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Competitive adsorption of perfluoroalkyl substances on anion exchange resins in simulated AFFF-impacted groundwater

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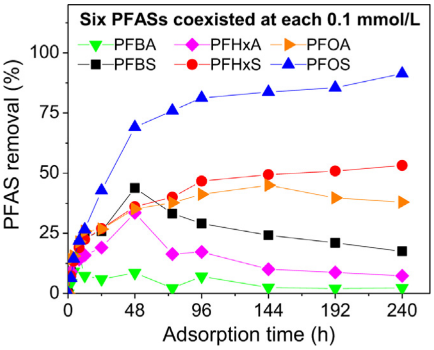
HIGHLIGHTS

- Strong base anion-exchange resin IRA910 is effective for PFASs removal.
- Competitive sorption follows the order of PFOS > PFHxS > PFOA > PFBS > PFHxA > PFBA.
- PFASs with short C-F chain are exchanged by those with long C-F chain.
- Competitive sorption is related to hydrophobicity and molecular size of PFASs.
- Coexisting organic anions decrease the removal efficiency of PFHxS.

GRAPHICAL ABSTRACT



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ABSTRACT

The historical use of aqueous film forming foams (AFFF) containing perfluoroalkyl substances (PFASs) for firefighting and training activities has resulted in groundwater contamination. The competitive adsorption of PFASs and the effect of co-existing compounds on the removal of PFASs by anion-exchange resins were studied in this study. Perfluorohexane sulfonate (PFHxS) was selected as the representative PFAS, and resin IRA910 was found to be effective for PFHxS removal. When PFHxS was co-removed with other PFASs in bisolute system, it replaced the adsorbed PFASs with shorter C-F chains on the IRA910, while perfluorooctanesulfonate (PFOS) was not replaced by PFHxS. The competitive adsorption among PFASs decreased in the order of PFOS > PFHxS > PFOA > PFBS > PFHxA > PFBA, closely related to the hydrophobicity and functional groups of PFASs. The nonionic organic compounds could not interfere with the PFHxS removal, while ionic ones can reduce the sorption amount and their influence to the sorption of PFHxS was concentration dependent. The presence of inorganic anions slightly decreased the removal efficiency of PFHxS and the influence of different inorganic anions was similar due to multiple effects including competitive anion, screening effect, and salting-out effect in the adsorption process.

1. Introduction

Perfluoroalkyl substances (PFASs) are a class of organic compounds that hydrogen atoms are fully substituted by fluorine atoms. Their perfluoroalkyl moiety imparts their enhanced properties including stronger thermal, acidic, basic, and redox stability, lower surface

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tension, water and oil repellency compared to their hydrocarbon counterparts because of the strong electronegative fluorine atoms which shield carbon backbone from physical and chemical attacks [1]. Thus, the PFASs are widely used in the manufacture of industrial and commercial products, surfactants, surface protecting agents, and aqueous film forming foams (AFFFs) [2,3]. The large-scale releases of AFFF during extinguishing hydrocarbon-fuel fires and fire training exercise have resulted in the contamination of groundwater with PFASs. Although PFOS, PFOA, and their related compounds were the most widely used fluorinated surfactants in AFFF [4,5], the recent studies have found that they are not always the most abundant PFASs in AFFF-impacted groundwater [6–8] since actions to reduce the release of long-chain PFASs and precursors have been taken by industry and regulators due to their undesired impacts on humans and the environment [9]. Recently, the high concentrations of perfluorohexane sulfonate (PFHxS) have been also detected in AFFF contaminated groundwater [6–8] probably because of the degradation of newly-identified fluorotelomer and electrofluorination based alternatives [6,7]. PFHxS also belongs to long-chain PFASs and possesses a longer half-life in humans than PFOS and PFOA [9,10].

Adsorption is an efficient method to remove PFASs [11–13], and some effective adsorbents such as activated carbon [13–15], anion-exchange resin [16–18], fluorinated clays [19,20], modified biomass [21,22], and β-cyclodextrin polymer [2] have been used to remove PFASs. Among them, activated carbon and anion-exchange resins have been the most widely used [11,13,23,24]. Activated carbon is effective for the long-chained ones [24], while anion-exchange resins can remove both long- and short-chained PFASs, but the long-chained PFASs are difficult to diffuse into some resins [23]. Several studies have also been carried out to examine the adsorption of PFASs using different anion exchange resins [1,15,16,23,25]. Besides the porosity and functional groups, the resin matrix also had significant effect on the sorption kinetics and capacity of PFASs on six different anio-exchange resins, and polyacrylic resins exhibited faster and higher sorption capacity for PFOS than polystyrene resins [16]. It has been reported that the presence of one hydroxyl group close to the quaternary nitrogen can make macroporous strong base polystyrene resin more hydrophilic and provide a more open structure [25], favorable for PFOS adsorption. However, most of the previous researches focused on PFOS, PFOA, PFBS and PFBA, and few studies investigated the removal of PFHxS in AFFF-contaminated groundwater by resins [6–8]. Furthermore, different PFASs usually exist in AFFF-impacted groundwater and some researchers found that the longer-chain PFASs competed with the shorter-chain ones [26], but the competition between different PFASs such as perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) has not been fully explored. Besides, other AFFF components, unburned jet fuel components, chlorinated solvents and dissolved organic matters found in AFFF-impacted groundwater [3,27,28] may affect the adsorption behavior of PFASs. However, very few study investigated the effect of co-existing contaminants effect, and the influence of DOM on removal of PFASs by granulated AC and anion exchange resin was recently reported [13].

In this study, we selected the optimal resin IRA910 to remove six PFASs from simulated AFFFs-impacted groundwater. The competitive adsorption among different PFASs and the effects of co-existing organic and inorganic compounds in groundwater were investigated, and the underlying adsorption mechanism was discussed. The exchange of short C-F chain PFASs by long C-F chain PFASs was fully clarified. This study is useful to select effective adsorbents for the removal of PFASs in AFFF-impacted groundwater.

2. Materials and methods

2.1. Chemicals and materials

Perfluorooctanesulfonate (PFOS), perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS) (all potassium salts, purity > 98%), and PFOA (≥96%), perfluorohexanoic acid (PFHxA, ≥97%), and perfluorobutanoic acid (PFBA, ≥98%) were purchased from Sigma-Aldrich (St. Louis, MO). Their structures are showed in Table 1. HPLC-grade methanol was purchased from Fisher Chemical (USA). Other chemicals including humic acid (HA), trichloroethylene (TCE), methylbenzene (MB), and sodium dodecyl sulfate (SDS) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). Four anion exchange resins including Amberlite IRA 67, IRA 96, IRA 400, and IRA 910 were purchased from Rohm and Haas Company, and their main properties are shown in Table S1. All resins were used in the chloride form [29] and dried at 50 °C until constant weight before the sorption experiments.

Table 1
Physicochemical properties of the PFASs used in this study.

PFASs	Chemical formula	Molecular length (nm)[a]	Solubility (g/L)[a]	pK_a[b]	LogK_{ow}[c]
PFBA	$CF_3(CF_2)_2COOH$	0.60	NA	0.4	−0.66
PFBS	$CF_3(CF_2)_3SO_3K$	0.81	46.2	0.14	0.03
PFHxA	$CF_3(CF_2)_4COOH$	0.81	15.7	−0.16	0.7
PFHxS	$CF_3(CF_2)_5SO_3K$	1.07	1.4	0.14	1.24
PFOA	$CF_3(CF_2)_6COOH$	1.11	3.4	−0.2	1.9
PFOS	$CF_3(CF_2)_7SO_3K$	1.33	0.57	−3.27	2.45

[a] The molecular lengths of PFASs in anion form were calculated in ChemBio3D Ultra software at minimal energy mode.

[b] [30].

[c] The log K_{ow} of anionic species of PFASs [31].

2.2. Adsorption experiments

Adsorption experiments were conducted at 25 °C with a shaking speed of 160 rpm for 240 h in an orbital shaker excluding kinetic adsorption experiments. The solid/liquid ratio performed in all adsorption experiments was 0.1 g/L except the multi-solute system. All solutions were adjusted to pH 6 with NaOH and HCl except for the pH effect experiments. In the adsorption isotherm experiments, 100 mL of different PFASs solutions with concentrations from 50 to 400 mg/L and IRA910 were added into conical flasks. For the sorption kinetics of single-solute systems, 250 mL of PFASs solution with the initial concentration of 0.5 mmol/L and IRA910 were added into conical flasks for adsorption. The competitive sorption experiments of PFHxS with other five different PFAS were also carried out in the bisolute system and multi-solute system. In bisolute system, the initial concentration of each PFAS was 0.5 mmol/L, while it was 0.1 mmol/L and the solid/liquid ratio was 0.05g/L for the multi-solute system. The pH effect experiments were conducted at pH 6 and pH 9 and other conditions were the same as single solute kinetic adsorption experiments.

To investigate the influence of coexisting organic matters in AFFF impacted ground water on PFASs removal, humic acid (HA), trichloroethylene (TCE), methylbenzene (MB), and sodium dodecyl sulfate (SDS) were selected as coexisting organic compounds. TCE as a chlorinated solvent, was repeatedly used to create fires for fire-fighter training exercises [28,32]. SDS as anionic hydrocarbon surfactant, is one of the ingredients of AFFF formulation [3]. MB is one of soluble compositions of hydrocarbon fuel [27]. Humic acid represented as the natural organic matter which is ubiquitous in groundwater [33]. PFHxS was dissolved with different organic compounds separately at 0.5 mmol/L. The concentrations of coexisting organic compounds were set to be in the range of 0–5 mmol/L and all are under the solubility of these substance (Table S6). For HA, the concentration was in the range of 0–200 mg/L.

In consideration of the influence of inorganic anions existed in groundwater including nitrate, sulfate, bicarbonate and phosphate, the adsorption experiments of PFHxS on resin IRA910 in the presence of

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