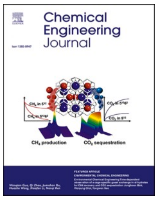
Chemical Engineering Journal 446 (2022) 137019

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej



Chemical Engineering Journal

Enhanced sorption of perfluorooctanoic acid with organically functionalized layered double hydroxide

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ARTICLE INFO

Keywords:
Layered double hydroxide
Organics functionalization
PFAS
PFOA
Adsorption
Water treatment

ABSTRACT

Sorption is recognized as an effective and economical approach for the practical treatment of water contaminated with per- and polyfluoroalkyl substances (PFAS). In this study, we reported the development, characterization, and evaluation of a family of new organically functionalized layered double hydroxide (LDH) adsorbents for PFAS removal with a primary focus on perfluorooctanoic acid (PFOA). The organic functional groups were introduced to the Zn-Al LDH by covalent bonding through a post-grafting process. The organically functionalized LDHs were very efficient for PFOA adsorption, likely due to the synergy of the positively charged structural layers of LDHs that provide strong electrostatic interactions and the modified organic functional groups that provide enhanced hydrophobic interactions to capture PFOA. Specifically, our adsorption kinetics and isotherm studies found that organically functionalized LDHs exhibited faster adsorption kinetics and greater adsorption capacities for PFOA than the unmodified LDH. Furthermore, organically functionalized LDHs showed substantially improved performance for PFOA removal under various water chemistry conditions in comparison to the unmodified LDH, and remained more effective following repeated adsorption-regeneration cycles. The best-performed organically functionalized LDH also exhibited high efficiency for the treatment of a mixture of PFAS with varied fluoroalkyl chain lengths and functionalities. Results of this work suggested that organically functionalized LDHs hold great promises for the treatment of PFAS-contaminated water.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) represent a large class of synthetic chemicals typically consisting of a hydrophobic fluorinated carbon chain and various types of hydrophilic end/head functional groups such as alcohol, carboxylate, sulfonamide, sulfonate, and phosphonate [1,2]. Because of their unique amphiphilic properties as well as their high chemical and thermal stability, PFAS have been used since the 1940s in a wide range of consumer, commercial, and industrial applications such as electronic manufacturing, industrial surfactants, paper and textile water proofing, metal plating and etching, surface treatment and protection, and firefighting foams [2–5]. Many PFAS, such as perfluoroalkyl acids (PFAAs) and perfluoropolyether carboxylic acids (PFECAs), are remarkably persistent in nature, negatively charged under ambient pH conditions, and highly soluble in aquatic environments [6–8]. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the two most examined PFAS within both scientific and regulation communities, and they have been detected in soil, groundwater and surface water [9,10]. PFOS, PFOA, as well as their precursors, are currently listed under the Stockholm Convention on Persistent Organic Pollutants [11]. The United States Environmental Protection Agency (USEPA) set the drinking water health advisory level of 70 ng/L for PFOS and PFOA in 2016 [12]. The USEPA's fifth Unregulated Contaminant Monitoring Rule (UCMR5) further required the public water systems in the United States to monitor 29 PFAS between 2023 and 2025, including PFOS and PFOA [13].

Because of its ease of operation and proven effectiveness, adsorption has been recognized as an economical approach for the treatment of water contaminated with PFAS [14,15]. Adsorption may be either employed as a stand-alone method or be incorporated into a treatment train for *ex situ* PFAS treatment [16,17]. The adsorbents that have been extensively investigated for PFAS removal over the past decades include activated carbons, ion exchange resins, natural and synthetic polymers, mineral-based materials, metal organic frameworks (MOFs), and

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https://doi.org/10.1016/j.cej.2022.137019
Received 18 March 2022; Received in revised form 12 May 2022; Accepted 13 May 2022

organic–inorganic composite materials [18–26]. Among them, activated carbons and ion exchange resins represent the most popular engineered adsorbents for practical PFAS treatment with demonstrated effectiveness in a number of field applications [17,18]. However, conventional adsorbents such as activated carbons and/or ion exchange resins also exhibited limitations such as reduced efficiency in the presence of dissolved organic matters and other water constituents, slow adsorption kinetics, difficulty for regeneration, and lack of selectivity [27,28]. For example, it was reported that up to 10 days were required for PFOS and PFOA adsorption by granular activated carbon (GAC) and ion exchange resins to reach equilibrium [28,29]. In addition, although some ion exchange resins were effective for PFAS treatment, they are often designed for single use and cannot be easily regenerated and reused [30,31].

Layered double hydroxides (LDHs), also known as anionic clays, are a family of layered minerals with a typical formula of $[M^{2+}_{1-x}N^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$. The M^{2+} and N^{3+} are metal cations occupying the octahedral centers of the positively charged brucite-like structural layers, and A^{n-} is an exchangeable anion within the interlayers [32,33]. Because of the high positive charge of the structural layer, LDHs generally exhibit positive surface charges over a range of environmentally relevant pH conditions, making them suitable for the adsorptive removal of anionic pollutants [34]. A few previous studies have investigated the removal of PFOS and PFOA with the use of Mg-Al LDHs and demonstrated the important role of exchangeable anion composition [35–37]. We recently reported that the cation composition of LDHs could also strongly affect PFOA adsorption and Zn-Al LDH exhibited higher efficiency than Mg-Al LDH [38]. However, LDHs are generally hydrophilic and the electrostatic interactions between LDHs and PFAS was considered the primary adsorption mechanism [35,37,38]. As a result, the presence of common anions such as sulfate and carbonates, as well as increased salinity have been reported to substantially reduce the performance of LDHs in PFAS removal [37–39], which could become a major limiting factor in the practical use of LDHs for PFAS treatment.

It was previously demonstrated that modification of minerals with organic functional groups could enhance the adsorption of organic pollutants [40,41]. Methods that have been used to incorporate organic functional groups into LDHs include the introduction of organic anions via non-covalent bonding during the LDH synthesis process and anion exchange with the inorganic anions within the interlayers of the LDHs [42,43]. For instance, Ding et al. developed a sodium dodecyl sulfate (SDS)-modified Mg-Al LDH through non-covalent bonding for the adsorption of chlorinated polyfluoroalkyl ether sulfonate (F–53B) [44]. There were, however, concerns about the stability of the organic functional group because of the non-covalent bonding nature between the organic functional groups and the LDHs. This is particularly true in complex environmental matrices and when the adsorbents were regenerated with the use of an organic solvent [33,45]. It is thus desirable to modify the surface of LDHs using organic materials that can form covalent bonding, such as silane coupling agents [46]. To the best of our knowledge, however, the development of organically modified LDHs through covalent bonding has not been explored for PFAS adsorption.

The primary objectives of the present work were to (1) develop new and efficient LDHs modified with organic functional groups through covalent bonding tailored for PFAS adsorption, and (2) quantify and compare the performance of organically functionalized LDHs with unmodified LDH for PFAS removal under various water chemistry conditions. Nitrate-intercalated Zn-Al LDH was used as a model LDH substrate for organic modification because of its demonstrated performance for PFAS adsorption [38]. Two organic functional groups, namely alkyl chain and polyfluoroalkyl groups, were used to modify the LDH to enhance the affinity with targeted PFAS. PFOA was selected as a representative PFAS for detailed examination of the adsorption behavior, because of its widespread environmental presence, known toxicity, and recalcitrant nature [9,47,48]. The adsorption affinity of PFOA was also usually weaker than that of PFOS with various adsorbents [18,28]. In addition, LDH modified with polyfluoroalkyl groups, which was more effective in PFOA removal, was investigated for the adsorption of a mixture of PFAS with different fluoroalkyl chain lengths, structure, and functional groups.

2. Materials and Methods

2.1. Chemicals and materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$, Alfa Aesar), aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot 9H_2O$, EMD-Millipore), acetic acid ($C_2H_4O_2$, Fisher Scientific), formic acid (CH_2O_2, Fisher Scientific), ethanol (C_2H_5OH, VWR-BDH), hydrochloric acid (HCl, VWR-BDH), sodium hydroxide (NaOH, Fisher Scientific), ammonium formate (NH_4HCO_2, Fisher Scientific), sodium bicarbonate ($NaHCO_3$, Fisher Scientific), sodium chloride (NaCl, Fisher Scientific), sodium nitrate ($NaNO_3$, Fisher Scientific), sodium sulfate decahydrate ($Na_2SO_4\cdot 10H_2O$, Fisher Scientific), n-hexadecane ($C_{16}H_{34}$, Fisher Scientific), triethoxy(octyl)silane ($C_{14}H_{32}O_3Si$, Si-CH, Sigma-Aldrich), and 1H,1H,2H,2H-perfluorooctyltriethoxysilane ($C_{14}H_{19}F_{13}O_3Si$, Si-CF, Oakwood-Chemicals) were used as purchased without further purification. PFOA (Alfa Aesar), perfluorobutanoic acid (PFBA, Sigma-Aldrich), perfluoropentanoic acid (PFPeA, Oakwood Chemical), perfluoroheptanoic acid (PFHpA, Sigma-Aldrich), perfluorononanoic acid (PFNA, Sigma-Aldrich), perfluorodecanoic acid (PFDA, Oakwood Chemical), perfluorobutanesulfonic acid (PFBS, Sigma-Aldrich), perfluorohexanesulfonic acid (PFHxS) in potassium salt (Sigma-Aldrich), PFOS in potassium salt (Sigma-Aldrich), and 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid (HFPO-DA or GenX, Wellington Laboratories) were used as representative PFAS. Properties of the PFAS were shown in the Supplementary Material (Table S1 of the Supplementary Material). Suwannee River Natural Organic Matter (NOM) was obtained from the International Humic Substances Society and was used to prepare a stock solution of 300 mg C/L with the calibration of a TOC analyzer (Shimadzu). LCMS grade methanol and acetonitrile were purchased from Fisher Scientific. Ultrapure water (resistivity > 18.2 MΩ) was used to prepare solutions. A natural lake water sample was collected from Lake Michigan. The water was filtered with a 0.22-μm polyether- sulfone (PES) membrane (Millipore) before experimental use.

2.2. Preparation of raw and organically functionalized LDHs

Zn-Al LDH was synthesized following a standard aqueous co-precipitation method reported in our previous paper [38]. Briefly, a 50-mL mixed solution of 0.75-M $Zn(NO_3)_2\cdot 6H_2O$ and 0.25-M $Al(NO_3)_3\cdot 9H_2O$ was prepared (Zn^{2+}/Al^{3+} molar ratio = 3:1) and added into 50 mL of a 2-M NaOH solution under vigorous stirring in a dropwise manner. Once the reaction was completed, the white slurry was aged for 24 h at room temperature, followed by centrifugation to collect the solids. The solids were washed with water several times, dried in an oven at 60 °C, and preserved for future use.

Organically functionalized Zl-Al LDHs were prepared through post-grafting of an organosilane onto the Zl-Al LDH based on the approach modified from previous research [49]. Specifically, Zl-Al LDH was modified with two organic functional groups, including an alkyl chain group (CH) and a polyfluoroalkyl group (CF), with the use of the corresponding organosilanes (Si-CH and Si-CF, **Figure S1** of the Supplementary Material), respectively. Both organic groups had a carbon chain length of 8 and were selected because of their hydrophobic nature and the convenient availability of the organosilane precursors. Briefly, the alkyl-modified LDH (i.e., denoted as LDH-CH) was prepared by dispersing ~ 12.5 mmol of Zn-Al LDH in 60 mL of ethanol. Then, a desired amount of the organosilane (molar ratio of Si-CH/LDH = 1:1) was added dropwise into the suspension under stirring, followed by adding 2 mL acetic acid. After 24 h of reaction, the solids were collected via centrifugation, and washed with ethanol and water 3 times, respectively. The obtained solids were dried in an oven at 60 °C and preserved for future use. The polyfluoroalkyl-modified LDH (i.e., denoted as LDH-CF) was prepared following the same method with the use of Si-CF as the organosilane and a smaller Si-CF/LDH molar ratio of 0.2 because of the strong hydrophobicity of Si-CF.

2.3. Material characterization

The structure of the raw and organically modified LDHs was characterized using powder X-ray diffraction (XRD) with a Bruker D8 Discover A25 diffractometer with copper Kα radiation. The scan speed and step size were 6° per min and 0.02°, respectively. Scanning electron microscopy (SEM) imaging was performed to determine the morphology of the materials using a Hitachi Model S4800. Fourier-transform infrared spectroscopy (FTIR) measurements were acquired on a Shimadzu IRTracer100 Spectrometer to investigate the surface functional groups of the materials. The vibrations corresponding to the wavenumbers in the range of 600–4000 cm^{-1} were collected with a resolution of 4 cm^{-1}. The thermo-gravimetric analysis (TGA) was conducted on a Discovery SDT 650 thermo-gravimeter (TA Instruments) in a 50-mL/min air flow with a temperature ranging from 30 to 800 °C and a heating rate of 10 °C/min. Contact angle measurements of water and n-hexadecane were performed using a Ramé-Hart goniometer. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Perkin Elemer PHI 5440 ESCA system with an Al Kα X-ray source. Zeta potentials of the materials prior to and after PFOA adsorption were measured with a Malvern Zetasizer Nano ZS 90 at pH 3 – 11. Carbon contents of the materials were measured on a Fisons NA 1500 NCS elemental analyzer to determine the organic functional group loadings. Anion exchange capacity of the materials was measured based on a sulfate exchange approach described previously [38,50].

2.4. Batch adsorption experiments

PFOA adsorption experiments were performed under batch mode in polypropylene reactors placed on an orbital shaker (Thermo Scientific, 300 rpm) at room temperature (22 ± 2 °C). Experiments were conducted at an initial pH of 6 with an adsorbent loading of 1 g/L and a PFOA concentration of 500 μg/L, unless otherwise specified. The solution pH was not buffered, and the final pH was stable at 7.0 ± 0.5 at the end of the experiments. It was worth noting that high PFOA concentrations ranging from 220 – >6,000 μg/L have previously been observed in some contaminated waters near the source zone [51–53]. The relatively high PFOA concentration in the present work was also within the range of previous batch adsorption studies [54–56], and was used to compare the performance of raw and organically functionalized LDHs under various water chemistry conditions. Experiments were performed for 48 h to ensure that adsorption achieved equilibrium, except for the kinetics experiments where samples were collected at various time intervals (i.e., 2 min – 48 h). To determine the maximum adsorption capacity, adsorption isotherm experiments were conducted with a series of PFOA concentrations up to 350 mg/L with a reduced adsorbent loading of 0.25 g/L because of the large adsorption capacity for the organically functionalized LDHs. In addition, a set of experiments were performed to evaluate the effect of common water chemistry parameters on PFOA adsorption, including solution pH (3 – 9), ionic strength (provided by NaCl, 1–100 mM), coexisting anions (chloride, sulfate, carbonates, nitrate, 1 mM), and NOM (Suwannee River NOM, 1 mM as C). Furthermore, the performance of LDH-CF was evaluated for the removal of multiple PFAS under more environmentally relevant concentrations in both a simple lab-prepared solution (i.e., ultrapure water) and a natural lake water (Table S2 of the Supplementary Material). Specifically, experiments were conducted with waters amended with a mixture of 10 PFAS that included 6 perfluorinated carboxylic acids (PFCAs: PFBA, PFPeA, PFHpA, PFOA, PFNA, PFDA), 3 perfluorinated sulfonic acids (PFSAs: PFBS, PFHxS, PFOS), and GenX, each with a nominal concentration of 10 μg/L. All experimental conditions were run in at least duplicates.

Reuse of the raw and organically functionalized LDHs was determined by conducting PFOA adsorption/regeneration experiments for 3 cycles. In each cycle, adsorption experiments were first conducted at pH 6 with an adsorbent loading of 1 g/L and a PFOA concentration of 500 μg/L for 48 h. The PFOA-loaded adsorbents were then collected through centrifugation and regenerated in a freshly prepared methanol/water (50%/50%) mixture containing 1 wt% NaCl for 24 h. The regenerated adsorbents were collected through centrifugation, washed with water for 3 times, and reused in the next cycle.

2.5. PFAS measurement

In all experiments, the collected samples were immediately filtered with 0.22-μm PES syringe filters (SLGPX13NK, Millipore), and the filtrates were preserved for PFAS analysis. No significant PFAS loss was observed during the filtering process because of the small filter diameter (i.e., 13 mm) and the use of a pre-rinsing step (i.e., the first 3-mL sample was used to rinse the filter and wasted). The PFOA concentrations in the aqueous samples from the single-solute experiments were determined using a high-performance liquid chromatography (HPLC, UltiMate 3000, Thermo Scientific) couple with single quadrupole mass spectrometry (ISQ EM, Thermo Scientific) [38]. This method had a PFOA detection limit of 2 μg/L. The concentrations of the 10 PFAS mixture from the mixed-solute experiments were determined using an ultra-high-performance liquid chromatography (UHPLC) system coupled with a triple quadrupole mass spectrometry (LCMS-8040, Shimadzu) [54]. Detailed information of the analytical parameters and detection limits was described in the Supplementary Material (Section S1 and Table S3 of the Supplementary Material).

The PFAS adsorption amount and removal efficiency were calculated using Eqs. (1) and (2), respectively:

$$q_e = \frac{(c_0 - c_e)^{*}V}{m} \tag{1}$$

$$\text{Removal}\ (\%) = \left(1 - \frac{c_e}{c_0}\right) \times 100\% \tag{2}$$

where q_e (mg/g) is the amount of PFAS adsorbed onto the adsorbent at equilibrium, c_0 (mg/L) and c_e (mg/L) represent the initial PFAS concentration and the equilibrium PFAS concentration in solution, respectively, and m (g) and V (L) are the adsorbent mass and the PFAS solution volume, respectively.

3. Results and discussion

3.1. Materials characterization

Zn-Al LDH was modified with organic functional groups through a convenient one-step post-grafting process to prepare the functionalized LDHs (i.e., LDH-CH and LDH-CF, **Figure S2** of the Supplementary Material). The organically functionalized LDHs were characterized and compared with the unmodified Zl-Al LDH using various tools. Based on the SEM image, the unmodified LDH consisted of clutters of randomly stacked small thin flakes with clear and sharp edges (**Figure S3a** of the Supplementary Material). After modification, the edges of the LDH thin flakes became smoother, probably due to the coverage of the organic functional groups onto the surface of the functionalized LDHs (**Figures S3b and S3c** of the Supplementary Material). The contact angle analysis clearly suggested that modification with organic functional groups increased the hydrophobicity of LDHs. The unmodified LDH was quite hydrophilic in nature with a contact angle of water close to 0° (**Figure S4a** of the Supplementary Material). In contrast, the surfaces of LDH-CH and LDH-CF became quite hydrophobic with the water contact angles increasing to 136.6° and 133.3°, respectively (**Figures S4b and S4c** of the Supplementary Material). Meanwhile, modification of organic functional groups did not substantially alter the surface charge of LDHs, and both the unmodified and organically functionalized LDHs exhibited positive surface charges under a range of environmentally relevant pH conditions based on zeta potential measurements (**Figure S5a** of the Supplementary Material).

FTIR was employed to determine the functional groups of the unmodified Zn-Al LDH, LDH-CH, and LDH-CF (Fig. 1). All three materials showed a broad absorption peak at 3600–3200 cm^{-1}, which was ascribed to the hydroxyl groups within the LDH structure. Additionally, the peaks centered at ~1350 cm^{-1} and ~1635 cm^{-1} were assigned to the interlayer nitrate ions and adsorbed H_2O, respectively [37,42]. Compared to the pristine LDH, the FTIR spectrum of LDH-CH showed two new characteristic peaks at 2850–2940 cm^{-1}, which were attributed to the symmetric stretching and asymmetric mode of C–H of the alkyl groups [54]. For LDH-CF, the new peaks centered at ~1135 and 1205 cm^{-1} were related to the vibrations of the $-CF_3$ and $-CF_2-$ of the polyfluoroalkyl groups [38,57]. Interestingly, the peaks associated with C–H stretching were not clearly shown for LDH-CF in comparison to LDH-CH, which may be related to the small number of C–H bonds within the polyfluoroalkyl group, as well as the lower functional group molar loading of LDH-CF than LDH-CH. Additionally, the peak at ~1015 cm^{-1} for both LDH-CH and LDH-CF was assigned to the stretching vibration of Si-O [58], and it was stronger for LDH-CH than LDH-CF, probably because of the higher functional group molar loading within LDH-CH. The FTIR results thus suggested that the alkyl and polyfluoroalkyl groups were incorporated into LDH-CH and LDH-CF, respectively. Furthermore, based on the XPS analysis, a peak was observed in the Si 2p spectrum for both LDH-CH and LDH-CF with the binding energy at 102.1 eV (**Figure S6** of the Supplementary Material), which was consistent with the Si state within silane structure [59]. Thus, the XPS result consolidated the FTIR observation and suggested the successful modification of the LDHs with the corresponding organosilanes (i.e., Si-CH and Si-CF).

According to the carbon elemental analysis, the loadings of the alkyl and polyfluoroalkyl groups were 1.55 and 0.57 mmol/g for LDH-CH and LDH-CF, respectively. It should be noted that the functional group loading for LDH-CF was estimated based on the assumption of complete combustion of the polyfluoroalkyl groups within the NCS elemental analyzer operated at 980 °C with excessive oxygen. Previous studies suggested that fluoroalkyl groups may be completely mineralized under combustion at 900–1000 °C [60–62]. Meanwhile, since fluoroalkyl chemical combustion is a complex process that can be affected by various parameters, the generation of any byproducts cannot be fully excluded [63]. If the combustion were incomplete, the polyfluoroalkyl group loading for LDH-CF would be slightly underestimated. Nevertheless, the elemental analysis should provide a conservative estimation of the functional group loading for LDH-CF.

The thermostability of the materials was further investigated using TGA analysis (Fig. 2). For all three materials, the gradual weight loss at up to ~200 °C indicated the removal of adsorbed water, which would not affect the structural integrity of the LDHs [64]. The weight loss at higher temperature may be related to the decomposition of the nitrate anions within the interlayer, the degradation of the organic functional groups of LDH-CF and LDH-CH, and the dihydroxylation of the LDH structural layers [65–68]. The weight loss of the unmodified LDH and LDH-CH became minimal above ~500 °C, indicating the formation of stable end products such as (mixed) metal oxides. In contrast, a slight weight loss was observed for LDH-CF till 800 °C, which may be related to the complex thermal decomposition processes of polyfluoroalkyl groups [63]. Compared to the unmodified LDH, higher weight losses were observed for LDH-CF and LDH-CH at 800 °C, which were consistent with the high organic functional loadings for these two functionalized LDHs. Notably, because of the higher molecular weight of the polyfluoroalkyl group (i.e., $-(CH_2)_2(CF_2)_5CF_3$) within LDH-CF than the alkyl group (i.e., $-(CH_2)_7CH_3$) within LDH-CH, LDH-CF would have a higher mass loading of the functional groups than that of LDH-CH, resulting in a slightly higher weight loss in the TGA profile.

The crystalline structure of the LDHs prior to and after organics modification was compared using XRD (Fig. 3). For the unmodified LDH, a characteristic peak at 2θ of 10.2° was clearly observed, which represented the (0 0 3) reflection and confirmed the layered structure of the material. According to the Bragg equation, the basal spacing (d_{003}) of the unmodified LDH was 0.87 nm. Compared to the unmodified LDH, the (0 0 3) peak position of LDH-CF did not change, suggesting that the layered structure was retained with minimal change of the basal spacing after modification with polyfluoroalkyl groups. In contrast, in addition to the strong peak at 2θ of 10.2°, a small peak at 2θ of 4.4° appeared for LDH-CH, which indicated the formation of a new minor phase after modification with alkyl groups. The basal spacing corresponding to this new minor peak was calculated as 2.01 nm, suggesting a partial

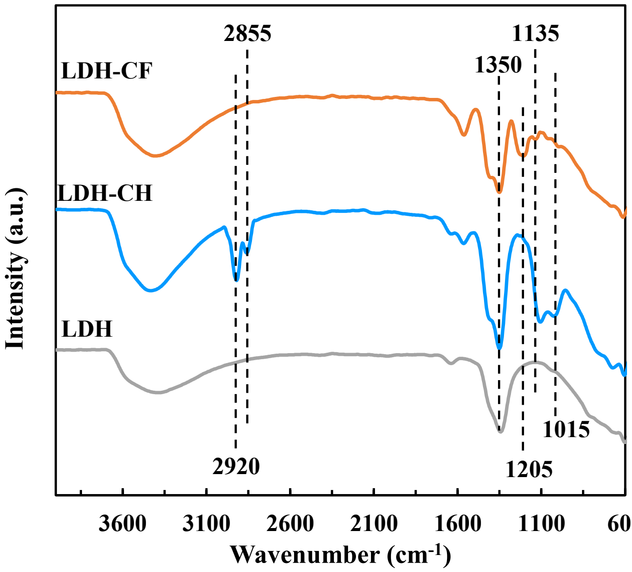

Fig. 1. FTIR spectra of pristine and organically functionalized LDHs.

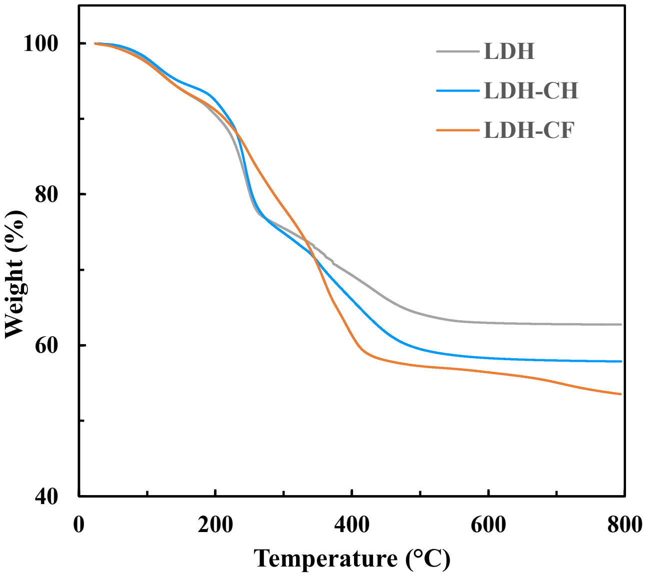

Fig. 2. TGA profiles of pristine and organically functionalized LDHs.

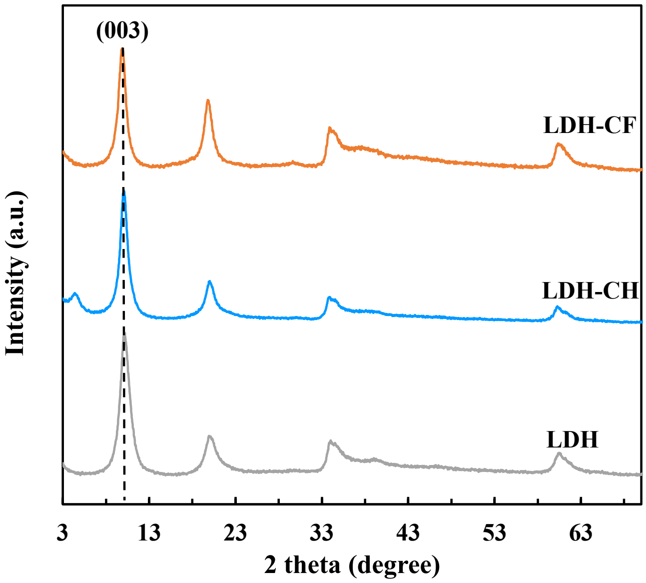

Fig. 3. XRD patterns of pristine and organically functionalized LDHs.

interlayer expansion for LDH-CH. In general, LDHs exhibited strong interactions between the adjacent structural layers, and thus a high organic functional group loading would be required to expand the interlayers and alter the stacking structure of LDHs [33,69]. For instance, Chang et al. previously determined the impact of PFOA loading on the structural change of Mg-Al LDH and reported that the interlayers only started to expand when the PFOA loading reached ~1.9 mmol/g [36]. In the present work, a partial interlayer expansion was observed for LDH-CH but not LDH-CF, which was consistent with the substantially higher molar loading of organic functional groups for LDH-CH than for LDH-CF.

3.2. *Adsorption kinetics and isotherms*

Adsorption kinetics and isotherm studies were first performed to investigate the adsorption behavior of PFOA onto the pristine and organically functionalized LDHs. Based on the kinetics experiments, all materials exhibited a rapid initial PFOA uptake, and then a gradually slower stage until adsorption reached equilibrium (Fig. 4). For the unmodified Zn-Al LDH, the equilibrium state was achieved within 2 h, which was comparable to different LDHs reported previously such as Mg-Al LDH and calcined hydrotalcite (i.e., Mg-Al-CO_3-LDH) [35,38,39]. Meanwhile, the organically functionalized LDHs exhibited faster adsorption kinetics and more complete PFOA removal than the unmodified LDH. Specifically, PFOA adsorption reached equilibrium within 5 and 30 min under the experimental condition for LDH-CF and LDH-CH, respectively. The observed faster adsorption kinetics of the organically functionalized LDHs than the pristine LDH suggested that modification with organic functional groups created more favorable conditions for PFOA adsorption, likely because of the change of the LDH surface properties that enhanced the interactions with PFOA. The organically functionalized LDHs, particularly LDH-CF, also showed substantially faster adsorption kinetics than various adsorbents reported in previous studies such as powdered activated carbon (PAC), GAC, ion exchange resins, fluoro-modified clay, and MIL-101-based MOF, onto which the equilibrium times for PFOA adsorption ranged from one hour to ten days [28,29,35,36,39,70,71]. Furthermore, PFOA adsorption kinetics onto all three materials in the present work can be well described by the pseudo-second order model (**Figure S7** and Table S4 of the Supplementary Material), which indicated that chemical sorption was involved in the adsorption process [72]. Overall, our kinetics results suggested that modification of LDHs with organic functional groups substantially accelerated PFOA adsorption, which may represent a major practical advantage over existing adsorbents.

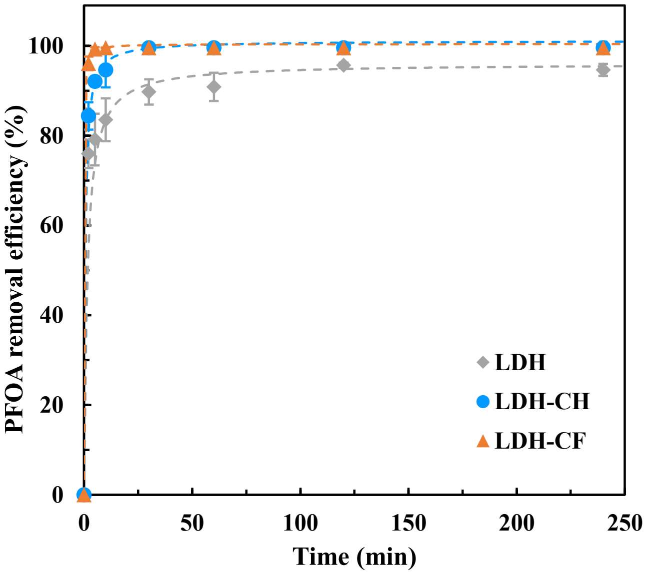

Fig. 4. Adsorption kinetics of PFOA onto pristine and organically functionalized LDHs at pH 6 with an initial PFOA concentration of 500 μg/L and an adsorbent loading of 1 g/L. Dash lines represent pseudo-second order model fits. Error bars represent one standard deviation of duplicate experiments.

Adsorption isotherms of PFOA onto the pristine and organically functionalized LDHs were obtained to determine the adsorption capacities and affinity (Fig. 5). The data were fitted with the classic Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models [73]:

$$Q_e = \frac{Q_{max}K_LC_e}{1 + K_LC_e} \tag{3}$$

$$Q_e = K_FC_e^{1/n} \tag{4}$$

where C_e (mg/L) is the equilibrium PFOA concentration in the solution, Q_e (mg/g) is the amount of PFOA adsorbed onto the (functionalized)

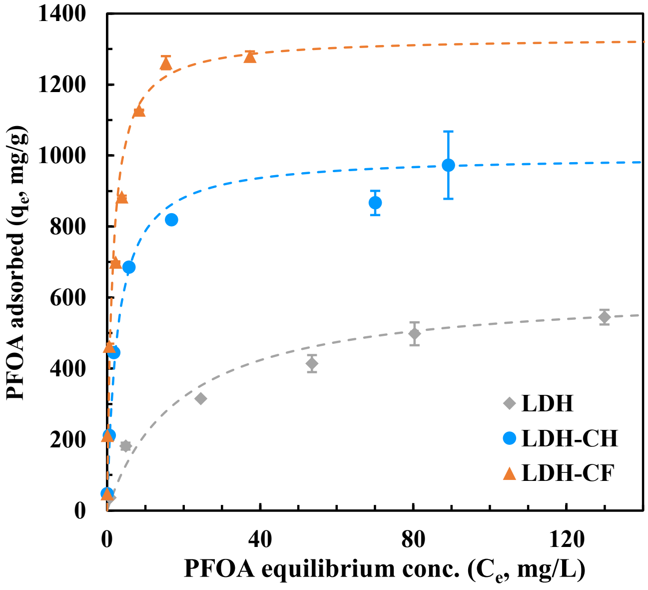

Fig. 5. Adsorption isotherms of PFOA onto pristine and organically functionalized LDHs at pH 6 with an adsorbent loading of 0.25 g/L. Dash lines represent Langmuir model fits. Error bars represent one standard deviation of duplicate experiments.

LDHs at equilibrium, Q_{max} (mg/g) and K_L (L/mg) represent the maximum adsorption capacity and the Langmuir constant related to the energy of adsorption, respectively, and K_F ((mg/g)·(L/mg)$^{1/n}$) and n are the Freundlich constant and a dimensionless indicator related to the adsorption heterogeneity, respectively.

Based on the R^2 values, the Langmuir model fitted the adsorption data slightly better than the Freundlich model for all three materials (Table S5 of the Supplementary Material). According to the Langmuir model, the maximum adsorption capacities of PFOA were 625 mg/g (1.51 mmol/g), 1,000 mg/g (2.42 mmol/g), and 1,333 mg/g (3.22 mmol/g) for the pristine LDH, LDH-CH, and LDH-CF, respectively. Compared to the pristine LDH, LDH-CF and LDH-CH increased the PFOA adsorption capacities by >110% and ~60%, respectively. Notably, the maximum PFOA adsorption capacity for LDH-CF was higher than the measured anion exchange capacity of LDH-CF (1.57 meq/g) or the loading of the polyfluoroalkyl groups (0.57 mmol/g). Thus, the result suggested that (1) the influence of the polyfluoroalkyl groups of LDH-CF may extend over multiple positively charged sites of the adsorbent, and (2) one surface site may be occupied by multiple PFOA molecules at high concentrations, probably because of the surfactant property of PFOA resulting in the possible formation of hemimicelles [29]. Similarly, a previous study also found that the maximum PFOA adsorption capacity was higher than the anionic exchange capacity of calcined hydrotalcite [36]. Furthermore, the Langmuir constant (i.e., K_L) is also an important parameter and reflects the adsorption affinity between adsorbents and adsorbates. Compared to the pristine LDH, the K_L values of LDH-CH and LDH-CF increased by over 7 and 14 folds, respectively (Table S5 of the Supplementary Material), suggesting that modification with organic groups substantially increase the adsorption affinity with PFOA, probably because of the enhanced hydrophobic interactions between PFOA and the adsorbents. It is noteworthy that despite of the lower organic functional group loading, LDH-CF showed both higher adsorption capacity and stronger affinity with PFOA than those of LDH-CH, which indicated that modification with polyfluoroalkyl groups can be more favorable than alkyl groups for PFOA adsorption.

Considering both Q_{max} and K_L, the performance of the organically functionalized LDHs was compared with a suite of conventional and advanced adsorbents reported in literature (Fig. 6). The organically functionalized LDHs, particularly LDH-CF, showed both superior adsorption capacity and strong adsorption affinity with PFOA, and outperformed various classes of adsorbents such as unmodified LDHs, PAC/GAC, ion exchange resins, polymeric materials, and organic–inorganic composites [20,29,35,38,54,56,70,71,74–86]. Although a few materials such as calcined hydrotalcite and special ion exchange resin also showed a high PFOA adsorption capacity >1,000 mg/g, their adsorption affinity with PFOA was 4 – 10 times lower than that of LDH-CF [29,36]. It is worth noting that the amount of PFOA captured by an adsorbent can be affected by both Q_{max} and K_L under practical conditions. Specifically, the Langmuir model can be simplified as Eq. (5) when the equilibrium concentration of PFOA in the aqueous solution is sufficiently low so that $K_L \cdot C_e \ll 1$:

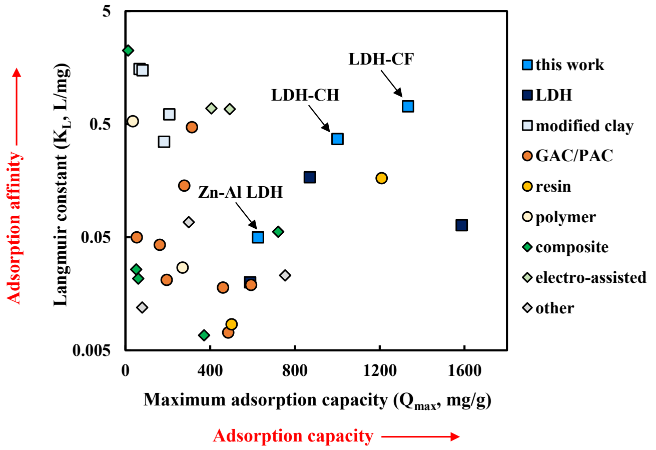

Fig. 6. Comparison of Langmuir fitting parameters among various classes of adsorbents reported in literature [20,29,35,36,38,54,56,70,71,74–86].

$$Q_e = Q_{max}K_LC_e \tag{5}$$

The product of Q_{max} and K_L (i.e., $Q_{max} \cdot K_L$) thus determines the partition of PFOA between adsorbent and aqueous phases at equilibrium, and a higher value of $Q_{max} \cdot K_L$ represents more favorable PFOA adsorption. Based on the calculated $Q_{max} \cdot K_L$ values, organically functionalized LDHs were among the best-performed adsorbents for PFOA removal (Table S6 of the Supplementary Material). Particularly, the $Q_{max} \cdot K_L$ value of LDH-CF was one to two orders of magnitude higher than a range of adsorbents.

3.3. Effect of water chemistry parameters

Compared to the unmodified LDH, organically functionalized LDHs consistently showed improved performance for PFOA removal in the presence of various anionic substances. Regarding the unmodified LDH, the presence of 1 mM of chloride, nitrate, and carbonates slightly inhibited PFOA adsorption, while PFOA adsorption was strongly inhibited with 1 mM of sulfate (Fig. 7a). PFOA is an organic acid and would be present predominantly as an anion under the experimental condition due to its low pKa (**Figure S8** of the Supplementary Material) [28]. Because of the positively charged structural layer and hydrophilic nature of pristine LDHs, PFOA adsorption onto the unmodified LDH may have occurred primarily through electrostatic interactions [35,37,38]. Since sulfate is present as a divalent anion, it may bind with the positively charged LDH surfaces more strongly through electrostatic attraction than that of monovalent anions, resulting in a strong inhibitory effect on PFOA adsorption [87,88]. The observation was consistent with previous studies showing that sulfate decreased the adsorption of PFOA and PFOS onto Mg-Al LDH by 70%–100% [37,38]. In contrast, both LDH-CF and LDH-CH showed superior performance in the presence of 1 mM of anions (Fig. 7a). Notably, the presence of 1 mM of sulfate had negligible inhibition on PFOA adsorption onto LDH-CF, which may be related to the modified organic functional groups that induced hydrophobic interactions in addition to electrostatic interactions between the adsorbent surface and PFOA. Even with a sulfate concentration as high as 10 mM that corresponded to a sulfate-to-PFOA molar ratio over 8,000, the PFOA removal efficiency could reach 75% with the use of LDH-CF (**Figure S9** of the Supplementary Material). Overall, our results suggested that modification of LDH with organic functional groups can greatly enhance the material affinity and selectivity with PFOA in the presence of competing inorganic anions.

NOM is widely present in aquatic environments and is generally negatively charged under ambient pH conditions [89]. As shown in Fig. 7a, the presence of 1 mM of NOM minorly reduced PFOA adsorption onto the pristine LDH to a level similar to that of 1 mM of chloride. Meanwhile, LDH-CH and LDH-CF showed different PFOA adsorption behaviors in the presence of NOM (Fig. 7a). For LDH-CH, NOM had a slightly larger inhibitory effect on PFOA adsorption than that of the unmodified LDH, which might be related to the competition of NOM with PFOA for the adsorption sites of LDH-CH through both electrostatic and hydrophobic interactions [27]. On the contrary, NOM had negligible impact on PFOA adsorption onto LDH-CF and nearly complete PFOA removal was observed under the experimental condition, suggesting the beneficial nature of the polyfluoroalkyl groups of LDH-CF for PFOA capture. Compared to LDH-CH, LDH-CF may have stronger adsorption affinity with PFOA, due to the unique fluorophilic interactions between the C-F chains of PFOA and the polyfluoroalkyl groups of LDH-CF [90,91]. The observed fluorophilic sorption was similar to those utilized in the chemical synthesis process for the separation of fluoro-containing products from reaction mixtures [92].

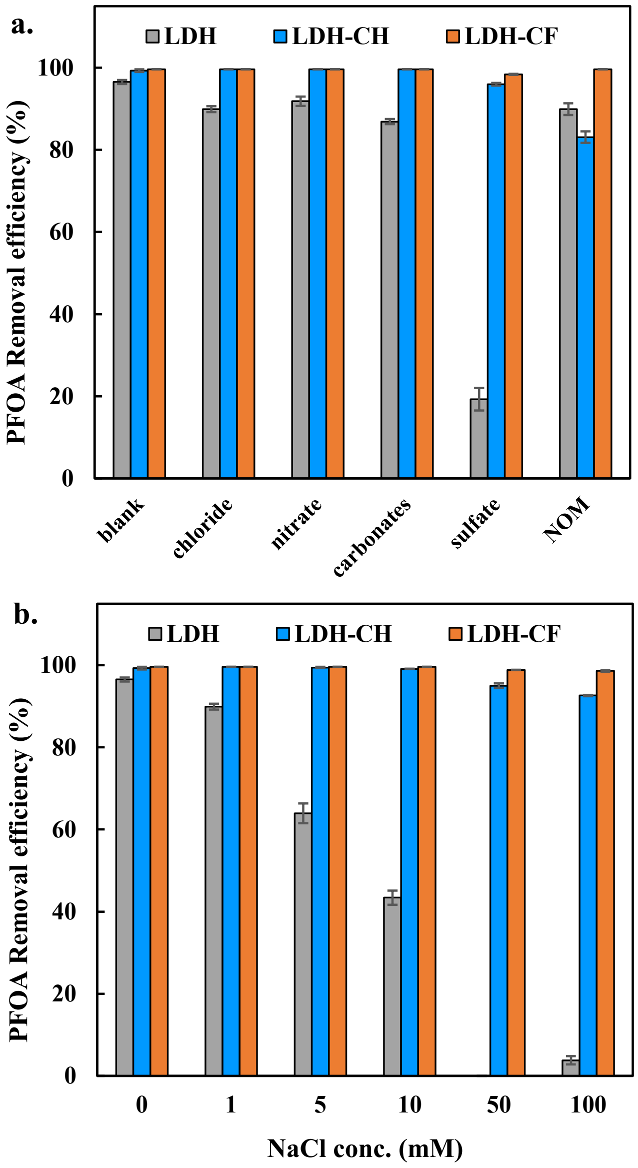

Fig. 7. Effect of (a) common anions (1 mM) and NOM (1 mM as C) and (b) ionic strength (provide by NaCl) on PFOA adsorption onto pristine and organically functionalized LDHs at pH 6 with an initial PFOA concentration of 500 μg/L and an adsorbent loading of 1 g/L. Error bars represent one standard deviation of duplicate experiments.

Additionally, PFOA adsorption was determined under a series of ionic strengths (provided by NaCl). For the unmodified LDH, the PFOA removal efficiency was dramatically reduced with increasing ionic strengths (Fig. 7b), further indicating the important role of electrostatic interactions for PFOA adsorption. An increase of ionic strength could compress the electrical double layer of the positively charged LDH surface, and thus decrease the electrostatic attraction between PFOA and the unmodified LDH [87,94]. Similarly, previous studies also reported that increased salinity strongly reduced the adsorption of PFOA and PFOS onto various LDHs [37,39]. In contrast, increasing ionic strengths had minimal impact on PFOA removal by the organically functionalized LDHs (Fig. 7b), particularly for LDH-CF where an ionic strength as high as 100 mM had negligible impact on PFOA adsorption. Notably, all LDHs also showed excellent PFOA removal efficiency over a range of pH conditions relevant to water treatment (**Figure S10** of the Supplementary Material). Our results suggested that organically functionalized LDHs, particularly LDH-CF, can be very efficient for PFOA removal under various water chemistry conditions.

3.4. Possible adsorption mechanisms

Overall, the improved performance of the organically functionalized LDHs demonstrated the important role of the modified organic functional groups that provided strong affinity with PFOA. Electrostatic and/or hydrophobic interactions have been recognized as main mechanisms for PFOA adsorption onto various types of adsorbents [18]. Based on the experimental results, the possible adsorption mechanisms of PFOA onto the unmodified and organically functionalized LDHs were proposed as follows. The unmodified LDH was hydrophilic and carried positive surface charges over a range of solution pH, according to the water contact angle and zeta potential measurements (**Figures S4 and S5a** of the Supplementary Material). Thus, electrostatic interactions may be the primarily mechanism for PFOA adsorption onto the unmodified LDH [35,37], which was evidenced by (1) the strong inhibitory effect of sulfate due to competitive adsorption and (2) the reduced PFOA removal efficiency with increased ionic strengths because of the compression of the electrical double layer of the LDH. In contrast, modification with organic functional groups increased the hydrophobicity but did not substantially alter the surface charge of the LDHs (**Figures S4 and S5a** of the Supplementary Material). Therefore, both electrostatic and hydrophobic interactions may contribute to the adsorption of PFOA onto the organically functionalized LDHs. The proposed mechanism was supported by the robust performance of the organically functionalized LDHs in the presence of coexisting anions or increased ionic strengths, which suggested that the organically functionalized LDHs showed much stronger affinity with PFOA than that of the unmodified LDH.

To further investigate the PFOA adsorption mechanisms, FTIR spectra of the unmodified and organically functionalized LDHs after PFOA adsorption were obtained. Compared to the materials prior to PFOA adsorption, a new peak centered ~ 1650 cm^{-1} related to C=O stretching of the carboxylate group was observed in the organically functionalized LDHs after PFOA adsorption (**Figure S11** of the Supplementary Material). Meanwhile, although the peak at ~ 1635 cm^{-1} that represented the bending vibration of adsorbed H_2O for the hydrophilic unmodified LDH could be partially overlapped with the C=O stretching peak, this peak shifted slightly to ~ 1650 cm^{-1} for the PFOA-loaded LDH, which suggested the adsorption of PFOA onto the unmodified LDH. Notably, the observed carboxylate C=O stretching in all PFOA-laden materials was redshifted in comparison to the C=O stretching of pure PFOA reported in literature (centered ~ 1750 cm^{-1}) [95], which may be due to the interactions between the positively charged LDH structural layers and the negatively charged carboxylate group of PFOA. Thus, the FTIR result confirmed that electrostatic interactions were likely present in both the unmodified and organically functionalized LDHs for PFOA adsorption.

Furthermore, zeta potential measurements were performed for the unmodified and organically functionalized LDHs after PFOA adsorption and results were compared with the PFOA-free adsorbents. For the unmodified LDH, PFOA adsorption did not substantially alter the point-of-zero charge (pH_{pzc}, **Figure S5** of the Supplementary Material), which indicated the formation of the relatively weak outer-sphere complexes where PFOA may bind with the unmodified LDH outside the shear plane [96]. This observation was consistent with previous spectroscopic study showing that electrostatic interactions would result in the formation of outer-sphere complexes for PFOA adsorption onto minerals [97]. In contrast, the pH_{pzc} of both LDH-CF and LDH-CH shifted from ~ 10 to ~ 6 after PFOA adsorption, suggesting the formation of strong inner-sphere complexes for PFOA adsorption onto the organically functionalized LDHs. Specifically, because of the extra hydrophobic interactions, PFOA may bind more strongly within the shear plane of the organically functionalized LDHs, which reduced the surface charges of the adsorbents and caused the shift of pH_{pzc} to more acidic values [98]. Therefore, zeta potential measurements further suggested that the organically functionalized LDHs had improved PFOA adsorption affinity in comparison to the unmodified LDH, likely as a result of the synergy of electrostatic and hydrophobic interactions.

It is worth mentioning that compared to LDH-CH, LDH-CF showed stronger adsorption affinity with PFOA (reflected by the higher Langmuir constant K_L) and more robust performance under different water chemistry parameters. The enhanced performance of LDH-CF may be attributed to the fluorophilic interactions between the polyfluoroalkyl groups of LDH-CF and C-F chains of PFOA. It has been found that C-F chains had much stronger interactions with C-F chains than C–H chains, because of the unique fluorous chemistry and the more rigid conformational C-F skeletons in comparison to that of the C–H skeletons [90]. Additionally, the unique properties of the polyfluoroalkyl groups of LDH-CF such as oleophobicity may also promote PFOA adsorption through the exclusion of competing anionic substances and NOM [70,93]. The oleophobic nature of LDH-CF was confirmed based on the large contact angle of n-hexadecane (110°, **Figure S12a** of the Supplementary Material); on the contrary, the n-hexadecane contact angle on LDH-CH was close to 0° (**Figure S12b** of the Supplementary Material). The observed fluorophilic sorption in the present work was consistent with previous studies reporting the improved adsorption selectivity and affinity between PFAS and fluoroalkyl-containing materials [70,91,93].

3.5. Regeneration and reuse

The unmodified and organically functionalized LDHs after PFOA adsorption were regenerated using a methanol/water (50%/50%) mixture containing 1 wt% NaCl as the regenerating solution. Nearly complete PFOA desorption was observed for all adsorbents (**Figure S13** of the Supplementary Material), because methanol and NaCl could weaken the hydrophobic and electrostatic interactions between PFOA and the adsorbents, respectively [30]. It was worth mentioning that the characteristic peaks of alkyl and polyfluoroalkyl functional groups were clearly observed in the FTIR spectra of regenerated LDH-CH and LDH-CF, respectively (**Figure S14** of the Supplementary Material), which suggested that the alkyl and polyfluoroalkyl groups were well retained following the adsorbent regeneration process due to the covalent bonding within the LDH substrate. Reuse of the unmodified and organically functionalized LDHs was then investigated by conducting the adsorption/regeneration experiments for three cycles. LDH-CH and LDH-CF had consistently better performance than the unmodified LDH, showing nearly complete PFOA removal for all three cycles (Fig. 8). On the contrary, the performance of the unmodified LDH was slightly reduced over the three cycles, which might be attributed to the possible NaCl accumulation during the material regeneration process that negatively impacted the electrostatic interactions between PFOA and the adsorbent.

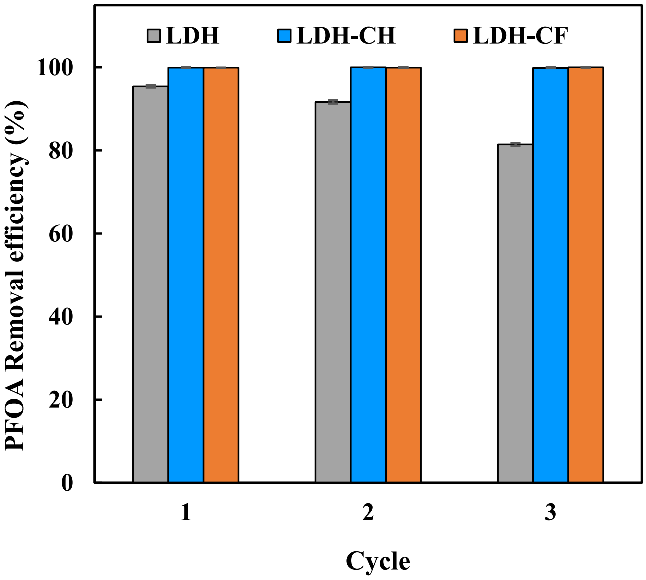

Fig. 8. Reuse of pristine and organically functionalized LDHs for PFOA removal (500 μg/L) at pH 6 with an adsorbent loading of 1 g/L. The adsorbents were regenerated after PFOA adsorption in each cycle with the use of a methanol/water (50%/50%) mixture containing 1 wt% NaCl.

3.6. Removal of multiple PFAS

Since LDH-CF exhibited stronger affinity, faster kinetics, and higher capacity for PFOA adsorption than those of LDH-CH and the unmodified LDH, it was further evaluated for the simultaneous removal of a suite of legacy and emerging PFAS under more environmentally relevant concentrations. Specifically, experiments were performed in a mixture of 10 PFAS that included 6 PFCAs, 3 PFSAs, and GenX, each with a nominal concentration of 10 μg/L. As shown in Fig. 9, >90% removal was achieved for most of the examined PFAS in pure water, suggesting the effectiveness of LDH-CF for the removal of PFAS with varied structures, fluoroalkyl chain lengths, and end functional groups. Even in a natural lake water, LDH-CF showed high removal efficiency of PFBA, PFHpA, PFOA, PFNA, PFDA, PFHxS, and PFOS that were comparable to those in pure water, and the removal efficiency of PFPeA, PFBS, and GenX was only slightly reduced. The result implied the strong adsorption affinity of LDH-CF with various PFAS despite the presence of various competing anionic constituents (Table S2 of the Supplementary Material). Overall, our initial evaluation indicated that LDH-CF may be used for the efficient removal of multiple PFAS.

4. Conclusions

In this study, alkyl chain (i.e., CH) and polyfluoroalkyl (i.e., CF) modified Zn-Al LDHs were developed through covalent bonding and were investigated for the adsorptive removal of PFOA for the first time. Compared to the unmodified LDH, modification with organic functional groups provided strong hydrophobic interactions that were synergistic with the electrostatic interactions of the LDH structural layers, resulting in the substantially improved performance for PFOA adsorption in terms of adsorption kinetics, capacity, and affinity. LDH-CF outperformed LDH-CH, which suggested the beneficial role of polyfluoroalkyl groups for PFOA adsorption likely through the unique fluorophilic interactions. Particularly, LDH-CF showed very fast PFOA adsorption kinetics with equilibrium achieved within 5 min, had a high PFOA adsorption capacity > 1,300 mg/g, and exhibited robust performance that resulted in nearly complete PFOA removal in the presence of various anionic substances, NOM, and a range of ionic strengths. Furthermore, LDH-CF can be readily regenerated and reused, and was efficient for the simultaneous removal of numerous PFAS with different structures. Results of this study suggested that modification of LDHs with organic functional groups may represent a promising approach for the development and application of LDH-based adsorbents for PFAS treatment. To facilitate technology development, future research may emphasize on (1) comprehensive investigation of the adsorption behaviors of various classes of PFAS onto organically functionalized LDHs, (2) elucidation of the impact of organic functional group composition (e.g., chain length) of the adsorbents on the removal of PFAS with different structures, (3) evaluation of the adsorbent performance with PFAS concentrations relevant to drinking water sources and more environmentally relevant settings, (4) development of multi-stage system or treatment train for complete treatment of PFAS, and (5) detailed techno-economic analysis to determine and improve the feasibility of technology.

Declaration of Competing Interest

The authors declare that they have no known competing financial

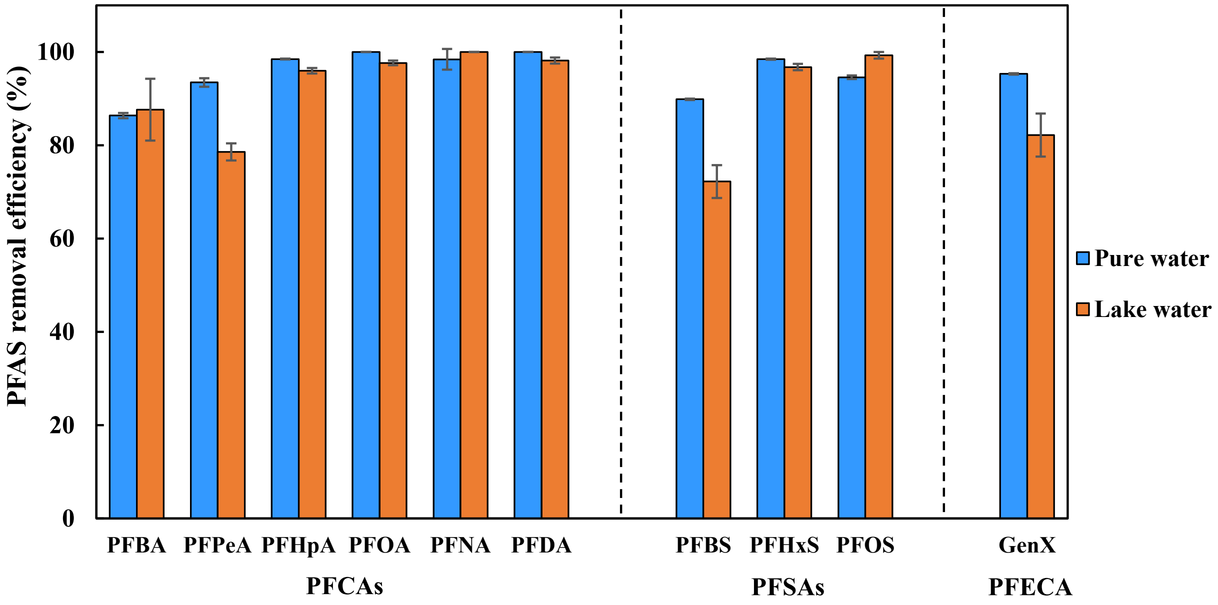

Fig. 9. Removal of a mixture of 10 PFAS (each with a nominal concentration of 10 μg/L) in pure water and lake water using LDH-CF (1 g/L). Error bars represent one standard deviation of duplicate experiments.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This project was supported by Water Equipment & Policy Research Center (WEP) located at University of Wisconsin-Milwaukee (UWM, IIP-2113857) and Marquette University (IIP-2113851). WEP operates under the auspices of the National Science Foundation Industry/University Cooperative Research Center Program. We acknowledge the use of FTIR, TGA, and zeta potential measurements in the Water Technology Accelerator at UWM. XRD and XPS measurements were conducted in the Advanced Analysis Facility. SEM was performed in the Department of Biological Sciences at UWM. We thank Mr. Patrick Anderson at UWM for his assistance with the carbon elemental analysis. LC-MS/MS analysis was performed in the Shimadzu Laboratory for Advanced and Applied Analytical Chemistry at UWM. We appreciate the comments of the three anonymous reviewers that improved the presentation of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2022.137019.

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