



Removal of Perfluoroalkyl Substances by PAC Adsorption and Anion Exchange [Project #4344]

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OBJECTIVES

The principal objective of this research was to assess the effectiveness of powdered activated carbon (PAC) adsorption and anion exchange processes for the removal of perfluoroalkyl substances (PFASs, also commonly referred to as perfluorinated chemicals or PFCs) from drinking water sources. Specific objectives were as follows:

1. Assess the effectiveness of commercially available PACs with a wide range of physical-chemical characteristics for PFAS removal
2. Determine whether enhanced PFAS removal can be accomplished with superfine PAC (S-PAC) as a result of faster PFAS adsorption kinetics and/or a larger PFAS adsorption capacity
3. Evaluate the effects of resin type and dose as well as background water quality on PFAS removal by anion exchange
4. Identify regeneration conditions that restore the PFAS removal capacity of anion exchange resins and measure the PFAS removal effectiveness of an anion exchange resin over multiple loading/regeneration cycles

Apart from the commonly studied perfluorooctanoic acid (PFOA or C8) and perfluorooctane sulfonate (PFOS), eight additional PFASs were evaluated: perfluorobutanoic acid (C4), perfluoropentanoic acid (C5), perfluorohexanoic acid (C6), perfluoroheptanoic acid (C7), perfluorononanoic acid (C9), perfluorodecanoic acid (C10), perfluorobutane sulfonate (PFBS), and perfluorohexane sulfonate (PFHS).

BACKGROUND

PFASs are organic compounds in which all carbon-hydrogen bonds are replaced with carbon-fluorine bonds. PFASs are surfactants that serve as active ingredients in stain repellents (e.g., Scotchgard) and firefighting foams. They are also used in the manufacture of such materials as non-stick coatings (e.g., Teflon), water repellent fabrics (e.g., GoreTex), and microwave popcorn bags. Two commonly studied PFASs are C8 and PFOS, two 8-carbon compounds. C8 and PFOS are of human health concern because they are probable human carcinogens and have

long half-lives in the human body (about 4 years for C8 and about 5 years for PFOS). Apart from C8 and PFOS, a wide range of additional PFASs has been detected in drinking water sources.

Because drinking water is an important PFAS exposure route, the U.S. Environmental Protection Agency (EPA) issued a drinking water Provisional Health Advisory for C8 and PFOS at 0.4 and 0.2 $\mu\text{g/L}$, respectively, which is meant to protect against subchronic exposure. The state of New Jersey has developed a more stringent C8 guideline of 0.04 $\mu\text{g/L}$ to protect consumers from adverse health effects associated with chronic C8 exposure.

Conventional drinking water treatment processes (coagulation, sedimentation, filtration, chlor[am]ination) are not effective for PFAS removal. Furthermore, advanced oxidation processes (ozone, UV/H₂O₂) are unable to oxidize PFASs because of the strength of the carbon-fluorine bond. Treatment processes that have shown promise for PFAS removal include activated carbon adsorption, anion exchange, nanofiltration, and reverse osmosis. The focus of the current research was on the former two treatment processes with the goal to fill the following knowledge gaps:

1. Quantify the removal of ten PFASs rather than focus only on the commonly studied C8 and PFOS
2. Determine treatment effectiveness at drinking water-relevant PFAS concentrations (500 ng/L for each PFAS rather than the higher concentrations used in most prior studies)
3. Assess treatment performance of unconventional PACs such as superfine PACs
4. Determine anion exchange resin performance over multiple uptake/regeneration cycles, which requires the determination of suitable resin regeneration strategies

APPROACH

Experiments evaluating PFAS removal were conducted with five commercially available PACs prepared from different base materials (wood, coconut shell, lignite, and bituminous coal) and with different activation methods (chemical and thermal). The five PACs were each wet-milled to produce a corresponding S-PAC. PFAS removal was also evaluated with four commercially available anion exchange resins certified for drinking water treatment. Resin types included strong and weak base anion exchange resins containing quaternary amine and tertiary amine groups, respectively. Both acrylic and styrene-divinylbenzene copolymer resins were studied in gel and macroporous forms. Experiments were conducted in salt-amended ultrapure water and in two drinking water sources (North Carolina reservoir water and Ohio River water) that were spiked with ~ 500 ng/L of each PFAS. The different water sources permitted the evaluation of background water matrix effects on PFAS removal by both (S-)PAC adsorption and anion exchange. Factors such as the presence and absence of dissolved organic matter (DOM), solution pH, and ionic strength were assessed. The performance of (S-)PACs was evaluated in batch kinetic tests, adsorption isotherm tests, and jar tests. PFAS removal by anion exchange resins was determined in batch kinetic tests and in sequential loading/regeneration experiments.

RESULTS/CONCLUSIONS

Powdered Activated Carbon Adsorption

PFAS Adsorbability by (S-)PACs with Different Physicochemical Properties

Batch kinetic tests in ultrapure water (UPW) were conducted to determine the adsorbability of PFASs in the absence of DOM. A 15 mg/L dose of (S-)PAC was added to salt-amended UPW with an ionic strength of 0.02 and pH 7. Regardless of the tested (S-)PAC, C4 removal was negligible, while PFOS removal was essentially complete. PFAS removal increased with increasing perfluorinated carbon chain length, and for a given perfluorinated carbon chain length, sulfonates were more adsorbable than carboxylates. PFAS adsorption rates on S-PAC were more rapid than on as-received PACs, primarily because of the smaller particle size of S-PACs. For PFAS uptake from UPW, the most effective adsorbents had a large primary micropore volume (pore width < 1 nm) and exhibited a net positive surface charge at pH 7.

The presence of DOM greatly reduced the effectiveness of (S-)PACs for PFAS removal. In North Carolina (NC) reservoir water, none of the as-received PACs removed >50% of any PFAS (PAC dose: 15 mg/L, t: 2 hours), and only two S-PACs (coconut-based and thermally activated wood-based) achieved >90% C10 and PFOS removal. A large mesopore volume helped reduce the adverse effects of DOM on PFAS adsorption. Surface charge of the virgin adsorbent appeared to have a smaller effect on PFAS adsorption when DOM was present, presumably because adsorbed DOM, which is anionic in nature, altered the adsorbent surface charge in a manner that negatively affected the adsorbability PFAS anions. While PFAS adsorbability increased with decreasing pH and ionic strength in UPW, pH and ionic strength had a negligible effect on PFAS adsorption from drinking water sources containing DOM.

Adsorption Isotherms

Adsorption isotherm experiments were conducted to measure PFAS adsorption capacities of thermally activated wood-based carbons in as-received and superfine forms. Adsorption capacities (q values) of the ten PFASs spanned ~3 orders of magnitude in UPW and ~2 orders of magnitude in the drinking water sources. Relative to results obtained in amended UPW, PFAS uptake capacities were lower in the two drinking water sources. For C6-C10 and the sulfonates, q values at an equilibrium aqueous phase concentration of 10 ng/L were 2.9-10.9% of those obtained in amended UPW, and, on average, were 45% larger in Ohio River water than in NC reservoir water. PFAS adsorption isotherms obtained in NC reservoir water were similar for the as-received and superfine carbons.

Jar Tests

The objective of the jar tests was to evaluate the removal of PFASs with (S-)PACs under coagulation conditions typically used by surface water treatment plants. At an adsorbent dose of 15 mg/L, PFAS removal percentages obtained in jar tests closely matched those obtained in batch kinetic tests, suggesting that the presence of aluminum hydroxide floc had a negligible effect on (S-)PAC performance. At a dose of 50 mg/L, the as-received wood-based PAC (thermally activated) was not able to remove measurable quantities of C4 and C5; C6 and PFBS removals were about 30%, and C10 and PFOS removals reached about 75%. At the same dose, the superfine

version of this carbon also failed to remove C4 and C5; C6 and PFBS removals were about 40%, and removals of the remaining PFASs (C7-C10, PFHS, PFOS) ranged from 78-95%. Coagulation pH (5.5, 6.2, 7.5) and was found to have little influence on PFAS removal.

Anion Exchange

Resin Type and Background Water Matrix Effects on PFAS Removal

Batch kinetic tests were conducted with three strong base anion (SBA) and one weak base anion (WBA) exchange resin. As was the case with PAC, PFAS uptake by the polyacrylic SBA resin (Resin 1) increased with increasing perfluorinated carbon-chain length of the carboxylates and sulfonates. However, removal of the three sulfonates by Resin 1 exceeded that of any of the seven tested carboxylates. Among the four tested resins, Resin 1 exhibited the fastest PFAS uptake kinetics, due in part to the small particle diameter of Resin 1 (180 μm). Different results were obtained for the styrene-divinylbenzene-based SBA resins (Resins 2 and 3), for which a general trend of increasing PFAS removal with decreasing molecular weight was observed. Overall, the highest PFAS removal percentages after a contact time of 2 hours were obtained with Resins 2 and 3 (>89% removal of all tested PFASs). At pH 7.5, the WBA resin performed more poorly with less than 82% removal for all PFASs. WBA resins are expected to perform more effectively at lower pH values, at which tertiary amine sites become protonated. Solution pH and DOM had a negligible effect on PFAS removal, but PFAS removal decreased with increasing ionic strength. At equivalent concentrations, the effect of individual anions on PFAS removal by Resin 1 was bicarbonate < chloride < sulfate < nitrate.

Anion Exchange Resin Regeneration and Cyclic Loading Tests

The effectiveness of regeneration strategies was assessed with Resin 1. Factors that were considered included (1) regenerant composition (chloride/sulfate, acidic/ambient pH, aqueous regenerant or water/methanol mixture), (2) regenerant batch volume (3 and 30 bed volumes per batch), and (3) number of sequential regenerant batches. Cyclic loading tests and associated mass balances showed that complete PFAS recovery was obtained after regeneration with four 30-bed volume batches of a 0.76 M NaCl in a methanol/water mixture (50/50). Based on PFAS removal results over six loading/regeneration cycles, the regenerant volume may be reduced by 90% to four 3-bed volume batches of the same regenerant without degrading PFAS removal. Longer-term studies are required to optimize resin regeneration strategies (e.g. aqueous NaCl for routine regenerations interspersed with NaCl in methanol/water for targeted PFAS removal).

APPLICATIONS/RECOMMENDATIONS

Overall, the results of this research illustrate that PFASs are difficult to remove by (S-)PAC adsorption and anion exchange. With respect to PFAS removal by (S-)PACs, jar test results illustrated that more than 50 mg/L of the most effective as-received PAC, a thermally activated wood-based carbon, would be required to achieve 90% removal of any of the tested PFASs. With the superfine version of the same carbon, doses between 40 and 50 mg/L would be required to reach 90% removal of C9, C10, and PFOS. Thus, if adsorption equilibrium is not obtained, as is the case for most conventional surface water treatment plants, 90% PFAS removal by both as-

received and superfine PACs requires adsorbent doses that are prohibitively high. If contact times are sufficiently long to approach adsorption equilibrium, 90% removal of C8-C10, PFHS, and PFOS is possible from NC reservoir water with PAC doses of 23 mg/L or lower, and from Ohio River water with PAC doses of 17 mg/L or lower. For situations in which 50% PFAS removal is sufficient, the use of (S-)PAC becomes more attractive. At the non-equilibrium conditions evaluated in jar tests, 28 mg/L of thermally activated wood-based PAC in as-received form or <15 mg/L in superfine form would achieve 50% removal of C8-C10, PFHS, and PFOS. At adsorption equilibrium, 50% removal starts becoming feasible for C6, C7, and PFBS. However, 50% C5 and C4 removal cannot be readily achieved by (S-)PAC adsorption.

Anion exchange processes show greater promise for PFAS removal, provided that resins are regenerated in a manner that restores, at least periodically, the PFAS removal capacity. Among the tested resins, the polyacrylic SBA resin exhibited the fastest PFAS uptake rates, while the polystyrene-based SBA resins were the only ones that permitted >90% C4-C6 removal at reasonable resin use rates (5 mL/L or 200 bed volumes). Regeneration with a 50/50 water/methanol mixture containing NaCl (0.76 M was tested in this study) is at least periodically required to restore the PFAS uptake capacity of Resin 1.

A possible alternative for PFAS removal could be a hybrid adsorption/anion exchange treatment approach, in which more strongly adsorbing PFASs are initially removed by activated carbon and the more weakly adsorbing PFASs subsequently by anion exchange. The hybrid approach may facilitate resin regeneration, which is more readily accomplished if only PFASs that interact more weakly with the resin need to be removed.