highlights

- PFAS removal by clay adsorbents was ranked using partition coefficient.
- Surfactant- and amine-modified clays remove remarkable quantity of PFAS.
- Hydrophobic interaction, electrostatic attraction and ligand exchange govern adsorption.
- pH, temperature, competing ions, organic matter and ionic strength influence removal.
- Clay-carbon composite materials hold potential as a future sustainable adsorbent.

Graphical abstract



Abstract

Poly- and perfluoroalkyl substances (PFAS) present globally in drinking-, waste-, and groundwater sources are contaminants of emerging concern due to their long-term environmental persistence and toxicity to organisms, including humans. Here we review PFAS occurrence, behavior, and toxicity in various water sources, and critically discuss their removal via mineral adsorbents, including natural aluminosilicate clay minerals, oxidic clays (Al, Fe, and Si oxides), organoclay minerals, and clay-polymer and clay-carbon (biochar and graphene oxide) composites. Among the many remediation technologies, such as reverse osmosis, adsorption, advanced oxidation and biologically active processes, adsorption is the most suitable for PFAS removal in aquatic systems. Treatment strategies using clay minerals and oxidic clays are inexpensive, eco-friendly, and efficient for bulk PFAS removal due to their high surface areas, porosity, and high loading capacity. A comparison of partition coefficient values calculated from extracted data in published literature indicate that organically-modified clay minerals are the best-performing adsorbent for PFAS removal. In this review, we scrutinize the corresponding plausible mechanisms, factors, and challenges affecting the PFAS removal processes, demonstrating that modified clay minerals (e.g., surfactant, amine), including some commercially available products (e.g., FLUORO-SORB®, RemBind®, matCARE^{TM}), show good efficacy in PFAS remediation in contaminated media under field conditions. Finally, we propose future research to focus on the challenges of using clay-based adsorbents for PFAS removal from contaminated water due to the regeneration and safe-disposal of spent clay adsorbents is still a major issue, whilst enhancing the PFAS removal efficiency should be an ongoing scientific effort.

Keywords: Clays and clay minerals; Poly- and perfluoroalkyl substances; Clay-biochar composites; Clean water and sanitation; Green and sustainable remediation.

1. Introduction

Poly- and perfluoroalkyl substances (PFAS) are aliphatic compounds originating from firefighting foams, aircraft, personal-care products, and water-proofing treatments for textiles and households [1]. The PFAS concentrations in aqueous media range from pg/L to µg/L and are found in lake-, waste-, river-, drinking-, storm-, and groundwater [2]. PFAS have varied carbon chain lengths, and in poly- and perfluoroalkyl acids, fluorine replaces hydrogen atoms linked to the carbon chain [3]. These substances also contain charged carboxylic or sulfonic acid groups in their structures. The perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are defined based on these terminal groups [4].

PFAS are grouped into long-chain (≥6 carbon atoms) and short-chain (≤5 carbon atoms) types [5]. Short-chain PFAS are more soluble, and show greater mobility in the aqueous phase than long-chain ones, thereby making the removal of the former from environmental media extremely challenging [6]. Another class of compounds are zwitterionic PFAS such as perfluoro sulfonamide amino carboxylates, perfluorooctane amido betaine (PFOAB), and 6:2 fluorotelomer sulfonamide betaine (6:2 FTAB), which constitute around 32% of the total emerging PFAS. The zwitterionic PFAS mainly originate from polyfluoroalkyl amides and polyfluoroalkyl sulfonamides [7]. Structurally, perfluoroalkyl chain is attached to the nonfluorinated moiety through an amide and sulfonamide group in zwitterionic PFAS [8, 9]. The dual nature of zwitterionic PFAS (i.e., possessing both positive and negative charges) under ambient conditions make them challenging to remove from the environment. Moreover, their fate and transport within environmental systems, and ecotoxicity towards living organisms are yet to be well understood.

To date, most remediation technologies have focused on removing long-chain PFAS compounds because the regulatory actions targets the long-chain ones over short-chain species as the former mostly drives research directions [10]. Nevertheless, their removal remains crucial irrespective of the chain length because they can accumulate in organisms, including humans, and cause serious adverse health effects. Epidemiological evidence indicates that perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in humans causes thyroid problems, high cholesterol, cancer, and hypertension [11]. Therefore, considering the high toxicity and persistent nature of these chemicals, the United States Environmental Protection Agency (USEPA) has set the critical PFCA and PFSA limit in water at 70 ng/L [12]. PFASs are harmful to the environment, including human health, and of emerging global concern [13]. To date, many treatment technologies to remediate PFAS-contaminated water, including biological degradation (aerobic and anaerobic), reverse osmosis (RO), adsorption [14], advanced oxidation processes (AOP), and photo-reductive destruction under UV irradiation [15] have been tried [6]. Unfortunately, most of these removal technologies suffer from excessive costs, energy consumption, and difficulty for field scale application [16]. Adsorption is proving to be the most cost-effective technique to remove PFAS from contaminated water, considering the selectivity and effectiveness of adsorbents for large-scale field applications [17].

Clay minerals and oxidic clays (Al, Fe, and Si oxides) have received widespread attention in contaminant remediation research because they are eco-friendly, inexpensive, and found in high abundance on all major continents [18, 19]. However, natural clay mineral adsorbents show low efficiency in removing bulk contaminants from aqueous systems. Therefore, mineral adsorbents are surface-modified with organic and inorganic agents containing various functional groups, improving selectivity, effectiveness, and surface functionality [19, 20].

Although a few scattered reports concerning adsorbents for PFAS removal from contaminated water is available [10, 21-24], no review paper till date has focused solely on PFAS removal using functionalized clays and clay minerals. The current review aims to provide insights into the opportunities and challenges of using clay-based materials for PFAS removal in water and wastewater, and propose future directions to ensure that this remediation technology becomes more effective and sustainable. Here we discuss the occurrence, distribution, and toxicity impact of PFAS and the mechanisms concerning their adsorption onto natural and modified clays and clay minerals. We shed lights on critical factors affecting the adsorption, such as pH, temperature, competing ions, and naturally occurring organic matter. Further, we evaluate the applications of various commercial clay products for PFAS removal, such as matCARE^{TM}, FLUORO-SORB®, and RemBind®, instantiate the challenges associated with clay mineral adsorbents, and propose future research directions to overcome them.

2. Occurrence, distribution, and toxicity impact of PFAS

Because of their unique chemical nature, PFAS have numerous applications in various industrial and consumer products, leading to their widespread distribution in air, water, sediment, and soil (Fig. 1) [1, 25-28]. The distribution is wide, ranging from high mountain lakes to polar regions [29, 30]. Once these chemicals reach the ecosystems, they disperse in the soil and water bodies, and are absorbed by plants [31] and animals [32, 33], and therefore, is biomagnified with high levels found in apex predators and humans (Fig. 1) [34-36]. Table 1 lists the global PFAS distribution in water bodies in developed countries, industrialized areas, and polar regions and highlights the severity of the contamination issue.

Long-chain PFAS (especially PFOS, >8 carbons) bio-magnify to a higher degree than short-chain PFAS, whereas short-chain PFAS has greater dispersal in the environment because of their high solubility [36, 51]. Humans are exposed to PFAS (biological half-life of 2.7–5.3 years) predominantly through food intake and drinking water [52, 53]. Contaminated fish and seafood, and crops, such as wheat, corn, soy, and vegetables, and potable water consumption significantly contribute to PFAS exposure in humans [54, 55]. At contaminated sites, drinking water could be the primary source of PFAS to the local population because wastewater treatment systems are inefficient in removing these compounds [36, 56]. The use of contaminated irrigation water for growing agricultural field crops and homegrown vegetables is another potential PFAS exposure pathway [57, 58]. Human exposure to PFAS could cause cardio-metabolic diseases including hypertension and high cholesterol, immuno-suppression, immune-toxicity, neuro-developmental effects, multiple sclerosis [35, 59], reduce fecundity and semen quality in male resulting in infertility, and adverse pregnancy outcomes in female [60, 61]. The above discussion signifies the urgency of developing new PFAS removal and remediation methods to reduce the potential risks and eco-toxicity of PFAS contaminants in the environment.

3. Clays and clay minerals for PFAS removal

Clays are naturally occurring materials composed primarily of fine-grained minerals showing plasticity under appropriate moisture conditions or hardening when dried [62, 63]. Soil clays are defined as "secondary inorganic compounds of clay (<2 μm) size in soil, regardless of their crystalline or nanocrystalline order, or their degree of disorder" [64]. In addition to aluminosilicate layered structure (phyllosilicate) clay minerals, soil clays include Fe, Al, Mn, and other metal oxides, hydroxides, and oxyhydroxides, and non-crystalline or nanocrystalline compounds, such as allophane and imogolite [65] (Fig. 2).

Among the layered structure aluminosilicate clay minerals, the kaolin (e.g., kaolinite, halloysite), smectite (e.g., montmorillonite (MMT)), and fibrous (palygorskite/attapulgite, sepiolite) clay mineral groups are popular adsorbents because of their easy availability, low cost, and high chemical affinity to contaminants [71]. The structures of these clay minerals are different, causing different charge densities. The kaolin group has one Si-tetrahedral sheet $[SiO_4]^{4-}$ and one Al-octahedral sheet $[AlO_3(OH)_3]^{6-}$ and is known as a 1:1 clay mineral. The smectite group has one octahedral sheet between two tetrahedral sheets known as a 2:1

aluminosilicate clay mineral [72]. The kaolin group minerals have relatively low negative charge arising on the edges of the mineral structure, while the smectite group minerals have high negative charge arising due to isomorphous substitution. Both the kaolin and smectite group minerals have pH-dependent charge due to the presence of –OH groups in their structures. The OH groups on the edge of kaolin and interlayer cations of smectite (e.g., Ca^{2+} and Mg^{2+}) are critical in adsorption through various mechanisms, including ligand exchange/substitution and electrostatic attraction. The smectite group of clay minerals is swellable (expanding type) in water, whereas the fibrous clay minerals (e.g., palygorskite, sepiolite) containing ribbons of the 2:1 aluminosilicate structure are non-swelling (non-expanding) [73].

Crystalline oxidic clays include goethite (α-FeOOH), magnetite (Fe_3O_4), and hematite (α-Fe_2O_3), whereas ferrihydrite ($Fe_2O_3.nH_2O$) is the most commonly occurring non-crystalline oxidic clay [67]. The non-crystalline oxidic clays have a higher surface area and, all oxides have variably charged surfaces. These clays include free and combined metal oxides (Al, Fe, Mn, and Si), such as allophane and imogolite, known as short-range order or nanocrystalline clays [65, 74].

3.1 PFAS removal by natural clays and clay minerals

3.1.1 Phyllosilicate clay minerals

The widespread availability, high exchange capacity, and low cost of naturally occurring clay minerals make them popular adsorbents for PFAS removal [72, 75]. However, the negative surface charge of phyllosilicate clay minerals (e.g., kaolinite, MMT) make them ineffective for anionic PFAS removal through electrostatic attraction. The exposed −OH at the edges of Al-octahedral and Si-tetrahedral layer structures of clay minerals is critical in PFAS adsorption on clay minerals such as kaolinite and MMT [75]. For example, PFOS adsorption on kaolinite and MMT from water reached 77.6 ± 3.3 and 54.5 ± 7.2 µg/g, respectively, for an initial PFOS concentration of 1.9 µmol/L and an adsorbent concentration of 5.0 g/L, and neutral pH [72]. Therefore, kaolinite provides a more reactive surface than that provided by MMT, and the point of zero charge (PZC) values of kaolinite and MMT are 3.2 and <2.0, respectively. At pH 5.0–7.0, both clay minerals are net-negatively charged. A mechanism other than electrostatic attraction could contribute to the adsorption of anionic PFOS by clay minerals. A Fourier-transform infrared (FTIR) spectroscopy study indicated that an outer-sphere complex was formed between PFOS and the kaolinite and MMT via ligand exchange [72].

PFOS adsorption onto kaolinite decreased with an increased pH because of its variable charge component. The maximum adsorption of PFOS (4.3 µg) was at pH 2.0 because of electrostatic attraction when organic carbon was not present in the medium [76]. Zhao et al. [77] obtained similar results when comparing hematite, kaolinite, and MMT for PFOS removal (Table 2). PFOS adsorption by these minerals reached equilibrium within 20 min at 600 µg/L initial adsorbate concentration with 0.4 g/L adsorbent loading, and followed the pseudo-second order kinetic model. The proposed mechanisms for PFAS adsorption onto these minerals include surface complexation (MMT, kaolinite), electrostatic attraction (kaolinite, MMT, goethite, and hematite), hydrogen bonding (kaolinite), and hydrophobic interaction between perfluoro alkyl acid chain and hydrophobic moiety of clay minerals [77]. Although, natural clay minerals are primarily hydrophilic in nature, the hydrophobic interaction could increase with increasing carbon chain length of PFAS compounds. However, the above-mentioned mechanisms were observed under different conditions such as pH, competing ions, and ionic strength. The order of PFAS adsorption capacity of the three minerals was hematite > kaolinite > MMT at an equilibrium concentration of 700 µg/L, and PFOS was more readily adsorbed on mineral surfaces than PFOA [77].

Xiao et al. [78] studied the adsorption of PFOS and several PFOAs on kaolinite surfaces (pH = 7.5; temperature = 22.2 °C, contact time = 48 h) and found greater adsorption affinity for PFOS than PFOA. Furthermore, the carboxylate group in PFAS is a relatively soft base, whereas hard bases are more readily adsorbed on oxide surfaces. In addition to adsorption, the photo-transformation of perfluorooctane sulfonamide (FOSA) to PFCA was studied because clay minerals could be effective electron donors under light irradiation. The oxygen atoms in the Si–O–Al bond of MMT had high electron density, thereby being an electron source for transforming contaminants to less toxic forms [79]. The transformation under sunlight irradiation was more pronounced in the presence of Ca-MMT than without Ca-MMT, thereby increasing concentrations of the degradation products, i.e., PFCAs [80]. The photo-transformation reaction was initiated by activating adsorbed oxygen molecules on the surface of MMT, generating superoxide anions and hydroxyl radicals. The hydroxyl radicals broke FOSA molecules adsorbed on the surface of MMT, indicating that the photodegradation of FOSA was a significant source of PFAS, i.e., its removal from contaminated systems was critical. However, the hydrophilicity, low adsorption capacity, and rapid contaminant desorption from pristine clay minerals (because of weak bonding strength) are some disadvantages of natural phyllosilicates in PFAS removal.

3.1.2 Oxidic clays

Metal oxides (oxides of Al, Fe, and Si) can remove PFAS from aqueous media because of their charged surfaces (Fe/Al oxides have positive surface charge and SiO_2 has negative charge) and high surface areas. For example, nano-hematite (α-Fe_2O_3) exhibited good PFOA and PFOS removal capacity at low pH (pH = 3.0) within 30 min [94]. The adsorption of PFOA and PFOS at 250 µM initial adsorbate concentration onto the nano-hematite was described by the pseudo-second order model, suggesting both chemisorption and covalent bonding adsorption mechanisms. Attenuated total reflection (ATR) FTIR spectroscopy data demonstrated that, in addition to electrostatic interactions, PFOA formed inner-sphere Fe-carboxylate complexes via ligand exchange, whereas the PFOS formed outer-sphere complexes and hydrogen bonds at the mineral surface [94]. Goethite formed electrostatic interactions during PFOS uptake at low pH (<5.0), with a positive mineral surface charge because of its high PZC [76]. Nano-silica (SiO_2) showed some PFOS uptake, but its interaction with PFOS was weak through van der Waals forces, and independent of pH and the background matrix [86] (Table 2). The nano-sized Al_2O_3, Fe_2O_3, TiO_2, and SiO_2 adsorbed a significant (pH = 7.0) amount of PFOS, which were much higher than those achieved using bulk oxides (Al_2O_3 and Fe_2O_3) [91]. The PFOS uptake mechanism of the nano-sized oxides depended on the medium’s pH, indicating adsorption via electrostatic attraction between the positively charged mineral surface and the negatively charged anionic PFOS molecules (Table 2). The surfaces of typical soil clays, such as Al_2O_3 and SiO_2, were also compared, but the PFAS was only adsorbed on alumina via electrostatic interaction because of its positively charged surface at low pH (< 5.0) [95].

Boehmite (γ-AlOOH), a hydrated aluminum oxide found in soils, was used for PFAS remediation because of its high surface area (~300 m^2/g). Because of the pH-dependent charge and positive charge, boehmite predominantly adsorbed negatively charged PFAS by electrostatic attraction at pH 7.0. However, boehmite also interacted with PFAS through ligand exchange with OH groups on the mineral surface [87]. Although natural oxidic clays have shown some success in PFAS removal because of their variable charge surface and high specific surface area, the commercial application of these oxidic clays suffers because of poor regeneration capacity and low adsorption affinity to PFAS compounds.

3.2 PFAS removal by modified clays and clay minerals

The adsorption affinity of natural clay minerals (0.08–0.31 mg/g) and oxidic clays (0.05–2.0 mg/g) (Table 2) to hydrophobic and anionic PFAS compounds is weak because the natural (unmodified) minerals are mostly negatively charged and hydrophilic (with exception of a few oxides such as Al (Al_2O_3) and Mn (MnO_2) oxides) in nature, rendering them industrially ineffective for hydrophobic PFAS compound adsorption [1]. The adsorption capacities of pristine clays and clay minerals could be improved by modifying with various agents, such as surfactants, polymers, amines, and micro- and nano-scale carbon particles [20, 96, 97].

3.2.1 Modified oxidic clays

Surface modification of oxidic clays (Fe, Al, and Si oxides) enhances their adsorption capacity due to additional surface functional groups, enhanced hydrophobicity, and increased specific surface area [96]. Organic modifiers, such as surfactants impregnated into mesoporous silica-based materials, also improve binding affinity and selectivity through molecular interactions with functional groups with higher affinity for PFAS compounds. Several organic compounds, including hexadecyl trimethylammonium bromide (HDTMA), 3-aminopropyltriethoxysilane, 1,8-bis(dimethylamino)naphthalene, and 1H,1H,7H-dodecafluoroheptyl methacrylate, were used to modify the silica surface and achieve PFAS uptake from water because of their inexpensive nature [22]. Furthermore, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3)-based nanoparticles were used to remove PFAS from water in SPE because of the high surface area covered by modifiers, strong magnetic properties (easy to remove from solution following use), and high separation ability [22]. These oxide clays have greater efficiency for PFAS removal than that of the silica materials. Therefore, SPE techniques based on modified iron oxides or silica for PFAS uptake are convenient, efficient, and deliver better performance toward the targeted PFAS than conventional solvent-based extraction methods [22]. For example, water-soluble starch-modified nano-Fe_3O_4 adsorbed nearly two times higher PFOA than unmodified nano-Fe_3O_4 (Table 2) [85]. The starch-modified nano-Fe_3O_4 reached equilibrium for PFOA adsorption within 30 min following the pseudo-second order kinetic model at 200 µg/L adsorbate concentration with 8 mg/L adsorbent loading, indicating that the adsorption process was rather a rate-limiting step than a diffusion. Electrostatic attraction and inner-sphere complexation mechanisms contributed to PFOA adsorption on bare and starch-modified nano-Fe_3O_4. The surface functional groups of starch-stabilized Fe_3O_4, including OH and C–O, and the zeta potential of the adsorbent and pH of the aqueous medium are critical for enhancing PFOA adsorption for modified Fe_3O_4 [85].

Similarly, magnetic iron oxides had often been impregnated into powdered-activated carbon to enhance the adsorption capacity of the activated carbon. The oxide-modified carbon adsorbent reached a ~90% perfluorinated compound removal within 120 min at 2.7 µg/L PFOA concentration through hydrophobic interaction and electrostatic attraction between the compounds and the adsorbent surface [98] (Table 2). Similarly, adding iron oxide (12%) to multiwall carbon nanotubes (MWCNT) resulted in increased PFOA adsorption than pristine MWCNT [99]. These adsorbents are highly pH-sensitive and show poor regeneration capacity following contaminant removal [100]. However, an adjustment of the pH value in the eluting system may improve the regeneration capacity of these modified oxidic clays.

3.2.2 Organoclay minerals

Natural phyllosilicate clay minerals often have weak bonding and low contaminant removal and retention capacities, especially for hydrophobic compounds such as PFAS [20]. Therefore, they have been chemically modified, enhancing their functionality (amino groups originating from the organoclay prepared with long alkyl chain surfactant) and improving the hydrophobic contaminant-removal capacity. Organoclays are prepared by incorporating long-chain cationic surfactants on the interlayers of clay minerals to enhance hydrophobicity, surface charge, and functional groups for hydrophobic contaminants, such as PFAS, removal (Fig. 3) [18, 20]. Pristine (unmodified) aluminosilicate clay minerals are hydrophilic and negatively charged, making them ineffective for anionic hydrophobic PFAS removal through electrostatic attraction [101]. However, after modification with a surfactant, the long alkyl chain of surfactant (surfactant loading ≥100% cation exchange capacity (CEC) of the clay mineral) enhances PFAS adsorption through hydrophobic interactions.

Yui et al. [102] attempted to intercalate polyfluorinated surfactants exceeding the exchange capacity of saponite on a saponite interlayer by exploiting the hydrophobicity of polyfluorinated substances. The intercalation depended on the increasing degree of the CEC of saponite and the number of carbon atoms in the polyfluorinated surfactants. However, HDTMA-modified MMT could remove PFOS using various concentrations. The HDTMA-modified MMT (loading of HDTMA: 2.65 mmol/g Na-exchanged MMT) adsorbed PFOS through hydrophobic interactions with a long alkyl chain cationic surfactant [24]. The PFOS adsorption by Na-MMT reached equilibrium faster (24 h) than HDTMA-MMT (32 h) following the pseudo-second order kinetic model. However, the PFOS adsorption capacity of HDTMA-MMT was almost double than Na-MMT at 100 mg/L initial PFOS concentration [24]. Another study showed that the HDTMA- and 2-aminoethanethiol hydrochloride (AET)-modified MMT (loading: 0.58 g HDTMA per g of Na-exchanged MMT, and 0.18 g AET per g Na-exchanged MMT) adsorbed almost two times higher PFOS via hydrophobic interactions than the previous study [81] (Table 2). Kambala and Naidu [23] explored a similar approach to synthesize HDTMA-MMT and amine-functionalized palygorskite. Almost complete removal of PFOS (initial concentration = 6.33 mg/L) and PFOA (initial concentration = 2.16 mg/L) was obtained using the amine-functionalized palygorskite in a fixed-bed column system with varying wastewater volumes. The ability of an octadecylamine-modified Na-exchanged mica to remove PFOA and PFOS was compared with the unmodified Na-exchanged mica [83]. Tests with spiked effluent wastewater indicated that PFOA and PFOS removals were achieved from an initial concentration of 10 µg/mL within 24 h (Table 2). The positively charged octadecylamine-modified mica adsorbed PFAS on the interlayer space of the clay mineral through both hydrophobic and electrostatic interactions [83]. However, organoclay minerals suffer from low regeneration capacity and disposal issues. Therefore, catalytic PFAS compound degradation using organoclay minerals could address those problems and prevent PFAS entry back into the environment.

Literature on catalytic degradation of PFAS by clay minerals is very limited. In a recent attempt to decontaminate PFOA via defluorination, a suspension of organoclay mixture containing MMT modified with HDTMA and poly-4-vinylpyridine-co-styrene (PVPcoS) was reported (Table 2) [93]. The organoclay mixture improved PFOA defluorination rate via reaction with hydroxyl radicals that were generated by the interaction of hydrated electrons with oxygen molecules within the MMT interlayers. Short chain compounds such as $C_6F_{13}COOH$, $C_5F_{11}COOH$, C_4F_9COOH, C_3F_7COOH, C_2F_5COOH and CF_3COOH were detected as the degradation intermediates following PFOA treatment with the organoclay mixture [93]. Similarly, an HDTMA-modified MMT was studied for hydrated-electron-induced photodegradation of PFOA, finding a complete degradation of 10 mg/L PFOA within 5 h at pH 3.0 in the presence of 10 mM 3-indole-acetic acid (IAA) [82, 105]. The hydrated electrons that formed in the reaction between the organoclay and IAA enhanced the degradation of the strong C–F bonds in PFOA. Further, the hydrophobicity of PFOA and IAA aided adsorption onto the organoclay. Among the surfactant-modified clays, HDTMA-MMT significantly accelerated PFOA degradation and defluorination rate (Table 2). Hence, HDTMA-MMT was effective to some extent for achieving PFAS degradation via hydroxyl radical reactions.

3.2.3 Clay-polymer composites

Hydrophilic clay minerals are modified with polymers to increase their removal efficiency of negatively charged hydrophobic contaminants, such as PFAS, through enhanced hydrophobicity. Poly(diallyldimethylammonium)chloride (PDADMAC), protonated PVPcoS polymers, and sodium alginate (alginate is a naturally occurring anionic polymer) were used to modify MMT and kaolinite [78, 90, 106], specifically via charge modification and inclusion of hydrophobic moieties (Table 2). Ray et al. [90] compared PFOA and PFOS adsorption on negatively and positively charged MMT clays that functionalized with these polymers. The positively charged amine-modified MMT had significantly higher PFOS and PFOA uptake than the negatively charged natural MMT (initial concentration: 5×10^3 to 5×10^6 ng/L). Similarly, Na-alginate-modified kaolinite also removed PFOA and PFOS by 0.36 and 1.16 L/kg, respectively [78, 106]. Nanocomposite membranes, composed of poly(*m*-phenylene isophthalamide) (PMIA) and organo-MMT (OMMT), were synthesized to remove PFOS [84]. The PFOS molecule rejection rates (% PFOS removed from feed water) using unmodified PMIA and nanocomposite membranes were more than 90% at neutral pH and operating pressure of 5.5×10^5 Pa (79.75 psi) with 50 µg/L PFOS concentration and 0.5g/L PMIA dosage. The rejection rate and flux proportionately varied with the OMMT concentration, and the maximum PFOS rejection was driven by electrostatic attraction between the negatively charged PFOS and positively charged OMMT (Table 2) [84]. Clay-polymer nanocomposite membranes have a tremendous scope to treat PFAS-contaminated wastewater. Hence, these novel functionalized materials should be explored for future research.

3.2.4 Magnesium aminoclays

Magnesium aminoclays (MgACs) are tailor-made water-dispersible aminopropyl-functionalized magnesium phyllosilicate (trioctahedral Mg $^{2+}$ sheet between tetrahedral Si sheets) materials with the formula $R_8Si_8Mg_6O_{16}(OH)_4$, (where R is $-CH_2CH_2NH_2$) [107]. The NH_2 group of 3-aminopropyltriethoxysilane enhances contaminant removal, making it a promising selective PFAS adsorbent. The MgAC material was used as a stabilizing agent for synthesizing nano-sized zero-valent iron (nZVI) [97]. In an adsorption followed by degradation mechanism, the MgAC-coated nZVI removed PFAS from wastewater with a remarkably better performance than bare nZVI. The surface charge of MgAC-coated nZVI was significantly higher at pH = 3.0, attracting PFAS to the surface [97]. The MgACs showed considerable PFAS removal without producing any harmful byproduct during the adsorption-degradation process. Future research is needed to optimize large scale application of this material for treating PFAS-containing wastewater.

3.2.5 Clay-carbon composites

Carbonaceous adsorbents, such as GAC, graphene oxide (GO), and carbon nanotubes (CNTs), have been extensively used for PFAS uptake from contaminated media [75, 96]. However, these materials have low adsorption capacity and rapid desorption rates [75, 108]. Therefore, carbonaceous materials have been modified with clay minerals and oxide materials to improve PFAS removal capacity [108]. An activated carbon/clay/alumina-based adsorbent, RemBind® (RemB), was evaluated for PFAS uptake and compared with pristine GO. The results showed that RemB removed 1.5-fold higher PFOA than bare GO. Hydrophobic interactions, with ligand exchange, contributed to the PFOA-removal mechanism because the RemB adsorption capacity was independent of the pH and ionic strength, and aluminum in RemB probably contributed to ligand exchange (Table 2) [108].

Recently, a composite of soil (comprising Fe_3O_4, ferrihydrites, and desilicated minerals) and sawdust-biochar was synthesized at a high pyrolysis temperature (600 °C) as an adsorbent for PFOS [109]. The composite removed more PFOS than the pristine sawdust biochar with the adsorption equilibrium reaching in 9 h following the pseudo-second order kinetic model. The maximum PFOS adsorption capacity was 188.67 mg/g with an adsorbent dose of 0.67 g/L. The authors speculated that hydrophobic and electrostatic interactions were involved for PFOS removal by the soil-biochar composite [109]. Although, biochar alone might have capability to remove PFAS from contaminated systems through hydrophobic interactions, the removal rate would be far below the mineral-biochar (carbonaceous materials) composite [110]. Thus, clay-modified carbonaceous materials are promising adsorbents, specifically because of the additional functional groups ($-NH_2$ groups from organoclays) and porous structure arising from the mineral components [111, 112], providing enhanced PFAS uptake capacity. However, research has predominantly focused on unmodified carbon materials [113, 114], including GAC [115, 116], with pore-clogging and regeneration issues. Moreover, separating these powdered carbonaceous materials from contaminated water is challenging; thus, further studies must focus on developing novel clay/biochar or clay/carbon materials for improving functionality and stability of pristine carbonaceous materials to remove PFAS from aqueous systems. Magnetic biochar prepared from mineral-biochar composites could be a way forward to address the issue of adsorbent separation from solution while simultaneously improving the PFAS removal efficiency [117, 118].

3.3 Partition coefficient: An approach to compare PFAS adsorption capacity of clay-based adsorbents

The performance of an adsorbent is measured by the equilibrium adsorption capacity. If the adsorbent is exposed to high adsorbate concentrations, the adsorbent exhibits higher adsorption capacity than under low adsorbate concentrations when sufficient active sorption sites are available. For a given study, where all tests were conducted at the same initial adsorbate concentration, the adsorption capacity is useful for comparing adsorbents under such limited conditions. However, it is inappropriate to make comparisons where studies are conducted under different initial adsorbate concentrations. Hence, adsorption capacity (usually in mg/g or mol/g) is not an objective metric to meaningfully assess the adsorbent performance. Furthermore, experimental conditions, such as the initial adsorbate concentration, the dosage of adsorbents used, and the contact time between the adsorbate and adsorbent significantly among published studies. Hence, the ideal evaluation of adsorbent performance should be made using a reliable concept for performance metrics, such as the partition coefficient (PC) (Eq. 1). The PC is derived from the ratio of the equilibrium adsorption capacity to the equilibrium adsorbate concentration in the media [119].

$PC = q_e/C_e$, (Eq. 1)

where, q_e is the equilibrium adsorption capacity, and C_e is the equilibrium adsorbate concentration. Comparison between PC values requires that sorption of the sorbate to the sorbent is linear over the concentration range of interest.

Using PC is reliable in assessing the adsorbent’s performance because it considers a normalization step for the key bias or arbitration controllable by setting the intentionally high initial loading conditions to achieve high adsorption capacity [119, 120]. Hence, Eq. 1 can also be written in the form of Eq. 2 to emphasize the effect of the initial adsorbate concentration [119, 120]. As such, the PC can be used as a reliable metric to judge the adsorbent’s performance relative to the adsorption capacity that is more sensitively affected by simple changes in the initial loading condition.

$$\mathrm{PC} = \frac{\mathrm{qe}}{Ci \times (1 - \mathrm{Removal\ rate})}, \qquad \text{(Eq. 2)}$$

where C_i is the initial adsorbate concentration and removal rate is expressed as in Eq. 3,

$$\text{Removal rate (\%)} = \frac{(Ci - Ce)}{Ci} \times 100 \quad . \qquad \text{(Eq. 3)}$$

Thus, the PC was calculated in Table 2 to compare the performances of various clay mineral-based adsorbents for PFAS removal in contaminated water. The three equilibrium concentrations (low, medium, and high) and their corresponding adsorption capacity values were selected from each study depending on the range of initial PFAS concentrations (data were extracted from adsorption isotherm figures available in the literature). Then, PC was calculated using Eq. 1 for each concentration (low, medium, and high), and Table 2 lists the mean PC values of each clay adsorbent. The surfactant (HDTMA)-modified montmorillonite and amine-modified palygorskite performed better than unmodified montmorillonite, kaolinite, Iranian bentonite, and magnesium aminoclay-coated nZVI (Table 2). Among oxidic clays, nano-magnetite (Fe_3O_4) was more suitable than other Fe and Al-based oxidic clays (Table 2).

4. Mechanisms of PFAS removal by clay-based adsorbents

The principal mechanisms in PFAS uptake by clay-based adsorbents are: (i) hydrophobic interaction between the PFAS perfluorocarbon chain and hydrophobic moiety on the adsorbent surface, (ii) electrostatic interactions between PFAS and positively charged surface of adsorbents, and (iii) ligand exchange between $–OH^{-}$ mineral groups (oxides and clay minerals) and PFAS compounds (Fig. 4). The PFAS adsorption mechanisms and adsorption capacity are governed by the physical and chemical characteristics of the natural and modified clay-based adsorbents (Table 3). The PFAS may offer both lipophobic and hydrophobic properties due to low polarizability of the fluorine atoms [121]. The increase in C chain length containing C-F bonds increases the lipophilic nature of PFAS (Gagliano et al., 2020). It could be speculated that some degree of lipophilic interaction may also occur between organoclay minerals and long-chained PFAS (perfluorotridecanoic acid (C_{12}), perfluoroteteradecanoic acid (C_{13}), PFOA (C_7), PFHxS (C_6)) during adsorption [122]. The negatively charged PFAS compounds can be adsorbed on negatively charged mineral surfaces if the interacting PFAS compounds are hydrophobic. Like lipophilicity, the hydrophobicity of PFAS increases with their increasing C chain lengths. Long alkyl-chained surfactant-modified organoclay having functional fluorophilic amide groups provide the basis of hydrophobicity of organoclay minerals (Table 3). The short-chain ($<C_6$) PFAS can be adsorbed irrespective of hydrophobicity of the adsorbents, whereas the long-chained PFAS ($>C_6$) can get adsorbed on hydrophobic organoclay surfaces through hydrophobic interaction [123]. Long chain PFAS was found outcompeting with short chain PFAS during adsorption onto organically modified kaolinite through hydrophobic interaction (Xiao et al., 2011). However, desorption rate of short-chain PFAS from RemBind® was found much higher due to the presence of carboxylic functional head groups leading to weaker adsorption in the short-chain than long-chain PFAS having sulfonic functional groups [124]. Hence, leaching and desorption of short-chain PFAS from the adsorbents may re-pollute the groundwater more frequently than long-chain PFAS, which need to be considered whilst developing an effective PFAS remediation strategy. Some polar functionalities (dipole), such as $–NH_2$ and –OH, could develop weak ion-dipole interactions with PFAS compounds, also considered as electrostatic attraction (Table 3; Fig. 4). In ligand exchange, inner-sphere covalent bonding between metal cations and ligands exchanged with carboxylic groups may occur (Fig. 4) [22].

Electrostatic attraction between the cationic clay-intercalated species and carboxylate or sulfonate groups of PFAS could drive PFAS adsorption on modified clay adsorbents (Table 2). Tang et al. [86] explained the mechanisms contributing to PFAS adsorption onto mineral surfaces as driven by solution parameters, such as pH, and ionic strength of the background electrolyte. Lowering the medium's pH below the PZC of the oxidic clays and clay minerals increases the positive surface charge attracting the anionic PFOS via electrostatic attraction. Adjacent PFOS molecules on the surface repel each other because of their similar charge characteristics. Thus, a solution having high ionic strength would enhance PFOS adsorption because of the suppressed electrostatic repulsive force. However, the aqueous system's pH does not affect the PFOS–PFOS electrostatic repulsion. Furthermore, hydrophobic interactions are independent of solution chemistry and pH. The hydrophobic interaction refers to the affinity between two non-polar hydrophobes that repel water due to lowering of energy of the system and formation of maximum H-bonds in an aqueous system [22]. Hydrophobic interactions also occur between the long hydrophobic chains of the PFAS molecules and hydrophobic chains or moieties on the clay minerals. For example, hydrophobic interaction occurs between the hydrophobic PFAS and long-chain (hydrophobic) surfactant-modified organoclays [77]. Gao and Chorover [94] explained the PFCA sorption mechanism on iron oxides and proposed that the $–COO^{-}$ group of PFCA formed inner-sphere complexes with Fe-carboxylate via ligand exchange.

5. Factors affecting PFAS removal using clay-based adsorbents

PFAS removal from aqueous media depends significantly on the solution pH, presence of natural organic matter (NOM), competing ions, ionic strength, and temperature. Furthermore, the carbon chain length of the PFAS significantly influences removal because it affects mobility and solubility, making short-chain PFAS more challenging to remove than long-chain PFAS [10]. For organoclays, the longer the hydrophobic chain length of the clay-modifying surfactant is, the higher the hydrophobicity of the obtained adsorbent, making the long-chain hydrophobic. Similarly, a gradual increase in surfactant loading in the organoclay increases the hydrophobicity of the clay product (Fig. 3), increasing PFAS adsorption [127]. Fig. 5 shows how the variation in the factors (pH, ionic strength, temperature, competing ions, and NOM) significantly affects the PFAS adsorption process on clay-based adsorbents in water.

5.1 pH

The solution pH is the most critical in the removal of polar contaminants from a system. Solution pH affects contaminant removal by altering the speciation of contaminants and the surface charge of adsorbents. Specifically, pH alters the surface charge on variably-charged minerals such as phyllosilicates and oxide clays [128]. For instance, in PFOS removal, using natural kaolinite and MMT is ineffective because the minerals were negatively charged at pH 5.0–7.0 because the PZC of kaolinite and MMT are 3.2 and 2.0, respectively [72]. Because of the anionic nature of PFOS ($pK_a = -3.27$) over a wide pH range, the electrostatic repulsion between PFOS and MMT is greater than that with kaolinite, reducing the PFOS uptake capacity of the clay minerals. Therefore, electrostatic attraction (Eq. 4) is not the primary mechanism unless cation bridging is involved in PFOS removal using natural kaolinite and MMT. Similarly, in organo-modified MMT (50% CEC of HDTMA-MMT), the removal rate of the PFAS is reduced at pH 6.0–6.6 because of the zeta potential decrease in the mineral surface because of modification and electrostatic repulsion between the sorbate and adsorbent (Eqs. 5 and 6) [24, 81]. Martín et al.[83] demonstrated that octadecylamine-modified (2 CEC of Na-Mica-4) Na-mica show a drastic reduction in PFOS removal at pH 12, whereas no significant reduction in PFOS removal was observed below this pH. Hence, the solution medium’s pH significantly affects PFAS removal when using clay minerals. However, in-depth research into the charge variability of clay adsorbents concerning pH for PFAS removal and formation of new molecules after the degradation process should be conducted to understand the underlying mechanisms, adsorption, and degradation mechanisms in detail.

At low pH: $M–OH + H^+ = M–OH_2^+$-------$PFAS^−$ (electrostatic attraction)(Eq. 4)

At high pH: $M^+–OH + OH^− = M–O^− + H_2O$ (Eq. 5)

$M–O^− + PFAS^− = M–O^{−}\cdots PFAS^−$ (electrostatic repulsion), (Eq. 6)

where, M is the octahedral metal cations ($Fe^{2+/3+}$, Al^{3+}, Mg^{2+}) in clay minerals.

5.2 Organic matter

Organic matter (OM) is an inseparable part of aqueous media defined as dissolved organic matter (DOM), and organic matter originating from wastewater treatment plants significantly affects PFAS removal [22]. The presence of OM reduces short-chain PFAS removal using clay mineral adsorbents from aqueous media [6, 129] because of a competitive hydrophobic interaction occurring between PFAS and DOM [130]. The OM can also be anionic with the presence of hydrophobic moieties (e.g., aromatic groups) that can show repulsive electrostatic interactions with PFAS. NOM adsorbs PFAS through hydrophobic interactions between the perfluoroalkyl end and NOM bound to the adsorbent surface [130, 131]. However, the interaction mechanisms between OM and PFAS in aqueous media are not well understood [6]. Fulvic and humic acids (FA and HA) have been used as DOM models to evaluate the impact of DOM on PFAS removal [72, 115]. Long-chain PFAS are preferentially adsorbed onto highly condensed domain of humin fraction of OM through hydrophobic interaction, whereas short-chain PFAS are preferentially adsorbed on the fulvic and humic acid fractions of humus through aggregate formation [6, 130]. As per conventional belief, NOM comprises HA, FA, hydrophilic acids, proteins, carboxylic, and amino acids [132]. However, the roles of OM species on PFAS removal have not been discussed in detail and only simulations of the natural environment using FA or HA coatings have been used, calling for in situ experiments. For instance, HA was coated on kaolinite and MMT (60 and 32 C/g, respectively) to simulate natural clay-OM complexes. The results revealed that HA coating decreased PFOS uptake by

19.8% on kaolinite and 25.3% on MMT. The authors explained that the adsorption decreased because of the sorption sites' saturation, HA lowering of the zeta potential, and the electrostatic repulsion between negatively charged HA and PFOS [72]. However, OM also competes with PFAS for the adsorption sites, inhibiting contaminant removal. This phenomenon is more pronounced for short-chain PFAS because of competition for active sites [133]. In contrast, hydrophobic OM showed strong adsorption of PFAS because of the formation of DOM-PFAS complexes when GAC was used as an adsorbent, but hydrophilic DOM did not affect PFAS adsorption when GAC and anion-exchange resin were used as adsorbents [134]. However, further experiments on varying fractions of OM (based on molecular weight) are needed to determine whether such OM-PFAS complexes are formed under field conditions.

5.3 Nature of competing ions and ionic strength

Competing inorganic and organic ions within the aqueous matrix affect contaminant removal using adsorbents because they can impact potential adsorption sites. The electrolyte composition, ionic strength, and charge characteristics of competing ions determine competition of target contaminants. For example, cations stimulate adsorbing anionic PFAS molecules on the adsorbent, but anions have the opposite effect, drastically reducing PFAS removal. A high background cationic (e.g., Ca^{2+}, Na^{+}) concentration reduced the diffuse double layer thickness and electrostatic repulsion between PFAS and kaolinite, favoring the adsorption of short-chain PFAS (PFHxA and PFBA) [78]. On the contrary, elevated level of NaCl (50 mM) reduced the short-chain PFAS adsorption on polymer-modified organo-silica adsorbent. The ionic strength of solution thus plays an important role for short-chain PFAS adsorption, and the chemistry of the adsorbent surface can affect the degree of adsorption [123]. Furthermore, di- and multivalent cations (e.g., Ca^{2+}, Mg^{2+}, $Fe^{2/3+}$) improve PFAS removal by cation-bridging effect, resulting in a more effective decrease of the electrical double layer thickness than in the case of monovalent cations (e.g., Na^+, K^+) [22, 77]. The di- and multivalent cations neutralize the surface negative charge of the clay minerals and form bridges between negatively charged groups (e.g., carboxylic, phenolic and hydroxyl groups) and PFAS anions [101]. However, the enthalpy of perfluorobutane sulfonic acid (PFBS) adsorption on smectite clay was comparatively less unfavorable in presence of Ca^{2+} (as background electrolyte) due to a monodentate stable lateral cation-bridging interaction between sulfonate head groups of PFBS and Ca^{2+} [135]. In contrast to cations, anions negatively affect PFAS adsorption because of competition for the adsorption sites [136]. Wang et al.[87] revealed that PFOS and PFOA adsorption on boehmite (γ-AlOOH) was reduced many folds in the presence of competing Cl^- anions (0.1–100 mM). Conversely, for other oxide clays, such as goethite, the uptake of negatively charged PFOS on the positively charged goethite surface significantly increased because of the enhanced electrostatic attraction in the high H^+ and Ca^{2+} concentrations [86]. An increase in ionic strength could reduce the electrostatic attraction between positively charged oxide clays (e.g., Al_2O_3, Fe_2O_3) and negatively charged PFAS by reducing the zeta potential and thickness of diffuse double layer [101]. For a poly(*m*-phenylene isophthalamide)/OMMT nanocomposite membrane, PFOS rejection (% removal of PFAS from feed water) from the nanomembrane increased with the increase in Pb^{2+} concentration at all transmembrane pressures because the complexation between Pb^{2+} and PFOS molecules is similar to that between Ca^{2+} ions and sulfonate functional groups in PFOS [84, 137]. However, Pb^{2+} in the feed water might have harmful effects on aquatic organisms and humans when used after purification. Further experiments therefore should be conducted to understand the simultaneous impacts of OM and competing inorganic anions at similar ionic strengths.

5.4 Temperature

Temperature is critical in influencing PFAS adsorption on clay adsorbents [138]. For example, the temperature effect on PFAS removal by MgAC-coated nZVI was studied at 20 °C and 55 °C. PFAS removal decreased with the increasing temperature of the reaction solution, indicating suitability for wastewater decontamination at 25 °C. This finding contrasted with a previous study [139], describing that 2,4,6-trinitrotoluene reduction using uncoated nZVI increased with increasing temperature. The contrasting result on the effect of temperature could be evidence of 2,4,6-trinitrotoluene adsorption as the first step before their reduction [139]. Because PFAS removal by MgAC-coated nZVI occurs via several mechanisms (predominantly adsorption and reduction), an in-depth study on thermodynamics should provide plausible evidence of the process [97]. Because of the scarcity of thermodynamic studies on PFAS removal by natural or organically modified clay minerals, comprehensive future studies are required.

6. Opportunities and challenges for clay mineral designs for PFAS removal

Currently, GAC is the most common adsorbent used for contaminant removal, including PFAS, from aqueous media. Main advantages of novel clay-based PFAS adsorbents in water are: (i) widespread natural abundance of clay materials, (ii) smaller physical space (minimum interval of the occupational distance between two clay particles) required for organoclay minerals in a wastewater treatment plant, (iii) higher removal capacity (99.65%) than GAC (approximately 90%) [140], (iv) easy separation of clay particles following contaminant adsorption, (v) low synthesis and operational costs (~$26/kg of organoclay compared to ~$88/kg for Amberlite resins, and ~$15/kg for GAC), and (vi) negligible harmful effects on the ecosystem [21, 129]. As an environment-friendly approach, clay-biochar composites composed of clay minerals, such as Na-montmorillonite/Na-bentonite and solid biowaste biochar, such as municipal solid waste, have been shown successful for ciprofloxacin and tetracycline (antibiotics) removal under alkaline conditions [111, 112, 141]. In these composites, the biochar serves as a porous structure supporting and hosting the distribution of clay minerals within its matrix. This characteristic can be exploited for developing innovative engineered biochar with clay minerals distributed within the biochar matrix to take advantage of clay minerals' good sorption ability [142]. The clay-biochar composites could be an effective adsorbent of zwitterionic PFAS which are otherwise difficult to remove from water. Biochar synthesized from mixed hard wood through slow pyrolysis was used to adsorb zwitterionic PFAS, namely PFOAB and 6:2 FTAB, at pH 8.1 in an aqueous solution (at initial 0.5, 2, 10, and 100 µg/L adsorbate concentrations) [143]. The biochar showed 9.52 and 31.2 µg/g adsorption capacity of PFOAB and 6:2 FTAB, with the distribution coefficients varying from 3.24 to 4.09 L/kg and 3.39 to 4.66 L/kg, respectively. The mechanisms of PFOAB and 6:2 FTAB adsorption were different due to their dual chemical nature. At pH = 8.1, 33.3% of PFOAB exists as neutral molecules and 66.7% as anions, and 99.9% of 6:2 FTAB exists as neutral molecules. The 6:2 FTAB was attracted on the biochar due to the compound's high molecular weight, neutral nature and strong hydrophobicity, whereas the amide group in PFOAB acted as a hydrogen bond acceptor due to the C=O dipole end supporting adsorption through hydrogen donation from the biochar [143]. However, the adsorption capacity of the biochar for those zwitterionic PFAS was quite poor showing substantial desorption potential (desorption distribution coefficient 4.62 and 3.90 L/kg for 6:2 FTAB and PFOAB). Mineral-biochar composites having various types of hydrophilic and hydrophobic reaction sites and uniquely porous structure could improve the removal of zwitterionic PFAS from contaminated water, which is worthwhile to investigate in the future.

Recently, magnetic biochars produced by incorporation of Fe-oxides were successful in stabilizing, and subsequently removing, arsenic, cadmium and lead in soil [117]. The mineral-biochar magnetic composites would provide easy separation of adsorbent from solution after

PFAS removal. New low-cost composite materials (from oxide clays and clay minerals) with enhanced value and functionalities can be used to remove anionic PFAS compounds from aqueous systems in the future. Furthermore, green polymers, such as cellulose microcrystals [144] derived from plant leaves (e.g., alginate) or chitosan, could be supporting agents to the clay-biochar composite for PFAS compound adsorption through hydrophobic interaction. Recently, calcinated hydrotalcite (a synthetic clay derived from talc) was used to remove PFOS from contaminated water. The commercial hydrotalcite was calcined at 450 °C for 3 h and used for PFOS removal. The calcinated hydrotalcite reached adsorption equilibrium within 30 min and adsorbed ~1400 mg/g PFOS (initial concentration 50–500 mg/L), 16 times higher than the raw hydrotalcite [145]. The modified hydrotalcite was superior to GAC and powdered-activated carbon, which adsorbed ~200 and ~560 mg PFOS/g, respectively [146]. The electrostatic attraction at low adsorbate loading (300 mg/g) was the principal mechanism in PFOS adsorption on calcined hydrotalcite, whereas hydrophobic interaction was the dominant mechanism at high PFOS loading (>600 mg/g) [145]. This study indicates that calcined hydrotalcite could be useful for PFAS removal, but the cost and energy incurred on the thermal modification process should be considered for future adsorbent design.

A few commercial clay adsorbents have been manufactured for effective PFAS removal from groundwater and sediments. For example, FLUORO-SORB®, a National Sanitation Foundation International (NSF International, University of Michigan, USA) certified product (predominantly granular formulation), can be used to remediate PFAS-contaminated sediment and groundwater. It can be used as a pre- or post-treatment medium for water treatment and used with activated carbon to improve its efficiency and reduce the remediation cost. Similarly, matCARE™ is a modified fibrous clay specifically designed to immobilize PFAS adsorbed from contaminated media. matCARE™ can effectively immobilize 99.97% PFOS in contaminated concrete. RemBind® is another mineral-based adsorbent consisting of kaolinite, activated carbon, and aluminum hydroxide having mixed charges and high surface area for PFAS adsorption via electrostatic attraction, hydrophobic interactions, and weak van der Waals force. RemBind® was developed in Australia by the Commonwealth Scientific and Industrial Research Organization (CSIRO) and is manufactured by RemBind Pty Ltd., a subsidiary of Ziltek Pty Ltd., as an in situ amendment for PFAS-contaminated soil. This adsorbent reduced the PFAS concentration in leachate by 90%–99%. In the last decade, AquaGate® (powder coating + aggregated core) has been combined with RemBind®, enhancing the adsorptive capacity of RemBind® for PFAS removal from contaminated water. The AquaGate® + RemBind® passive-barrier treatment system offers a new tool for in situ remediation of groundwater and sediment. These materials are commercially produced and, therefore, limited scientific information is available openly regarding their mode of action and mechanisms. Few challenges associated with clay-based adsorbents for PFAS removal are: (i) low adsorption capacity due to oleophobic and hydrophobic nature of PFAS and hydrophilic nature of natural clay minerals, (ii) poor selectivity and particle-size sensitivity [147], (iii) high desorption rate (which could otherwise facilitate regeneration of spent adsorbents) [148], (iv) high cost involvement during synthesis of some organoclays using specific type of surfactants, and (v) possible ecotoxic effects of some surfactant-modified organoclays [149, 150]. However, opportunities for sustainable PFAS remediation from water using clay adsorbents remain, as expounded in this paper.

7. Regeneration of clay-based adsorbents

The safe disposal of spent clay adsorbents can be an issue if not well managed. A low volume of concentrated PFOS waste could be incinerated for safe contaminant disposal [22], but it is energy-intensive and could emit CO_2 into the atmosphere, increasing the chances of global warming. The PFAS desorption rate of natural clay minerals is high because of the weak bonding or non-specific adsorption between clay and PFAS. Here, treatment with specific solvents, such as acid or alkali solutions, could regenerate the adsorbent. Clay-adsorbent regeneration techniques for other contaminants (dyes, pharmaceuticals, and heavy metals) include chemical treatment (desorption of contaminants using specific solvents), supercritical extraction (separation of extractant from the matrix), thermal degradation (>1000 °C), photocatalytic activity, and biological degradation [151].

Pyrolysis is being considered as a way to decompose PFAS in spent adsorbents. Pyrolysis temperature as low as 600 °C can be more effective and ecofriendly than thermal treatment of PFAS-loaded adsorbents at 1000 °C. This approach holds potential to regenerate clay materials where the mineral matrix containing PFAS (i.e., spent adsorbent) would be converted to chars which could be used for further adsorption of PFAS [152]. This indicates the opportunity to treat PFAS-adsorbed clay adsorbents for subsequent treatment of polluted water. However, limited literature is available on PFAS removal during pyrolysis. Kim et al. [153] conducted laboratory pyrolysis experiments with wastewater solids at 300 and 700°C and found no significant change of residual PFAS concentration in the biochar, although PFAS is reported to be volatilized at temperature <700°C. Contrarily, a pyrolysis operating at 850°C demonstrated PFAS removal to an undetected level, indicating transformation or volatilization of the compounds [154]. Kundu et al.[152] demonstrated PFAS destruction in biosolid through a pyrolysis reaction and subsequently used the biosolid biochar for removing short- and long-chain PFAS from contaminated water. The PFAS-contaminated biosolid was pyrolyzed at 600 °C under pre-heated air and N_2/CO_2 conditions. The pyrolysis-combustion integrated process was able to remove >90% PFOA and PFOS from the biosolid, and the resultant biochar with high stability (i.e., low H/C and O/C ratio) adsorbed >80% long-chain and 19-27% short-chain PFAS form contaminated water samples having PFAS concentrations in the range of 0.05 – 480 µg/L. The partially decomposed PFAS products volatilizing from the reactor as pyrolysis gas could also be used for combustion application for energy recovery resulting in further destruction of PFAS [155].

A number of techniques could be useful for PFAS destruction/removal in spent clay adsorbents. Organoclay/metal-based nanoparticles could be used as photocatalysts for PFAS degradation under visible or ultraviolet light irradiation since these methods have shown promise for degrading persistent chlorinated compounds [156]. In the above example, the organoclay mineral attracts the PFAS and accumulates on the particle surface. The photocatalyst catalyzes the degradation of the compounds in the subsequent oxidation process. This technique could be used to avoid incinerating spent adsorbents at high temperatures. Biological degradation of PFAS using microorganisms could be difficult and time consuming because of the long-chained C–F bonds in PFAS compounds. Future research should focus to eliminate the disadvantages of clay-based adsorbents such as safe disposal of spent adsorbents, and reuse the PFAS compounds following recovery where possible. Nevertheless, reusing spent clay adsorbents for PFAS removal seem challenging because of the need for a closed and improved infrastructure facility to regenerate the adsorbents for avoiding possible PFAS diffusion and dispersion, which could add extra operational cost for PFAS remediation. Novel clay-biochar composite materials prepared from biowaste may help to overcome the cost barrier for new adsorbents and improve PFAS adsorption capacity remarkably. Easy availability of biowaste will also facilitate the production of clay-biochar composites in large quantities paving ways to scale up their application in wastewater treatment at megacity level.

8. Conclusions and future research

PFAS enters the human food chain, plants, and soil via contaminated industrial wastewater, groundwater, drinking water, and soil pollution. Natural clay minerals and their counterparts modified with organic agents, such as long-chain surfactants, polymers, and amines, improve adsorbents' capacity for PFAS removal from water through electrostatic and hydrophobic interactions. The computed PC values indicate that the surfactant (HDTMA)-modified montmorillonite and amine-modified palygorskite perform better than unmodified montmorillonite, kaolinite, raw bentonite, and magnesium aminoclay-coated nZVI for PFAS removal from water. The principal factors in removal processes are solution pH, regulating the surface charge and determining the main adsorption mechanism, and competing cations and anions that can increase or decrease PFAS removal, respectively. Further, OM inhibits adsorption because of competition for adsorption because of their negative charge and the affinity of highly aromatic OM (high molecular weight) towards PFAS adsorption through hydrophobic interaction. High temperatures also inhibit PFAS removal using clay minerals. Thus, natural and designer clays meant for removing PFAS from water require investigation in the following prioritized research areas:

1. Removing short-chain PFAS is more challenging than long-chain PFAS. Thus, research should focus on developing clay-based materials for removing short-chain PFAS.
2. Removal of zwitterionic PFAS is challenging due to the presence of both positive and negative charges under ambient environmental conditions and relatively high desorption rate following adsorption. Clay-carbon composites using biochar might improve the bulk adsorption capacity of zwitterionic PFAS in aqueous systems, which warrants future research while also promoting circular economy and environmental sustainability.
3. Clay-assisted photocatalysts might destroy the adsorbed PFAS and overcome the problem of safe disposal of the spent adsorbent. Therefore, the catalytic activity of clay minerals should be further explored.
4. Bio-reactive clay minerals (surface-modified and bacteria-loaded) could be explored for removal of PFAS through 'hook and destroy' approach where the modified clay would accumulate PFAS on the surface, and PFAS-degrading bacteria (artificially cultured, inhabiting

within the clay structure) would acquire carbon from PFAS converting it to less toxic by-products.

5. Spectroscopic and microscopic characterization of clay materials before and after PFAS adsorption are recommended to elucidate the adsorption mechanisms.

6. Investigations into the impacts of competing ions (cations and anions), size and fraction of organic matter and temperature on PFAS removal using clay adsorbents are also required to optimize various process parameters in large scale wastewater treatment applications.

7. Some chemical modifiers of clay materials such as surfactants might be toxic to aquatic organisms. Future research is required to explore bio-based non-toxic agents for modifying clays, and to assess the toxicity of currently available chemically-modified clay adsorbents.

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Author contributions

BS conceptualized the work; RM and BS wrote the original draft, made formal data analysis and revised the manuscript; KNP, DJY, NSB, SJP, CS and YSO subsequently added some sections, critically reviewed and edited the manuscript.

Conflicts of Interest

There are no conflicts of interest to declare. The authors have no vested interest in commercial products presented in the paper.

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Legend of figures

Fig. 1. Source fate and transport of PFAS in terrestrial and aquatic ecosystems (adapted from Garg, Kumar [34]).

Fig. 2. Classification of soil clays and clay minerals (adapted from [66] and [67]). Images of chlorite and allophane, and hematite are reproduced from the 'Images of Clay Archive' of the [68] and [69], and [70], respectively).

Fig. 3. Hypothetical structure of 2:1 type clay mineral (a), and structural evolution of organoclays with monolayer (b), bilayers (c), pseudo-trimolecular layers (d), paraffin-type (d & e) orientations of alkylammonium cations in the interlayer of the clay mineral. The original clay mineral is hydrophilic with hydrated cations in the interlayer, while the hydrophobicity of organoclays gradually increases from b to e. (adapted from [103, 104]).

Fig. 4. Plausible mechanisms (electrostatic attraction, hydrophobic interaction and ligand exchange) of PFAS adsorption by natural and modified clay minerals.

Fig. 5. Factors (pH, temperature, competing ions, natural organic matter, ionic strength) affecting PFAS removal by clay-based adsorbents.

Title of tables

Table 1. Global PFAS distribution in water bodies in selected countries with relatively high PFAS concentrations.

Table 2. Natural and modified clays, clay minerals, and oxides for PFAS removal from aqueous systems.

Table 3. Physical and chemical properties of clay-based adsorbents for PFAS removal.

Figures

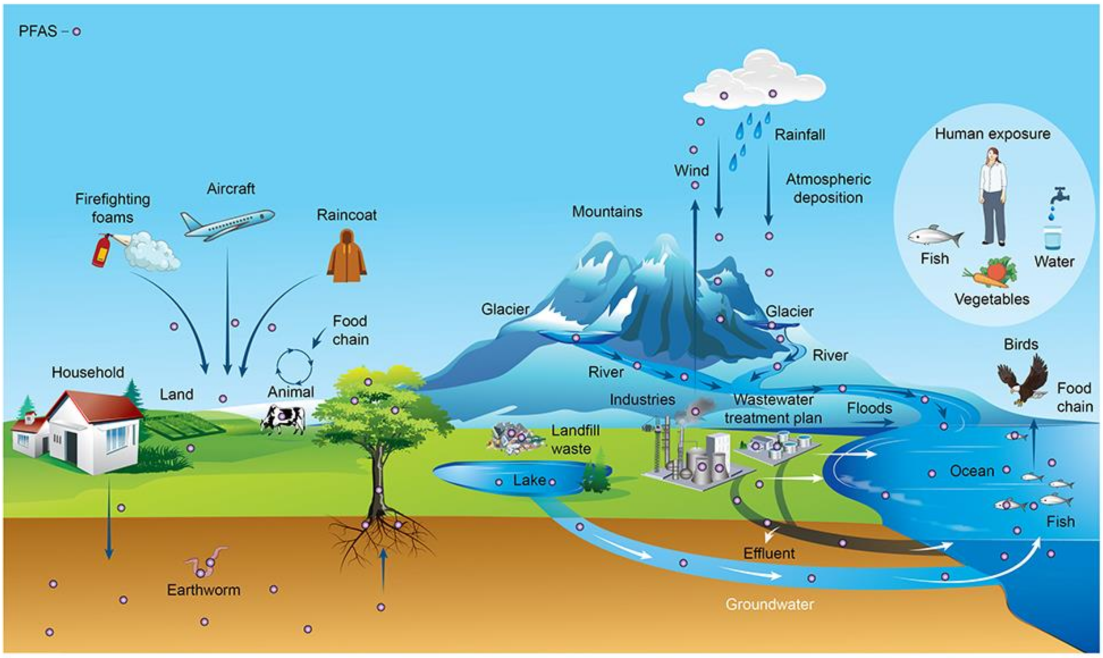

Fig. 1.

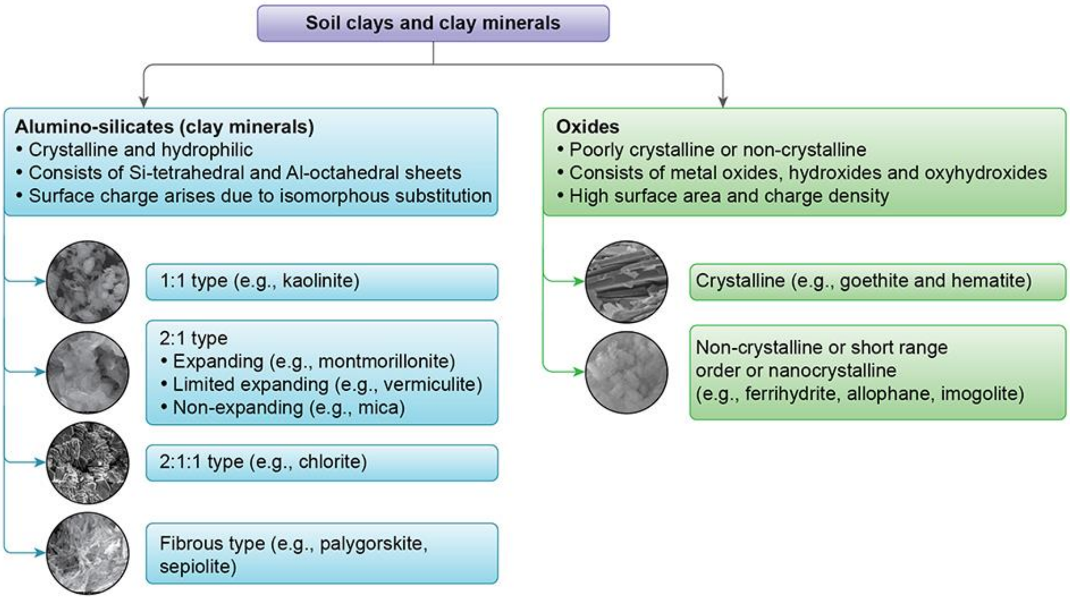
Soil clays and clay minerals
Alumino-silicates (clay minerals)
• Crystalline and hydrophilic
• Consists of Si-tetrahedral and Al-octahedral sheets
• Surface charge arises due to isomorphous substitution
1:1 type (e.g., kaolinite)
2:1 type
• Expanding (e.g., montmorillonite)
• Limited expanding (e.g., vermiculite)
• Non-expanding (e.g., mica)
2:1:1 type (e.g., chlorite)
Fibrous type (e.g., palygorskite, sepiolite)
Oxides
• Poorly crystalline or non-crystalline
• Consists of metal oxides, hydroxides and oxyhydroxides
• High surface area and charge density
Crystalline (e.g., goethite and hematite)
Non-crystalline or short range order or nanocrystalline (e.g., ferrihydrite, allophane, imogolite)

Fig. 2.

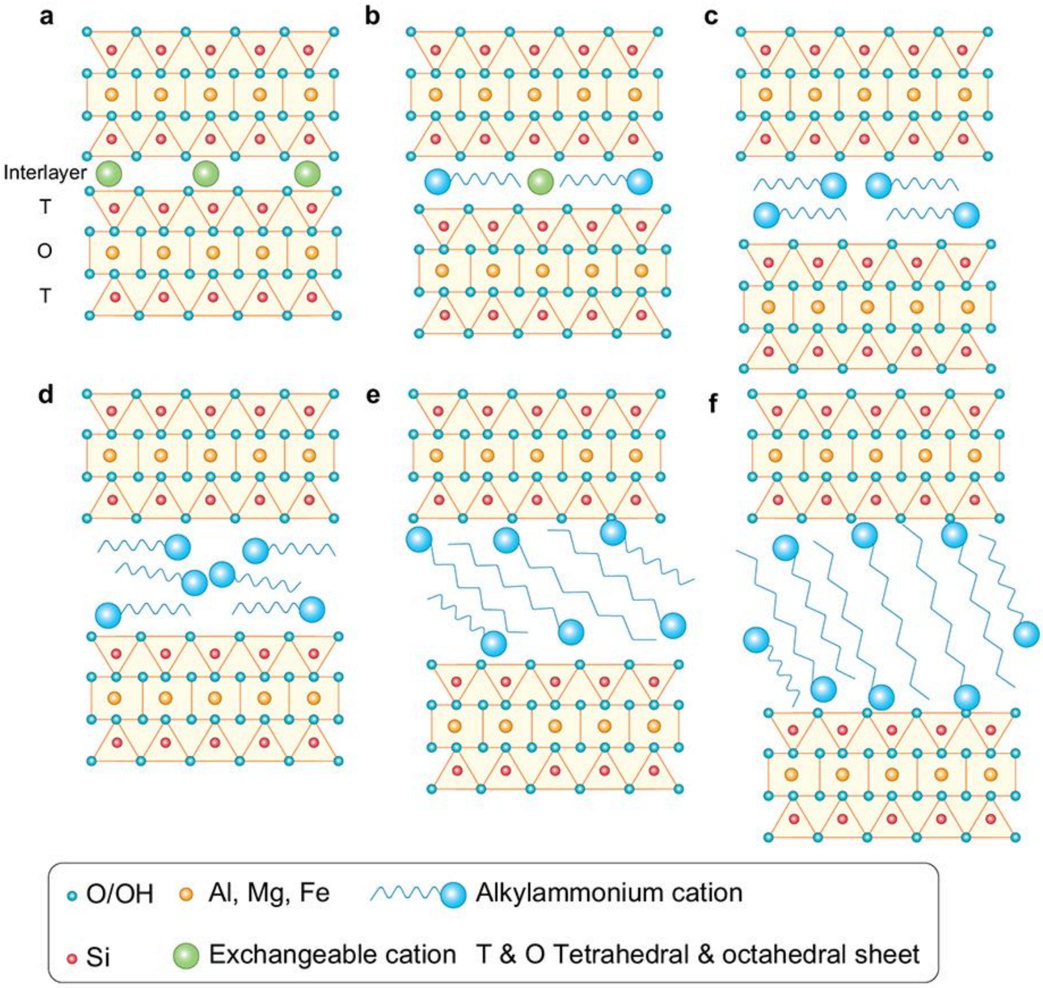
a
b
c
Interlayer
T
O
T
d
e
f
O/OH
Al, Mg, Fe
Alkylammonium cation
Si
Exchangeable cation
T & O Tetrahedral & octahedral sheet

Fig. 3.

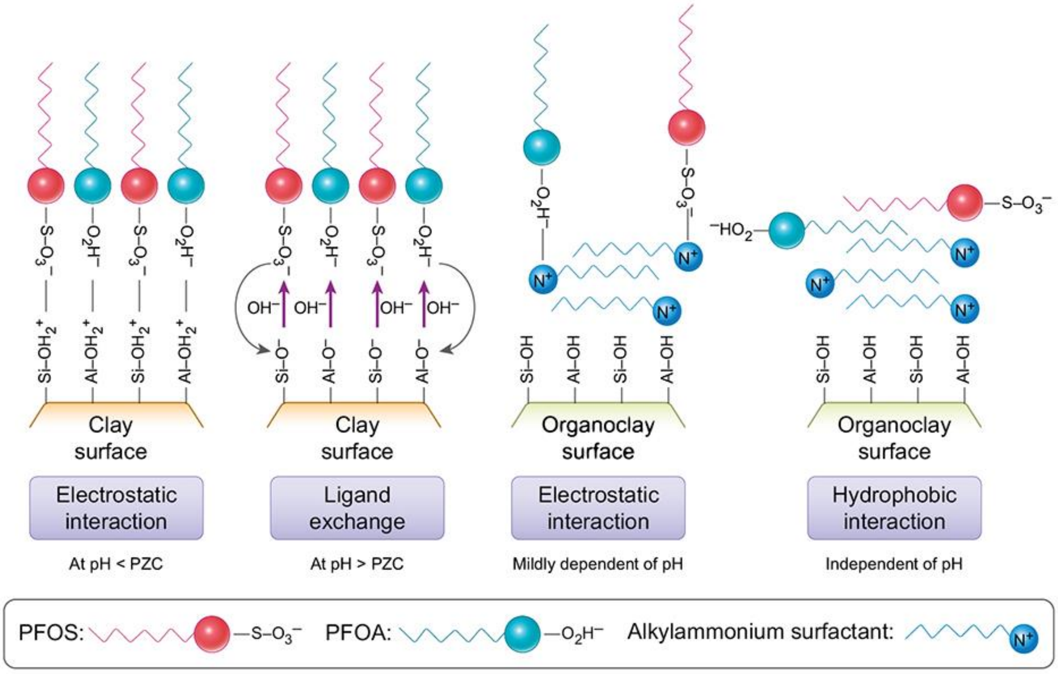
S–O3−
O2H−
Si–OH2+
Al–OH2+
OH−
Si–O−
Al–O−
Si–OH
Al–OH
N+
−HO2
Clay surface
Clay surface
Organoclay surface
Organoclay surface
Electrostatic interaction
At pH < PZC
Ligand exchange
At pH > PZC
Electrostatic interaction
Mildly dependent of pH
Hydrophobic interaction
Independent of pH
PFOS:
—S–O3−
PFOA:
—O2H−
Alkylammonium surfactant:
N+

Fig. 4.

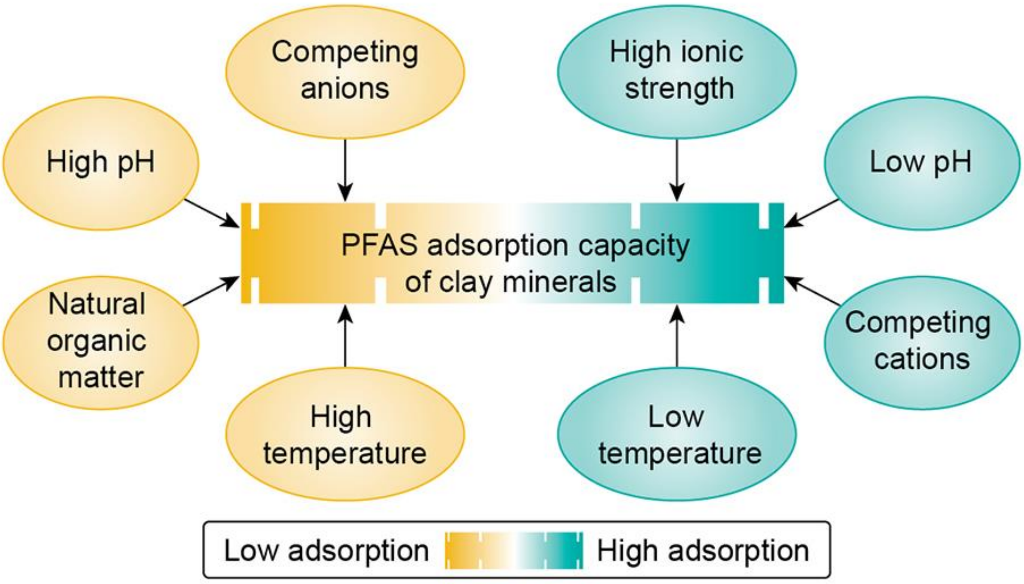
Competing anions
High ionic strength
High pH
Low pH
PFAS adsorption capacity of clay minerals
Natural organic matter
Competing cations
High temperature
Low temperature
Low adsorption
High adsorption

Fig. 5.

Tables

Table 1. Global PFAS distribution in water bodies in selected countries with relatively high PFAS concentrations.

Country	**Source**	**Compound**	**Concentration range** [a]		**Detection method**	**Reference**
			Lower	**Upper**		
Japan	Lake Biwa	PFOA	7.0 ng/L	17 ng/L	LC-MS/MS	[37]
		PFOS	0.8 ng/L	2.8 ng/L		
USA	Rivers and groundwater	PFOA	6.32 ng/L	112 ng/L	LC-MS/MS	[38]
		PFOS	2.28 ng/L	48.3 ng/L		
		PFHxS	0.86 ng/L	44.8 ng/L		
		PFBS	1.12 ng/L	11.1 ng/L		
China	Seawater (coastal areas) in	Σ_6PFAS	7.66 ng/L	11.98 ng/L	LC-MS/MS	[39]
	South China sea	Σ_6PFAS	2.12 ng/L	8.61 ng/L		
	Freshwater (reservoirs)					
China	South China Sea	Σ_{23}PFAS	0.195 ng/L	4.925 ng/L	UPLC-MS	[40]
Canada	Lake Ontario	PFOS	—	1.1 ng/L	LC-MS/MS	[41]
		PFOA	—	0.8 ng/L		
Germany	North Sea	Σ_{29}PFAS	4.7 ng/L	7.4 ng/L	HPLC-MS/MS	[42]
	Baltic Sea	Σ_{29}PFAS	1.6 ng/L	5.2 ng/L		
Italy	Western Mediterranean Sea	ΣPFAS	0.246 ng/L	0.515 ng/L	HPLC-MS/MS	[43]

Australia	Groundwater near wastewater treatment plant at Werribee South, Melbourne	$\sum_{20}$PFAS	0.03 ng/L	74 ng/L	LC-MS/MS-QQQ	[44]
Australia	Groundwater contaminated site at Fisherman’s Bend, Melbourne	$\sum_{17}$PFA	26 ng/L	5200 ng/L	LC-MS/MS	[45]
India	Ganges River	$\sum_{21}$PFAS	1.3 ng/L	15.9 ng/L	LC-MS/MS	[46]
—	North Atlantic Ocean	PFOS	0.0086 ng/L	0.036 ng/L	HPLC-MS/MS	[47]
		PFOA	0.052 ng/L	0.338 ng/L		
—	Northwestern Atlantic surface seawater	$\sum_{21}$PFAS	0.47 ng/L	3.97 ng/L	LC-MS/MS	[33]
	Northwestern Atlantic sub-surface seawater	$\sum_{21}$PFAS	0.66 ng/L	4.07 ng/L		
—	Eastern Pacific Ocean	PFOA	0.01 ng/L	0.06 ng/L	HPLC-MS/MS	[47]
	Western Pacific Ocean	PFOA	0.14 ng/L	0.50 ng/L		
—	Arctic Ocean	$\sum_{29}$PFAS	0.26 ng/L	—	LC-MS/MS	[48]
—	Western Antarctic Peninsula	Σ_2 PFOS	0.0011 ng/L	0.0033 ng/L	GC/MS	[49]
		Σ_2FOSE	0.0014 ng/L	0.013 ng/L		
Livingston Island (Antarctic)	Freshly deposited snow	$\sum_{14}$PFAS	0.76 ng/L	3.6 ng/L	UFLC-MS/MS	[50]
	Background surface snow	$\sum_{14}$PFAS	0.082 ng/L	0.43 ng/L		
	Seawater	$\sum_{14}$PFAS	0.094 ng/L	0.42 ng/L		

[a] ng/L is concentration in water and ng/m^3 is concentration in air; HPLC: High-performance liquid chromatography; LC: Liquid chromatography; UPLC: Ultra-performance liquid chromatography; MS: Mass spectroscopy; MS/MS: Tandem mass spectroscopy; QQQ: Triple quadrupole mass spectroscopy; GC: Gas chromatography; UFLC: Ultrafast liquid chromatography; GC-MS: Gas chromatography-mass spectroscopy.

1369 **Table 2**. Natural and modified clays, clay minerals, and oxides for PFAS removal from aqueous systems.

Clay and clay mineral	**Modifier**	**PFAS**	**Adsorption capacity or removal efficiency**	**Best fitted isothermal model**	**Best fitted kinetic model**	**Initial PFAS concentration**	**Clay and clay mineral dose (g/L)**	**Partition coefficient**	**System pH**	**Mechanism**	**Reference**
Kaolinite	—	PFOS	0.08 mg/g	—	—	1.0 mg/L	5.0	0.13 L/g	7.0	Outer-sphere complex	[72]
Montmorillonite	—	PFOS	0.05 mg/g	—	—	1.0 mg/L	5.0	0.07 L/g	7.0	Ligand exchange	[72]
Kaolinite	—	PFOA	0.10–0.11 mg/g	Langmuir	Pseudo-second order	10-1200 μg/L*	0.4	0.54 L/g	7.0	Surface complexation	[77]
Montmorillonite	—	PFOS	0.29–0.31 mg/g	Langmuir	Pseudo-second order	10-1200 μg/L*	0.4	0.17 L/g	7.0	Electrostatic attraction	[77]
Montmorillonite	HDTMA	PFOS	1.71 mmol/g	Freundlich	Pseudo-second order	50-500 mg/L*	—	23.78 L/g	6.3	Hydrophobic interaction	[24]
Montmorillonite	HDTMA	PFOS	890 mg/g	—	—	50 mg/L	4.0	16.25 L/g	3.0	Hydrophobic interaction	[81]

Clay and clay mineral	**Modifier**	**PFAS**	**Adsorption capacity or removal efficiency**	**Best fitted isothermal model**	**Best fitted kinetic model**	**Initial PFAS concentration**	**Clay and clay mineral dose (g/L)**	**Partition coefficient**	**System pH**	**Mechanism**	**Reference**
Montmorillonite	HDTMA and 3-indole-acetic acid	PFOA	100%	—	—	10 mg/L	2.2	—	3.0	Photodegradation by hydrated electrons by stabilizing effect of the montmorillonite on the indole radicals generated by photolysis	[82]
Na-mica	Octadecylamine	PFOA	91%	—	—	10 μg/mL	6.25	1.61 L/g	—	Hydrophobic interaction	[83]
Na-mica	Octadecylamine	PFOS	100%	—	—	10 μg/mL	6.25	—	—	Hydrophobic interaction	[83]
Palygorskite	Amine	PFOS	50 mg/g	Langmuir	—	300-1000 μg/mL*	2.5	18.08 L/g	—	Hydrophobic interaction	[23]

Clay and clay mineral	**Modifier**	**PFAS**	**Adsorption capacity or removal efficiency**	**Best fitted isothermal model**	**Best fitted kinetic model**	**Initial PFAS concentration**	**Clay and clay mineral dose (g/L)**	**Partition coefficient**	**System pH**	**Mechanism**	**Reference**
Montmorillonite	Poly(*m*-phenylene isophthalamide)/organic compounds	PFOS	>90%	—	—	25-200 μg/L*	4% wt.	—	7.0	Electrostatic attraction	[84]
Nnao-Fe_3O_4	Starch stabilized	PFOA	62.5 mg/g	Langmuir	Pseudo-second order	0-4000 μg/L*	8 mg/L	85.66 L/g	6.8	Inner-sphere complexation	[85]
Goethite	—	PFOS	1.4×10^{-3} molecules/nm^2	Langmuir	—	0.12-8 mg/L*	—	2.8–8.9 L/kg	4.0	Electrostatic attraction	[76]
Goethite	—	PFOS	2.4 μg/m^2	Langmuir	—	5-1000 μg/L*	0.417	0.011 L/m^2	7.0	Non-electrostatic attraction	[86]
Boehmite	—	PFOA	0.633 μg/m^2	Langmuir	Mass transfer (diffusion)	50-1000 μg/L*	5.0	0.002 L/m^2	7.0	Electrostatic attraction	[87]

Clay and clay mineral	Modifier	PFAS	Adsorption capacity or removal efficiency	Best fitted isothermal model	Best fitted kinetic model	Initial PFAS concentration	Clay and clay mineral dose (g/L)	Partition coefficient	System pH	Mechanism	Reference
Alumina	—	PFOA	0.16 µg/m^2	Langmuir	Mass transfer (diffusion)	40-400 µg/L*	10.0	0.001 L/m^2	4.3	Electrostatic attraction	[88]
Boehmite	Humic acid	PFOS	0.17 µg/m^2	Langmuir and Freundlich	—	50-1000 µg/L*	5.0	0.0001 L/m^2	7.0	Hydrophobic interaction	[89]
Montmorillonite	Quaternary ammonium	PFOA & PFOS	—	—	—	0-500 µg/L*	0.5	—	7.6	Electrostatic attraction	[90]
Al_2O_3	—	PFOS	1.1 µg/m^2	—	—	0.1-2.0 µmol/L*	0.2	0.02 L/m^2	7.0	Electrostatic attraction	[91]
Fe_2O_3		PFOS	4.0 µg/m^2					0.19 L/m^2			

Clay and clay mineral	Modifier	PFAS	Adsorption capacity or removal efficiency	Best fitted isothermal model	Best fitted kinetic model	Initial PFAS concentration	Clay and clay mineral dose (g/L)	Partition coefficient	System pH	Mechanism	Reference
Iranian bentonite	Arquad® 2HT-75 (IBA)	PFOS	99.9 mg/g	Freundlich for both IBA and IBAP	—	5-300 mg/L[*]	2.5	1.49 L/g	7.8	Hydrophobic interaction and electrostatic attraction	[92]
	IBA modified with palmitic acid (IBAP)	PFOS	78.1 mg/g					0.89 L/g	7.8	Hydrophobic interaction	
Montmorillonite	HDTMA and poly-4-vinylpyridine-co-styrene mixture	PFOA	>90% defluorination	—	Pseudo-first order	10 mg/L[**]	2.2	—	—	Catalysis through hydroxyl radicals as a result of the reaction between hydrated electron and oxygen	[93]

'—' indicates data not available.

[*] Concentration range reported for isotherm adsorption experiment.

[**] Initial concentration in adsorption kinetic experiment.

Table 3. Physical and chemical properties of clay-based adsorbents for PFAS removal.

Clays and clay minerals	**Physical properties**	**Chemical properties**	**Reference**
Natural clays and clay minerals	Surface area: montmorillonite = 67.5 m^2/g, kaolinite = 23.1 m^2/g, hematite = 9.9 m^2/g; Porous structure.	CEC: montmorillonite = 111 cmol/kg, kaolinite= 34 cmol/kg, hematite = 78 cmol/kg; Net negative surface charge due to isomorphous substitution in phyllosilicates; Variable charge under varying pH values in oxides and phyllosilicates; PZC: kaolinite = ~3.6, montmorillonite = 7.2, hematite = 5.9; Exposed –OH groups (e.g., in kaolinite) for H-bonding.	[72, 76, 78]
Starch-modified oxidic clays	Increased surface area from 3.98 m^2/g to 8.21 3.98 m^2/g after modification; Chemically stable modified product; Intact magnetic properties after modification.	Reversal of surface charge from -23 mV at pH = 6.5 to slightly positive values at pH = 2-9 after modification; Enhanced surface functional groups such as OH$^-$, -COO$^-$ and C–O after modification.	[85]
Organoclay minerals	Decreased surface area after modification (e.g., 44 m^2/g of organopalygorskite against 97 m^2/g of pristine palygorskite due to pore blocking by surfactant molecules)	Reversal of surface charge from negative to positive values (e.g., -19.9 mV in pristine palygorskite against 30.6 mV after organic modification of palygorskite); Increased amino (-NH$_2$) functional groups; Increased hydrophobicity due to long chain alkyl group of surfactants.	[20, 24, 125, 126]

Clay-polymer composite	Highly porous in nature; Small particle size (e.g., 100-300 µm for PDADMAC-MMT composite).	High positive charge on surface (e.g., -40.3 mV for MMT against 41.0 mV for PDADMAC-MMT at pH 7.6); Enhanced surface functional groups; Presence of hydrophobic moieties due to the inclusion of polymer.	[90]
Magnesium aminoclays (MgAC)	Water dispersible particles; Decreased hydrodynamic diameter (e.g., 508 nm for MgAC coated nZVI against 5130 nm for bare nZVI)	Increased surface positive charge (e.g., 23.5 mV for MgAC coated nZVI against 14.5 mV for bare nZVI); Selective affinity towards hydrophobic PFAS due to enhanced $–NH_2$ functional groups.	[97]
Clay-carbon composite	Highly porous structure; Decreased particle size (e.g., 2.27 nm for MSW-BC-MMT composite against 17.96 nm for MMT); Increased surface area (e.g., 8.72 m^2/g for MSW-BC-MMT composite against 4.33 m^2/g for MSW-BC).	Enhanced hydrophobicity and functional groups (e.g., $-OH^-$, $-NH_2$) due to carbonaceous materials (e.g., GO, biochar) and clay minerals	[111, 112]

PDAMAC: Poly(diallyldimethylammonium) chloride; nZVI: Nano zero valent iron; MgAC: Magnesium aminoclay; BC: Biochar; MSW: Municipal solid waste; MSW-BC: Municipal solid waste biochar.