



Behavior and mechanisms for sorptive removal of perfluorooctane sulfonate by layered double hydroxides



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HIGHLIGHTS

- The maximum PFOS uptake capacity was 865 mg/g for the nitrate-LDH.
- Fast kinetics were observed with an equilibrium time of 20 min at 1 mg/L PFOS.
- Competing sulfate and carbonate anions reduced PFOS sorption by LDHs.
- Both anion exchange and surface adsorption played a role in the sorption mechanism.

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ABSTRACT

Perfluorooctane sulfonate (PFOS) is known to be extremely persistent and is toxic to wildlife and humans. In this study, we evaluated the sorptive removal behavior of PFOS from aqueous solution using three forms of layered double hydroxides (LDHs), namely, nitrate-, carbonate- and chloride-intercalated LDHs. Batch experiments showed that the sorption process was very fast with an equilibrium time of 10–60 min. The nitrate-LDH had the greatest ability to remove PFOS with a removal rate of 99.7% at an initial concentration of 100 mg/L and the maximum uptake capacity reached 865 mg/g. The sorption kinetic and equilibrium data could be fitted well with the pseudo-second-order model and Langmuir model, respectively. The intraparticle diffusion model suggests that both external diffusion and intraparticle diffusion are the rate-limiting processes for PFOS sorption onto the LDHs. The initial pH, background electrolyte concentration and coexisting ions influenced the sorption of PFOS by the LDHs. It was concluded that both surface adsorption and anion exchange were involved in the PFOS sorption onto the LDHs.

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1. Introduction

Perfluorinated compounds (PFCs) have been used worldwide since the 1950s in a variety of applications, such as surfactants, coatings and firefighting foams, due to their unique physicochemical properties. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the two most commonly detected PFCs in all environmental media. In addition to PFOS and PFOA being universally found in wildlife (Kannan et al., 2001a, 2001b; Müller et al., 2011; Reiner et al., 2011; Greaves et al., 2012), they are also

the two dominant PFCs found in human breast milk (So et al., 2006). However, it has been recognized that PFOS is much more bioaccumulative than PFOA (Kannan et al., 2005). PFOS has been defined as an emerging contaminant and is listed in Annex B of the Stockholm Convention on Persistent Organic Pollutants (Wang et al., 2009). It was reported that PFOS tends to reside in surface waters, especially oceans (Paul et al., 2009), and it has the potential to enter groundwater (Murakami et al., 2009). Therefore, PFOS in aquatic environment is a significant threat to ecosystems and human health.

PFOS is highly persistent due to its strong C–F binding energy (110 kcal/mol) and is resistant to most conventional treatment technologies. Different from PFOA, PFOS does not undergo any

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transformation when treated with activated persulfate (Park et al., 2016) and irradiated by ultraviolet–visible light (Hori et al., 2006). So far, there have been some studies on the PFOS remediation technologies. For example, sonochemical degradation of PFOS through cleavage of the perfluorocarbon chain has been observed, generating products with lower toxicity (Moriwaki et al., 2005). The catalytic reductive dehalogenation of PFOS by employing a biomolecule was first reported in 2008 (Ochoa-Herrera et al., 2008). In the presence of zero valent iron as a reducing agent, PFOS was efficiently decomposed to a fluoride ion in subcritical water (Hori et al., 2006). Kwon et al. firstly reported aerobic biodegradation of PFOS by a specific microorganism after 48 h of incubation, although there was some debate over the validity of its conclusions (Kwon et al., 2014).

In addition to energy-consuming chemical treatments, moderate physical treatments, including reverse osmosis and nanofiltration (Tang et al., 2007), enhanced coagulation (Xiao et al., 2013) and sorptive removal using various sorbents (Du et al., 2014), have also been investigated for PFOS treatment. Activated carbons and resins (Yu et al., 2009), cross-linked chitosan beads (Zhang et al., 2011) and surfactant-modified montmorillonite (Zhou et al., 2010) were proved to be effective in removing PFOS from water. Due to their ease of implementation and cost-effectiveness, novel and effective sorbents for the removal of PFOS have been of interest recently.

Layered double hydroxides (LDHs), a class of ionic lamellar compounds made of positively-charged brucite-like layers with an interlayer region containing charge compensating anions (Wang and O'Hare, 2012), can serve as inorganic minerals and sorbents, capable of removing toxic oxyanions in water, owing to their significant anion exchange capacity. Their layered structure has been studied extensively (Lv et al., 2006; Grover et al., 2009) and can be described by the formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are metal cations occupying the octahedral centers in the infinite hydroxide layers and A^{n-} is an exchangeable anion. LDHs, as well as calcined LDHs, have been used to remove anions, like arsenite (Grover et al., 2009), chromate (Alvarez-Ayuso and Nugteren, 2005), selenite (Liu et al., 2009), phosphate (Das et al., 2006), chloride (Lv et al., 2006) and so on. The sorption behaviors of various forms of LDHs when treating different oxyanions have been reviewed in detail (Goh et al., 2008). In addition, calcined LDHs can be effective as a result of the memory effect, where the layer structure disappears after calcination and recovers through anion uptake from an aqueous solution. Furthermore, materials derived from LDHs exhibit significant ability in reducing sulfur oxides (Cantú et al., 2005), nitrogen oxides (Yu et al., 2007) and carbon dioxide (Wang et al., 2008). With a low pKa value of -3.27 , PFOS in water usually exists in an anion form. Thus, there is the potential for LDHs to remove PFOS in aqueous solution.

The objective of this work is to study the removal of PFOS in aqueous solution using different forms of LDHs via sorption kinetics and isotherm batch experiments. The effect of solution chemistry on PFOS removal is also investigated. In addition, the mechanisms for PFOS sorption by the LDHs are explored.

2. Materials and methods

2.1. Chemicals and reagents

Magnesium nitrate ($Mg(NO_3)_2$, 99%), aluminum nitrate ($Al(NO_3)_3$, 99%), potassium nitrate (KNO_3 , 99%), calcium nitrate ($Ca(NO_3)_2$, 99%), magnesium chloride ($MgCl_2$, 98%), aluminum chloride ($AlCl_3$, 97%), sodium carbonate (Na_2CO_3 , 99.8%), potassium carbonate (K_2CO_3 , 99%), potassium sulfate (K_2SO_4 , 99%), nitric acid (HNO_3 , 65–68%), sodium hydroxide ($NaOH$, 96%), aqueous

ammonia solution (NH_3 , 25–28%), ammonium acetate (CH_3COONH_4 , 98%) and acetic acid (CH_3COOH , 99.5%) were of analytical grade and were purchased from Sinopharm Chemical Reagent Corporation Ltd. (Beijing, China). The PFOS used was of potassium salt and was purchased from Adamas Reagent, Ltd. (Shanghai, China). Chromatographically pure methanol was used for chromatographic analysis. The ultrapure water ($18.3 M\Omega \cdot cm$) used in this study was generated by a Milli-Q system.

2.2. Synthesis and characterization of LDHs

LDHs with nitrate, carbonate and chloride ions in the interlayers were prepared based on coprecipitation procedures described elsewhere (Olanrewaju et al., 2000; Lv et al., 2006; Grover et al., 2009), where the LDHs were prepared for inorganic anion sorption. For the nitrate-LDH, a 100-mL mixed solution of 1.2 M $Mg(NO_3)_2$ and 0.4 M $Al(NO_3)_3$ was prepared with the molar ratio $Mg^{2+}/Al^{3+} = 3:1$. The mixed salt solution was then introduced to 100 mL of a 6 M ammonia solution in a dropwise manner under vigorous stirring conditions. After completion of the reaction, the white slurry was aged at room temperature for 24 h and then centrifuged to collect the solids. The solids were washed with distilled water several times to remove dissolved impurities and lyophilized in a vacuum freeze drier at $-50^\circ C$. The obtained solids were ground fine with a pestle and mortar, and sieved with a 150-mesh sieve. The powder was stored in a desiccator before use. Similarly, a mixed solution of $MgCl_2$ and $AlCl_3$ was introduced into a 6 M NaOH solution to synthesize the chloride-LDH. For the carbonate-LDH, a mixed solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ was introduced into a mixed solution of 6 M NaOH and 0.8 M Na_2CO_3 . Typically, the nitrate-LDH with a Mg^{2+}/Al^{3+} molar ratio of 3:1 was denoted as Mg_3Al-NO_3 .

The point of zero charge (pH_{pzc}) of the LDHs was determined using the pH drift method (Srivastava et al., 2011). Briefly, 0.01 g of LDHs powder and 100 mL of 0.01 M NaCl solution, with various pH values ranging from 6 to 12, were introduced into conical flasks. After adequate shaking for 24 h, the final pH values were measured and plotted versus the initial pH values. The point on the curve where the initial pH value is equal to the final pH value was denoted as the pH_{pzc} .

X-ray diffraction (XRD) patterns of all LDH samples were obtained by employing an X'TRA powder diffractometer (ARL, Ecu-blens, Switzerland) operated at 40 kV and 40 mA with $CuK\alpha$ radiation starting from 3° to 80° at a scanning rate of $0.6^\circ/min$. Fourier transform infrared (FTIR) spectra were recorded with a Nexus 870 spectrometer (Nicolet, Madison, WI, USA). An ASAP 2020 Accelerated Surface Area and Porosimetry system (Micromeritics, Norcross, GA, USA) was used to conduct the N_2 adsorption-desorption studies for different LDHs. The specific surface area was obtained using the Brunner-Emmett-Teller (BET) method, while the porosity was analyzed with the Barret-Joyner-Halenda method.

2.3. Batch experiments

Batch experiments were conducted by introducing 40 mL of a PFOS working solution into 50 mL polypropylene centrifugal tubes with 0.01 g of LDH powder. The tubes were then placed into a horizontal shaker at 150 rpm with a constant temperature of $25^\circ C$. The LDHs with different intercalated anions were used for comparative studies. Each test was done in triplicate.

In the kinetics study, a stock solution of 100 mg/L PFOS was introduced into polypropylene centrifuge tubes to make diluted working solutions. Samples were extracted at designated time intervals. For the isotherm study, concentrated solutions ranging

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