

ABSTRACT

AREVALO PEREZ, ELISA CAROLINA. Removal of Perfluorinated Compounds by Anion Exchange: Factors Affecting Resin Performance and Regeneration. (Under the direction of Detlef R.U. Knappe).

Perfluorinated compounds (PFC) are organic compounds in which all carbon-hydrogen bonds are replaced with carbon-fluorine bonds. PFCs are used in the production of stain repellants, non-stick coatings, and firefighting materials. Two important PFC classes are perfluorocarboxylic acids (PCAs) such as perfluorooctanoic acid (C8, PFOA) and perfluorinated sulfonic acids (PSAs) such as perfluorooctane sulfonate (PFOS). C8 and PFOS are the most commonly studied PFCs because of their toxicity, persistence, and long half-lives in humans. The EPA issued a drinking water Provisional Health Advisory for C8 and PFOS at 0.4 and 0.2 $\mu\text{g/L}$, respectively. Apart from C8 and PFOS, a wide range of additional PFCs have been detected in drinking water sources. Both PCAs and PSAs are strong acids and therefore occur predominantly in anionic form at common water treatment pH values. Objectives of this research were to (1) assess the effectiveness of a magnetic anion exchange resin for the removal of seven PCAs and three PSAs, and (2) identify regeneration strategies that effectively restore the PFC uptake capacity of the spent anion exchange resin.

Batch and sequential loading experiments were conducted to identify factors that affect the removal of seven PCAs and three PSAs. A commercially available magnetic anion exchange resin certified for drinking water treatment was evaluated. The selected strong base anion (SBA) exchange resin has a polyacrylic, macroporous matrix and contains quaternary amine groups as ion exchange sites. Experiments were conducted in salt-amended ultrapure

water and in two drinking water sources that were spiked with 500 ng/L of each PFC. The effects of dissolved organic matter (DOM), solution pH, and ionic strength on PFC removal were assessed. Resin regeneration was evaluated in batch tests, and factors such as regenerant anion type, pH, and solvent matrix were investigated.

PFC uptake increased with increasing perfluorinated carbon-chain length, and PSAs were more effectively removed than PCAs. At typical resin operating conditions (500-1,000 bed volume equivalents), removal of perfluorobutanoic acid (C4) ranged from ~30-55% while that of PFOS exceeded 95%. Solution pH and DOM had a negligible effect on PFC removal, but PFC removal decreased with increasing ionic strength. At equivalent concentrations, the effect of individual anions on PFC removal generally was bicarbonate < chloride < sulfate < nitrate for PCAs and bicarbonate < chloride ~ sulfate < nitrate for PSAs.

Regarding regeneration strategies, results from cyclic loading tests and associated mass balances showed that complete PFC recovery was obtained when regenerating the resin with four 30-bed volume batches of a 0.76 M NaCl in a methanol/water mixture (50/50). Alternatively, the regenerant volume may be reduced by 90% to four 3-bed volume batches of the same regenerant without degrading PFC removal over six loading/regeneration cycles. Longer-term studies are required to optimize resin regeneration strategies.

Overall, the results of this research illustrate that >90% removal is feasible at typical operating conditions for the tested PSAs and for PCAs with seven or more perfluorinated carbons. To maintain the PFC removal capacity, the resin needs to be regenerated in a manner that restores, at least periodically, the PFC removal capacity.

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Removal of Perfluorinated Compounds by Anion Exchange: Factors Affecting Resin
Performance and Regeneration

by
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DEDICATION

Quiero dedicar esta tesis a mis papás, Martha y Luis, por apoyarme y amarme incondicionalmente; y a Juan por estar siempre en mi corazón.

(I would like to dedicate this thesis to my parents, Martha and Luis, for supporting and loving me unconditionally; and to Juan for always staying in my heart.)

BIOGRAPHY

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CHAPTER 1 : INTRODUCTION AND OBJECTIVES

MOTIVATION

Perfluorinated compounds (PFCs) are organic compounds in which all carbon-hydrogen bonds are replaced with carbon-fluorine bonds. Two classes of PFCs that are of ecotoxicological and human health concern are perfluorocarboxylic acids (PCAs) and perfluorosulfonic acids (PSAs). PFCs are surfactants used as active ingredients in stain repellents (e.g. Scotchgard) and firefighting foams. They are also used in the manufacture of materials such as non-stick coatings (e.g. Teflon), water repellent fabrics (e.g. GoreTex), and microwave popcorn bags. PFCs are released into the environment directly by fluorochemical production facilities and indirectly through consumer use of products.

PFCs are of concern because of their toxicity and their persistence in the environment and the human body. Perfluorooctanoic acid (C8, PFOA) and perfluorooctane sulfonate (PFOS) have been detected globally in humans and wildlife. For example, measurable PFOS concentrations were found in the black-footed albatross in remote oceanic locations, and ten-fold higher PFOS concentrations have been measured in cormorants and herring gulls from the industrialized North American Great Lakes region (Giesy and Kannan 2002). In addition, PFCs have been measured in human blood serum collected from both fluorochemical industry workers and the general population. Fluorochemical industry workers can have PFOS and/or C8 blood serum levels that are one to two orders of magnitude higher than those found in the general population (Lau et al. 2007; Steenland and Woskie 2012). Once

present in human whole blood or serum, C8 and PFOS have half-lives of 3.8 and 5.4 years, respectively (Betts 2007).

In terms of human health effects, a variety of adverse health conditions have been putatively associated with PFC exposure. Among them are cancer, decreased birth weight in newborns, immunotoxicity, thyroid disease, chronic kidney disease, and decreased sperm count (Barry, Winquist, and Steenland 2013; Fei et al. 2007; Melzer et al. 2010; Shankar, Xiao, and Ducatman 2011; Joensen et al. 2009). Recent findings suggest that populations with elevated C8 blood serum levels, such as those working in or living near C8 production facilities, have an elevated risk of developing testicular and kidney cancers (Barry, Winquist, and Steenland 2013). A Johns Hopkins University study showed a correlation between PFOS and C8 levels in newborn infants and decreased birth weight and head circumference (Betts 2007). Furthermore, a recent study showed that PFC exposure in children from birth to age 5 years reduced the immune response to diphtheria and tetanus vaccinations to the point of antibody concentrations being below the level needed for long-term protection (Grandjean et al. 2012). Some studies have shown a positive correlation between C8 exposure and increased cholesterol, uric acid, and liver enzyme levels in adults; however, effects are not consistent across all studies (Steenland, Fletcher, and Savitz 2010).

As drinking water is one important exposure route, the USEPA has issued a drinking water Provisional Health Advisory (PHA) for C8 and PFOS at 0.4 and 0.2 µg/L, respectively (US Environmental Protection Agency 2009). The PHA was developed to protect consumers against adverse effects from short-term C8 and PFOS exposure. In New Jersey, a health-based C8 guideline of 0.04 µg/L was developed as a protective measure against lifetime C8

exposure. C8 levels of 0.04 µg/L are not uncommon in drinking water sources. In addition, the USEPA is seeking occurrence data for six PFCs [C8, PFOS, perfluoroheptanoic acid (C7), perfluorononanoic acid (C9), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHS)] in U.S. drinking waters as part of the third Unregulated Contaminant Monitoring Rule (UCMR3). As more information about PFC occurrence and the effects of PFCs on human health becomes available, it is important to concurrently identify treatment methods that are capable of protecting human health by limiting PFC exposure through drinking water.

OBJECTIVES

The principal objective of this research was to assess the effectiveness of anion exchange processes for the removal of perfluorinated compounds (PFCs) from drinking water sources. Specific objectives included to

1. assess the effectiveness of a commercially available magnetic anion exchange resin for PFC removal,
2. evaluate the effects of background water quality on PFC removal by anion exchange,
3. identify regeneration conditions that restore the PFC removal capacity of anion exchange resins and measure the PFC removal effectiveness of an anion exchange resin over multiple loading/regeneration cycles.

Apart from the commonly studied perfluorooctanoic acid (C8, PFOA) and perfluorooctane sulfonate (PFOS), eight additional PFCs [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)] were evaluated.

CHAPTER 2 : LITERATURE REVIEW

PERFLUORINATED COMPOUNDS

Characteristics

PFCs are organic compounds in which all carbon-hydrogen bonds are replaced with carbon-fluorine bonds. They are often grouped with polyfluorinated compounds, in which the hydrogen atoms have been partially replaced by fluorine (Rahman, Peldszus, and Anderson 2013). Figure 2.1 shows the generic chemical structures of two important PFC classes, the perfluorocarboxylic acids and perfluorosulfonic acids.

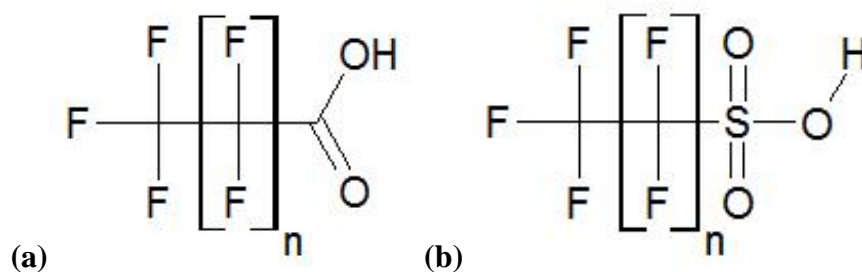


Figure 2.1 General chemical formulas for (a) perfluorocarboxylic acids (b) perfluorosulfonic acids

Figure 2.1 shows linear perfluorinated structures, but PFCs can also be branched (Lindstrom, Strynar, and Libelo 2011). PFCs are surfactants used as active ingredients in stain repellents (e.g. Scotchgard) and firefighting foams. They are also used in the manufacture of non-stick coatings (e.g. Teflon) and water repellent fabrics (e.g. GoreTex). PFCs are released into the environment directly by fluorochemical production facilities and

indirectly through consumer use of products. PFCs are manufactured by electrochemical fluorination and telomerization. The production of PFCs by electrochemical fluorination produces a mixture of the target PFC and homologues with additional or fewer perfluorinated carbons, while telomerization produces primarily linear compounds with an even number of carbons, like C8 (Post, Cohn, and Cooper 2012). PFCs work well as surfactants because of the hydrophilic acid head and hydrophobic carbon-fluorine tail that can not only repel water but also fats and oils. The hydrophobic/hydrophilic characteristic, as well as high water solubility at circumneutral pH and low volatility, contribute to the presence of PFCs in all aquatic environments and even in rain water (Rahman, Peldszus, and Anderson 2013). Physical/chemical properties of the ten PFCs studied in this project are summarized in Table 2.1.

Large differences in the physical/chemical properties of PFCs with varying carbon chain length leave questions about how to predict the fate and transport of PFCs in the environment (Rayne and Forest 2009). Values for log K_{OW} range from 1.69 for PFBS to 7.9 for C10; however, these values are difficult to determine because of the likelihood that PFCs aggregate at the water/octanol interface (Rahman, Peldszus, and Anderson 2013). Similarly, log D values at pH 7 range over ~6 orders of magnitude, from -1.81 for PFBS to 4.15 for C10. With respect to aqueous solubility at pH 7, C4 and C5 are essentially miscible while the solubility of C10 is predicted to be 670 mg/L. Overall, the solubility of PFCs at circumneutral pH is orders of magnitude higher than the sub-microgram per liter levels of concern from a standpoint of drinking water safety.

Table 2.1
Chemical properties of PFCs studied

Compound	Formula	CAS #	MW	pK _a (25°C)	log K _{ow} ^a	log D ^b (25°C, pH 7)	Intrinsic Solubility of Molecular Form (g/L)	Solubility at pH 7 (g/L)
Perfluorobutanoic acid (C4)	C ₄ HF ₇ O ₂	375-22-4	214.0	0.37 ^c , 0.39 ^d	3.39 ^c , 2.14 ^e	-0.36 ^c	1.1 ^c , 1.37 ^e	1000 ^c
Perfluoropentanoic acid (C5)	C ₅ HF ₉ O ₂	2706-90-3	264.1	0.40 ^c , 0.57 ^d	4.39 ^c , 2.81 ^e	0.64 ^c	0.19 ^c , 0.196 ^e	1000 ^c
Perfluorohexanoic acid (C6)	C ₆ HF ₁₁ O ₂	307-24-4	314.1	0.42 ^c , 0.84 ^d	4.98 ^c , 3.48 ^e	1.24 ^c , 0.70 ^f	0.047 ^c , 0.027 ^e	260 ^c
Perfluoroheptanoic acid (C7)	C ₇ HF ₁₃ O ₂	375-85-9	364.1	0.47 ^c	5.71 ^c , 4.14 ^e	1.97 ^c	0.011 ^c , 0.0036 ^e	58 ^c
Perfluorooctanoic acid (C8, PFOA)	C ₈ HF ₁₅ O ₂	335-67-1	414.1	0.50 ^c , 1.01- 2.80 ^d	6.44 ^c , 4.81 ^e	2.69 ^c	2.3 x 10 ^{-3c} , 4.8x10 ^{-4e}	13 ^c , 9.5 ^g
Perfluorononanoic acid (C9)	C ₉ HF ₁₇ O ₂	375-95-1	464.1	0.52 ^c , 2.58 ^d	7.17 ^c , 5.48 ^e	3.42 ^c , 2.57 ^f	5.1 x 10 ^{-4c} , 6.2x10 ^{-5e}	3 ^c
Perfluorodecanoic acid (C10)	C ₁₀ HF ₁₉ O ₂	335-76-2	514.1	0.52 ^c , 2.61 ^d	7.90 ^c , 6.15 ^e	4.15 ^c , 2.90 ^f	1.2 x 10 ^{-4c} , 8x10 ^{-6e}	0.67 ^c
Perfluorobutane sulfonate (PFBS)	C ₄ HF ₉ SO ₃	375-73-5	300.1	-3.57 ^c	1.69 ^c , 1.82 ^e	-1.81 ^c	0.9 ^c , 0.344 ^e	999 ^c
Perfluorohexane sulfonate (PFHS)	C ₆ HF ₁₃ SO ₃	355-46-4	400.1	-3.34 ^c	3.05 ^c , 3.16 ^e	-0.45 ^c	0.048 ^c , 0.006 ^e	150 ^c
Perfluorooctane sulfonate (PFOS)	C ₈ HF ₁₇ SO ₃	1763-23-1	500.2	-3.27 ^c	4.51 ^c , 4.49 ^e	1.01 ^c , 2.45 ^f	2.4 x 10 ^{-3c} , 1x10 ^{-4e}	7.5 ^c , 0.68 ^h

^a octanol/water partition coefficient of molecular form

^b pH-dependent octanol/water partition coefficient

^c SciFinder Scholar (values were calculated with Advanced Chemistry Development (ACD/Labs) Software)

^d Experimental values (Ding and Peijnenburg 2013)

^e US EPA. 2012. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.10. United States Environmental Protection Agency, Washington, DC, USA.

^f Experimental values at pH 6-7 (Jing, Rodgers, and Amemiya 2009)

^g Measured values (Kauck and Diesslin 1951)

^h Based on OECD 105, OPPTS 830.7840 (OECD 2002)

Occurrence

As mentioned above, PFCs are used in numerous industrial and consumer products, and their presence in the environment is attributed in part to emissions associated with the consumer use of products. For example, PFCs were found in 27 out of 30 consumer product samples collected from Norway and Sweden (Herzke, Olsson, and Posner 2012). Samples included waterproofing agents, paint, coated fabrics (paper, textiles, leather and carpets), non-stick ware, electrics and electronics, and firefighting agents. Firefighting agents are probably one of the products that contribute the most to PFC emissions because of the direct introduction of PFCs into the environment when extinguishing fires. Coated textiles are another important source since PFCs can be released during cleaning or through wear (Herzke, Olsson, and Posner 2012). For example, 3M estimates that 95% of PFOS loss can occur over a carpet's useful life. The fact that products treated with PFCs have a longer service life than untreated products leads to considerable amounts of PFCs being released to the environment during the life of the product (Herzke, Olsson, and Posner 2012).

Studies have shown the global presence of PFCs in the environment. PFCs have been detected in surface water, groundwater, wastewater, as well as in raw and finished drinking water. Results of a selection of these studies are summarized in Table 2.2. The presence of PFCs in remote areas can be attributed to atmospheric transport of volatile precursors and to long-range aqueous transport of emitted PFCs by currents on the ocean's surface (Post, Cohn, and Cooper 2012).

Table 2.2
PFC occurrence

Location	Type of Water	C8 (ng/L)	PFOS (ng/L)	Total PFC (ng/L)	Source
USA (data from 7 utilities)	Drinking water	ND-30	ND-57	up to 102	Quiñones and Snyder 2009
USA (data from 18 utilities)	Drinking water	ND-57	ND-61	up to 244	Appleman et al. 2013b
England and Wales	Drinking water	ND-240	ND-130	-	Atkinson et al. 2008
N.E. Spain	Drinking water	ND-30	3.0-71	-	Flores et al. 2013
Ruhr region, Germany	Drinking water	ND-519	ND-22	up to 598	Skutlarek et al. 2006
Fuxin, China	Drinking water	0.3-1.7	ND	up to 2.7	Bao et al. 2011
Osaka, Japan	Drinking water	2.3-84	0.16-22	-	Takagi et al. 2008
Osaka, Japan	Drinking water	6.5-48	ND-3.7	-	Takagi et al. 2011
Yodo River basin, Japan	Drinking water	12-47.5	3.9-9.4	up to 76	Shivakoti et al. 2010
South East Queensland, Australia	Drinking water	ND-2.29	ND-8.07	up to 25.4	Thompson et al. 2011
New Jersey	Groundwater	ND-140	-	-	Post et al. 2009
Fuxin, China	Groundwater	4.85-524	ND-0.73	up to 1,400	Bao et al. 2011
Cape Fear River basin, NC	Surface water	ND-287	ND-132	up to 942	Nakayama et al. 2007
Decatur, AL	Surface water and wells	ND-11,000	ND-151	up to 31,906	Lindstrom et al. 2009
Great Lakes	Surface water	15-70	11-121	up to 203.1	Boulanger et al. 2004
New Jersey	Surface water	ND-40	-	-	Post et al. 2009
Tennessee River, AL	Surface water	ND-598	16.8-144	-	Hansen et al. 2002
Ruhr region, Germany	Surface water	ND-3640	ND-193	up to 4,385	Skutlarek et al. 2006
Fuxin, China	Surface Water	27.2-668	0.28-0.54	up to 713	Bao et al. 2011
California	Treated WW	12-190	20-190	90-470	Plumlee et al. 2008
Pacific Northwest	Treated WW	8.2-15	15-34	-	Schultz et al. 2006
River Elbe basin, Germany	Treated WW	12.3-77.6	ND-82.2	30.5-266.3	Ahrens et al. 2009
Minnesota	Treated industrial WW	62,400	19,200	2.91*10 ⁵	Oliaei et al. 2006
Minnesota	Landfill leachate-impacted groundwater	ND-41,600	ND-2,690	up to 1.28*10 ⁶	Oliaei et al. 2006
US landfills	Landfill leachates	380-1,000	56-160	up to 7,414	Huset et al. 2011

C8 and PFOS are two of the most frequently detected PFCs, and they range from non-detect to well above the U.S. Provisional Health Advisory. However, as the regulations around C8 and PFOS become more stringent it is probable that the use and environmental levels of other PFCs, especially those with a shorter carbon chain length, will increase (Rahman, Peldszus, and Anderson 2013).

While the source of PFC contamination in many areas is not clear, some of the studies were conducted near PFC production facilities (e.g., Decatur, AL; Cottage Grove and Washington County, MN; Fuxin, China). Table 2.2 also illustrates the degree of global PFC contamination with PFCs detected in waters of the United States, Germany, Japan, and China. PFCs have also been detected in the waters of many other countries (Ahrens et al. 2009).

Health Effects

PFCs are of increasing public health concern because of their toxicity and persistence. The persistence of a PFC in the environment and human body is directly related to the length of the carbon chain. For example, perfluorobutane sulfonate (PFBS) with 4 carbons can be eliminated from the human body in a little over 1 month, while C8 and PFOS require 3.8 and 5.4 years, respectively, for elimination (Betts 2007). Drinking water is an important PFC exposure pathway, and for C8, a serum:drinking water concentration ratio of about 100:1 can be expected (Post, Cohn, and Cooper 2012).

In the United States, PFOS and C8 concentrations measured in whole blood samples from the general population averaged 30.4 ng/mL and 5.2 ng/mL, respectively (Calafat et al.

2007). Globally, PFOS has been detected in whole blood at concentrations as high as 116 ng/mL (Lau et al. 2007). In humans living in the industrialized world, C8 concentration in blood serum range from 2-8 ng/mL. Serum samples from California women collected in 1960, 1980, and 2010 showed that PFOS levels decreased over the fifty years from 45.9 to 9.44 ng/mL (Wang, Park, and Petreas 2011). The decrease from 1980-2010 is consistent with the phase-out of PFOS manufacturing in 2002. For C8, there was an increase from 0.3 ng/mL to 3.17 ng/mL from 1960-1980, but a decrease to 2.21 ng/mL in 2010. In addition, a steady increase in longer chain PFCs like perfluorononanoic acid and perfluorodecanoic acid occurred over the fifty years. The consistent build-up of longer chain PFCs could be because of their continued production and emission, and the longer half-lives compared to C8. Unlike other persistent organic pollutants like polychlorinated biphenyls (PCBs), which are lipophilic and accumulate in fatty tissue, PFCs accumulate in organs such as the liver and kidney, in muscle, and attach to serum proteins in blood.

While it has been established that PFCs are present in the environment and in humans, to date, epidemiological studies on human health effects are limited. Research efforts have provided information about the toxicokinetic effects in animals such as rats and monkeys, but these differ significantly between species. For example the half-life of C8 is 3.8 years in humans, but ranges from 4 hours in female rats to 6 days in male rats to 17-19 days in mice (Lindstrom, Strynar, and Libelo 2011). The difference in toxicokinetics is mainly due to differences in renal clearance rates (Post, Cohn, and Cooper 2012), and it makes extrapolation from animal data to humans difficult. Presented here are human and animal epidemiological studies that point to possible adverse health effects of PFC exposure.

An important case of PFC exposure is that of several mid-Ohio River Valley communities affected by C8 released from the Washington Works plant in Parkersburg, West Virginia. The released C8 contaminated local drinking water sources by entering the groundwater supply. The communities near the Washington Works plant in West Virginia initiated a lawsuit against DuPont that resulted in a Settlement Agreement, which included the initiation of the C8 Health Project. The objective of this project was to gather health information and collect blood samples from about 69,000 people, including community residents and plant workers. Also, a C8 Science Panel, formed by three epidemiologists, was established to assess whether or not there would be a probable link between C8 exposure and disease in the community. An epidemiological study conducted as part of the C8 Health Project considered 32,254 participants, including DuPont plant workers. In this study, 2,507 validated cancers (21 cancer types) were reported, and C8 exposure was associated with kidney and testicular cancer. The association between thyroid cancer risk and C8 was positive and significant in DuPont workers but not in community residents (Barry, Winquist, and Steenland 2013). The C8 Science Panel concluded that there is a probable link between C8 and kidney cancer, testicular cancer, diagnosed high cholesterol, ulcerative colitis, pregnancy-induced hypertension, and thyroid disease (C8 Science Panel 2012). C8 was classified as “likely to be carcinogenic in humans” by the USEPA Science Advisory Board.

Apart from the findings of the C8 Health Project, a number of other health effects associated with PFC exposure have been identified. For example, a positive correlation between C8 exposure and increases in uric acid, and liver enzymes in adults has been determined (Steenland, Fletcher, and Savitz 2010). A study of U.S. adults showed a positive

association between increased C8 and PFOS levels and chronic kidney disease. Adults with >5.9 and >29.5 ng/mL blood serum concentrations of C8 and PFOS, respectively, were almost twice as likely to have chronic kidney disease (Shankar, Xiao, and Ducatman 2011). Increased PFC blood serum levels have also been linked to insulin resistance and high serum uric acid levels, which are also associated with the development of chronic kidney disease.

A study on data collected as part of the National Health and Nutrition Survey from 1999-2006 showed a correlation between adults with thyroid disease and C8 and PFOS concentrations in blood serum (Melzer et al. 2010). Women with C8 blood serum concentrations ≥ 5.7 ng/mL were more than twice as likely to have thyroid disease as women with ≤ 4 ng/mL. A similar increase in thyroid disease was observed in men with ≥ 7.3 ng/mL C8 in their blood serum compared to those with ≤ 5.2 ng/mL. For PFOS, blood serum concentrations ≥ 36.8 ng/mL compared to ≤ 25.5 ng/mL resulted in men being over 2.5 times more likely to develop thyroid disease. No correlation between PFOS concentration and thyroid disease was observed in women (Melzer et al. 2010).

A study of Danish pregnant women found a negative correlation between birth weight and maternal plasma C8 concentrations (Fei et al. 2007). In addition, a Johns Hopkins study showed a correlation between higher PFOS and C8 levels in newborns and lower birth weight and head circumference (Betts 2007). Also, an association was observed between prenatal C8 exposure and increased risk of overweight/obesity and changes in metabolic hormones in 20-year old women (Halldorsson et al. 2012).

A study of sperm count in Danish men found that elevated levels of C8 and PFOS in blood serum resulted in significantly lower spermatozoa levels in semen. Average PFOS and

C8 blood serum concentrations were 4.9 and 24.5 ng/mL, respectively. Men in the highest quartile based on C8 and PFOS concentration in blood serum had 6.2 million total morphologically normal semen compared to 15.5 million in the lowest C8 and PFOS concentration group (Joensen et al. 2009).

In children from birth to age 5 years, elevated exposure to PFCs, as measured by PFC levels in blood serum, reduced the immune response to immunizations for diphtheria and tetanus to the point of antibody concentrations being below the level needed for long-term protection (Grandjean et al. 2012). A two-fold increase in PFOS exposure was associated with a decrease in antibody concentration in blood serum by 39% at age 5 years. A cumulative two-fold PFC exposure in children was associated with a decrease of 49% of antibody concentrations in blood serum, with PFOS and C8 representing the main culprits (Grandjean et al. 2012). The same study also showed that postnatal PFC exposure from birth until age 7 years was more strongly associated with decrease in antibody concentration than prenatal exposure. Exposure of infants to C8, either through water ingestion or through breast milk, is higher than in adults that consume the same drinking water, especially due to a higher fluid consumption on a body weight basis (Post, Cohn, and Cooper 2012).

Studies have also been conducted to determine the potential adverse health effects of PFC exposure in animals. Exposure to C8 in female rats resulted in decreased body weight gain, decreased erythrocytes, and decreased hemoglobin concentration (Post 2007). A study of C8 exposure in Rhesus monkeys caused an increase in liver weight. A study of rats exposed to C8 showed an increased incidence of Leydig cell adenomas in male rats and an increase in mammary fibro adenomas in female rats. Male rats exposed to C8 also had an

increased incidence of hepatic and pancreatic adenomas and carcinomas (Post 2007). Studies of mice showed that prenatal exposure to PFOS and C8 caused increased incidence of neonatal mortality. Mice were born appearing to be healthy but would die shortly after birth (Betts 2007). Studies in animals have shown that C8 and PFOS can bind to the peroxisome proliferator-activated receptor (PPAR), which is a receptor associated with carcinogenesis. The activation of PPAR is believed to be related to the cause of liver and pancreatic tumors in mice and the effects seen on fetal growth and immune response (Betts 2007). While there is a plethora of studies reporting adverse health effects of PFCs in animals, extrapolating these results to humans is controversial because of the considerably shorter PFC half-life in animals compared to humans.

Health advisories and regulatory framework

As drinking water is one important PFC exposure route, the USEPA has issued a drinking water Provisional Health Advisory (PHA) for C8 and PFOS at 0.4 and 0.2 µg/L, respectively (US Environmental Protection Agency 2009). The PHA was developed to protect consumers against adverse effects from short-term C8 and PFOS exposure. In New Jersey, a health-based C8 guideline of 0.04 µg/L is in effect to protect against adverse health effects from a lifetime of exposure to drinking water containing C8 (Post et al. 2009). To derive the 0.04 µg/L C8 guideline, New Jersey used a method relating the external C8 dose (drinking water concentration) to the blood level of C8 in humans. A concentration factor of 100 from drinking water to blood was used. By evaluating toxicity studies in a variety of animal types (adult rats, pregnant female rats, non-human primates, rat pups) that modeled

animal blood levels after long-term exposure to C8, no observed adverse effect levels (NOAEL) and lowest observed adverse effect levels (LOAEL) were correlated to blood C8 concentration in animals. Different toxicity endpoints were used in each study, such as decreased body weight and hematology in adult female rats and increased liver weight and possible mortality in adult non-human primates. After applying uncertainty factors that were study-specific, a target human blood level was extrapolated from the animal blood level. To this target human blood level, the concentration factor of 100 was applied. In addition, it was assumed that the drinking water contribution to C8 exposure was 20%. The six health-based concentrations calculated ranged from 0.04 – 0.26 µg/L, and the most conservative of these values was selected for the health-based guidance (Post 2007; Post et al. 2009). C8 levels of 0.04 µg/L are not uncommon in drinking water sources (Table 2.2).

The USEPA has also included C8 and PFOS in the third drinking water contaminant candidate list (CCL3) of 32 compounds being considered for further regulatory studies (US Environmental Protection Agency 2011). Furthermore, C8, PFOS, C7, C9, PFBS, and PFHS are analytes in the third Unregulated Contaminant Monitoring Rule (US Environmental Protection Agency 2012c). The UCMR3 requires nationwide monitoring to obtain occurrence data needed for regulatory decision-making. The USEPA Office of Pollution Prevention and Toxics also developed Action Plans to address PFC risks (US Environmental Protection Agency 2013b), and the USEPA recently issued a rule requiring companies to report all new uses of long-chain PFCs and their intent to import carpets containing these substances (US Environmental Protection Agency 2013a).

Furthermore, due to its persistence, bioaccumulating and biomagnifying properties, potential for long-range environmental transport, and adverse health effects, PFOS was classified as a Persistent Organic Pollutant by the Stockholm Convention (United Nations Environment Programme 2005). In 2002, the 3M Company, a major PFOS producer in the US, completed its voluntary phase-out of PFOS production in the United States, and PFOS is no longer produced in the US. However, China remains an important producer of PFOS, and PFOS can be imported into the US for specific limited uses (US Environmental Protection Agency 2012a). For C8 and related chemicals, eight companies have committed to 95% reductions in emissions and product contents by 2010 followed by complete elimination by 2015 (US Environmental Protection Agency 2012a).

Effectiveness of water treatment processes for PFC removal

Multiple studies have shown that coagulation, flocculation, and filtration are ineffective for PFC removal (Vecitis et al. 2009; Quiñones and Snyder 2009; Appleman et al. 2013b). Oxidation processes such as chlorination, ozonation, and advanced oxidation (AOP) are also ineffective. Fluorine is the most electronegative element, making it thermodynamically unfavorable for oxidants to break carbon-fluorine bonds and release fluoride ions (Vecitis et al. 2009). Furthermore, if PFC precursors (e.g., polyfluorinated compounds) are present, they could get oxidized to terminal compounds, such as C8 or PFOS; thus, increasing their concentration in the finished water (Rahman, Peldszus, and Anderson 2013).

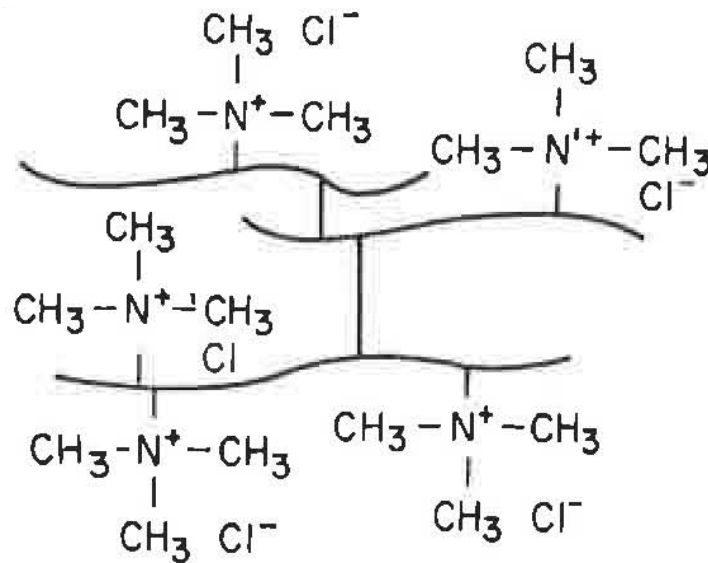
Takagi et al. (2008) presented results of a sampling survey of PFCs in 14 Japanese water treatment plants. Only a treatment plant utilizing granular activated carbon (GAC) that was changed regularly removed PFCs effectively. Plants utilizing chlorination, ozonation, slow-sand filtration, and rapid filtration were not effective at removing PFOS and C8. Similar results were obtained in U.S. full-scale water treatment systems, where ozonation, packed tower aeration, potassium permanganate, ultraviolet (UV) treatment, UV/H₂O₂ advanced oxidation, chlor(am)ination, and chlorine dioxide proved ineffective for the control of PFCs (Appleman et al. 2013b). In treatment systems where coagulation was followed by dissolved air flotation instead of sedimentation, 49% removal of PFOS was observed (Appleman et al. 2013b). According to the authors, treatment systems using anion exchange and GAC preferably removed longer-chain PFCs, while those using reverse osmosis were effective for the removal of all compounds considered in the study (a total of 23 poly- and perfluoroalkyl substances). The effectiveness of reverse osmosis treatment was also observed by Quinones and Snyder (2009) and by Tang et al. (2007), but high energy requirements make reverse osmosis a costly option for PFC removal. Nanofiltration has also been shown to be effective, resulting in 90-99% removal of PFOS (Tang et al. 2007) and >93% removal of C4, C5, C6, C8, C9, C10, PFBS, PFHS, and PFOS (Appleman et al. 2013a).

ION EXCHANGE

Ion exchange is a process in which exchangeable ions on a resin are displaced by ions in solution. Ion exchange is typically used in drinking water treatment for water softening as well as for the removal of sulfate, nitrate, bromide, and natural organic matter (NOM).

Anion exchange resins

The resin is an insoluble support matrix for the exchangeable ions and can be natural or synthetic. Synthetic resins tend to be more durable and can be regenerated with a salt or acid/base solution. Synthetic resins are spherical beads and come in a variety of bead sizes. Typical sizes are 16x40, 16x50, and 20x50 U.S. mesh. The backbone of the resin is made up of a network of cross-linked polymers to which charged or ionizable functional groups are covalently bonded. Cross-linking is typically accomplished with the use of divinylbenzene. The most common polymers for making the resin matrix are polyacryl and polystyrene. Figure 2.2 shows the generic structure of an anion exchange resin with crosslinked polymer backbone.



Source: (Clifford, Sorg, and Ghurye 2011)

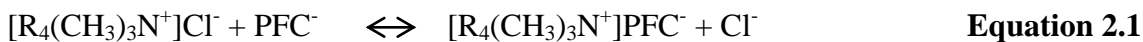
Figure 2.2 Strong-base anion exchange resin

Resins are classified as gel type or macroporous resins. Gel-type resins typically have approximately 8% cross-linking, which results in an open pore structure that can result in faster kinetics of ion exchange. Macroporous resins typically have 20-25% crosslinking. The degree of cross-linking affects the resistance of the resin to swelling or shrinking. Macroporous resins retain their pore structure when dried, whereas gel-type resins lose their pore structure upon drying. Dry gel-type resins typically have very low BET surface areas while macroporous resins have BET surface areas of 7-600 m²/g resin (Crittenden and others 2005). Macroporous resins are more resistant to swelling, and the moisture content of these resins is lower. Gel-type resins have higher water content, and the more open pore structure allows for more swelling. Swelling due to ion exchange can be reversible, but repeated swelling and shrinking can cause beads to fracture.

Resin quantities are often measured on a volumetric basis, which includes water within the resin pores. For gel-type resins with their more open pore structure and higher water content, the amount of actual resin measured by volume will be less than with a macroporous resins. Resin capacities are expressed in equivalents per liter, which is dependent on the quantity of functional groups per wet-volume of resin. The wet-volume depends on the moisture content of the resin (Crittenden and others 2005).

Anion exchange resins are grouped into strong base anion (SBA) and weak base anion (WBA) resins. The distinction is in the pK values of the functional groups, which are >13 for strong base and 5.7-7.3 for weak base anion exchange resins (Crittenden and others 2005). A common functional group in SBA resins is the quaternary amine group, which carries a positive charge over almost the entire pH range of 0 to 14. In WBA resins, tertiary

amines are the most common functional group, which does not become appreciably protonated until the pH falls below the pK. The general exchange reactions for a SBA and WBA resins are presented in Equations 2.1 and 2.2, respectively.



In Equation 2.1, $[\text{R}_4(\text{CH}_3)_3\text{N}^+]$ represents the anion exchange site of SBA resin which is originally in the chloride form. For SBA resins, the anion in solution (e.g. PFC^-) will exchange with a chloride ion on the functional group. In Equation 2.2, $[\text{R}_3\text{N}]$ represents the tertiary amine functional group of the WBA resin. It is only ionized in the acidic pH region, at which point it is able to serve as an anion exchange site (Clifford, Sorg, and Ghurye 2011).

Effectiveness of anion exchange for PFC removal

Ion exchange resins have shown promise for PFC removal. Macroporous styrene-divinylbenzene (DVB) resins were effective for PFOS removal in column tests (Senevirathna et al. 2010) as were gel-type polystyrene DVB resins in batch experiments (Chularueangaksorn et al. 2013). With a polyacrylic quaternary amine SBA resin at a dose of ~1.7 g/L, both PFOS and PFBS reached >95% of their equilibrium uptake after 4 hours elapsed (Carter and Farrell 2010). Similar removal trends among PFCs were observed with ion exchange resins as with activated carbon. PFOS uptake on resins was greater than PFBS,

perhaps due to the greater hydrophobicity of the longer fluorinated PFOS chain (Carter and Farrell 2010). Resin type has also been shown to play a role in PFOS removal. Polyacrylic resins exhibited faster uptake kinetics and higher capacity compared to polystyrene resins, regardless of whether the resins were tested in gel-type or macroporous form (Deng et al. 2010). The faster uptake kinetics and higher capacity were attributed to the more hydrophilic properties of the polyacrylic resin. Differences in gel-type and macroporous resins have been observed in polystyrene-DVB resins. Faster uptake kinetics were observed with macroporous polystyrene-DVB resins compared to gel-type polystyrene-DVB resins (Deng et al. 2010). The PFC removal effectiveness of ion exchange resins can be affected by the presence of other ions in solution. Deng et al. (2010) showed that the presence of sulfate decreased the availability of ion exchange sites for PFOS.

A magnetic anion exchange treatment process, employed to remove total organic carbon, was examined for the removal of PFCs in a U.S. water treatment plant facility (Appleman et al. 2013b). Although this process showed little to no removal of any of the PFCs evaluated, the results from column operation and bench-scale studies indicate that it is a promising technology (Appleman et al. 2013b). The poor field performance was attributed by the authors to continual regeneration, insufficient capacity due to improper operation, and/or kinetics. Also, the pH of drinking water (typically 6-9) is not expected to affect the PFC removal by SBA resins due to the ionization of the compounds (Rahman, Peldszus, and Anderson 2013).

An important consideration with respect to anion exchange is the regeneration and reusability of the resin. Several authors have investigated strategies to regenerate the resins

(Chularueangaksorn et al. 2013; Deng et al. 2010; Rokicki and Boyer 2011), and Chularueangaksorn et al. (2013) confirmed the efficacy of 1% and 5% NaCl in MeOH/deionized water (7:3) regenerant solution for PFOS removal and the reusability of the tested resin over six loading/regeneration cycles.

SUMMARY

Based on the literature reviewed, it is clear that common water treatment processes such as coagulation, sedimentation, filtration, chlor(am)ination, and ozonation are not effective for PFC removal. Among the water treatment processes that show promise for PFC removal (activated carbon adsorption, anion exchange, nanofiltration, reverse osmosis), anion exchange was selected for further study to fill the following knowledge gaps: (1) removal of ten PFCs rather than only the commonly studied C8 and PFOS, (2) treatment effectiveness at drinking water relevant PFC concentrations (500 ng/L for each PFC rather than the higher concentrations used in most prior studies), and (3) anion exchange resin performance over multiple uptake/regeneration cycles, which required the determination of suitable resin regeneration strategies.

CHAPTER 3 : FACTORS AFFECTING THE REMOVAL OF PERFLUORINATED COMPOUNDS BY ANION EXCHANGE

ABSTRACT

Perfluorinated compounds (PFC) are anthropogenic substances that have been measured in drinking water, wastewater, groundwater, and landfill leachates. In addition, PFCs have been measured in human blood serum collected from both fluorochemical industry workers and the general population. These compounds are of increasing concern because of their toxicity, persistence, and bioaccumulating/biomagnifying properties. Once present in human whole blood or serum, it can take several years for PFCs to be completely removed from the body. In this study, batch kinetic tests were performed to evaluate the effectiveness of an anion exchange resin for the removal of ten PFCs at environmentally relevant concentrations. Seven perfluorocarboxylic acids (PCAs) and three perfluorosulfonic acids (PSAs) were evaluated at drinking water relevant concentrations. Experiments were conducted in salt-amended ultrapure water and in two drinking water sources (North Carolina reservoir water and Ohio River water). For both PCAs and PSAs, uptake increased with increasing perfluorinated carbon-chain length. Furthermore, removal of the three PSAs exceeded that of any of the seven tested PCAs. Solution pH and DOM had a negligible effect on PFC removal, but PFC removal decreased with increasing ionic strength. At equivalent concentrations the effect of individual anions on PFC removal was generally bicarbonate < chloride < sulfate < nitrate for PCAs and bicarbonate < chloride ~ sulfate < nitrate for PSAs.

INTRODUCTION

In recent years, there has been a growing interest in understanding the fate, occurrence, and treatment of perfluorinated compounds (PFCs). These substances are an emerging class of environmental contaminants that have been detected in the aquatic environment, including raw and finished drinking water. PFCs are surfactants used as active ingredients in stain repellents (e.g. Scotchgard) and firefighting foams. They are also used in the manufacture of non-stick coatings (e.g. Teflon) and water repellent fabrics (e.g. GoreTex). The presence of PFCs in the environment is attributed in part to direct releases from fluorochemical production facilities and in part to emissions associated with consumer use of products.

Two of the most commonly studied PFC classes are the perfluorocarboxylic acids and the perfluorosulfonic acids. PFCs are of concern because of their toxicity, their persistence, and their biomagnifying properties. Once present in human whole blood or serum, perfluorooctanoic acid (C8) and perfluorooctane sulfonate (PFOS) have half-lives of 3.8 and 5.4 years, respectively (Betts 2007). Additionally, a variety of adverse health conditions have been putatively associated with PFC exposure. Among them are cancer, decreased birth weight in newborns, immunotoxicity, thyroid disease, chronic kidney disease, and decreased sperm count (Barry, Winquist, and Steenland 2013; Fei et al. 2007; Melzer et al. 2010; Shankar, Xiao, and Ducatman 2011; Joensen et al. 2009).

To protect consumers against adverse health effects from short-term C8 and PFOS exposure, the EPA issued a Provisional Health Advisory (PHA) for C8 and PFOS at 0.4 and 0.2 µg/L, respectively (US Environmental Protection Agency 2009). In New Jersey, a health-

based C8 guideline of 0.04 µg/L was developed as a protective measure against lifetime C8 exposure. The EPA has also included C8 and PFOS in the third drinking water contaminant candidate list (CCL3) of 32 compounds considered for further regulatory studies (US Environmental Protection Agency 2011). Furthermore, these compounds were included in the third Unregulated Contaminant Monitoring Rule (UCMR3), along with C7, C9, PFBS, and PFHS (US Environmental Protection Agency 2012c).

Conventional water treatment processes have proven to be ineffective for PFC removal (Vecitis et al. 2009; Quiñones and Snyder 2009; Appleman et al. 2013b). Therefore, a better understanding of alternative treatment approaches, such as anion exchange, is required. According to Senevirathna et al. (2010), macroporous styrene-divinylbenzene (DVB) resins were effective for PFOS removal in column tests. Also, gel-type polystyrene DVB resins showed promise for PFOS removal, when tested in batch experiments (Chularueangakorn et al. 2013). A polyacrylic quaternary amine SBA resin at a dose of ~1.7 g/L achieved >95% removal of PFOS and PFBS in four hours (Carter and Farrell 2010). Polyacrylic resins exhibited faster uptake kinetics and higher capacity for PFOS compared to polystyrene resins, regardless of whether the resins were tested in gel-type or macroporous form (Deng et al. 2010). The faster uptake kinetics and higher capacity were attributed to the more hydrophilic properties of the polyacrylic resin. Differences in gel-type and macroporous resins have been assessed with polystyrene-DVB resins, and faster uptake kinetics were observed with macroporous polystyrene-DVB resins (Deng et al. 2010).

Furthermore, PFC removal effectiveness of ion exchange resins can be affected by background water matrix constituents, especially by the presence of other anions in solution.

However, limited data are available to date. Deng et al. (2010) showed that the presence of sulfate and hexavalent chromium in wastewater decreased the availability of ion exchange sites for PFOS. The authors also showed that pH had little effect on a polyacrylic macroporous resin, but there was a significant impact on a polyacrylic gel type resin at pH above 10. Most ion exchange studies that have been conducted to date focused on PFOA and PFOS and evaluated PFC concentrations in the mg/L range. Therefore, the objectives of this research were (1) to assess the effectiveness of an anion exchange resin for the removal of ten PFCs (seven perfluorocarboxylic acids, C4-C10, and three perfluorosulfonic acids, PFBS, PFHS, and PFOS) at environmentally relevant concentrations, and (2) to evaluate background water matrix effects on PFC removal.

MATERIALS AND METHODS

Materials

Experiments were conducted in salt-amended ultrapure water (UPW), Cane Creek Reservoir water (Carrboro, NC), and Ohio River water (Cincinnati, OH). For batch kinetic tests, the ionic strength (IS) of UPW was adjusted with NaHCO_3 and NaCl (Table 3.1) to 0.002 (low IS UPW) and 0.02 (high IS UPW) and adjusted with HCl or NaOH to pH 5.5, 7.0, and 8.5. As a reference, the ionic strength of terrestrial waters typically ranges from 0.001 to 0.01. Water quality parameters of the studied matrices are summarized in Tables 3.1 and 3.2.

Table 3.1
Background water matrix constituents for amended UPW and two surface waters

	Ionic Strength	Cl⁻ (mg/L)	HCO₃⁻ (mg/L)	SO₄²⁻ (mg/L)	NO₃⁻ (mg/L)
Low IS UPW	0.002	53.2	30.5	<0.5	<0.5
High IS UPW	0.02	532	305	<0.5	<0.5
CCR	0.0017*	9.6	52.5	4.9	3.5
ORW	0.0057*	21.3	87.8	62.6	<0.5

* Based on specific conductance measurements
 (IS=1.6 x 10⁻⁵ x specific conductance (µS/cm), Snoeyink 1980)

Table 3.2
Water quality parameters for drinking water sources

	CCR	ORW
pH	7.5	7.7
TOC (mg/L)	4.5	3.9
UV₂₅₄	0.150	0.125
Alkalinity (mg/L as CaCO₃)	37	72
Hardness (mg/L as CaCO₃)	35	127
Turbidity (NTU)	30	71
Sulfate (mg/L)	4.6	64

Experiments were conducted with a magnetic anion exchange resin (MIEX, Orica) that is NSF-certified for use in drinking water treatment. Resin properties are presented in Table 3.3. The strong base anion (SBA) resin was tested in the chloride form. Prior to experiments, the resin was prepared by rinsing resin beads in a glass column with at least 20 bed volumes of deionized water. Rinsed resin was stored at room temperature in deionized water until use.

Table 3.3
Resin properties

Matrix		Functional Group	Anion Exchange Capacity (eq/L)	Dry Resin Bed Density (mg/mL)	Mean Diameter (µm)
Polyacrylic	Macroporous	Quaternary amine (strong base)	0.52	213	180

Seven PCAs and three PSAs were studied (Table 3.4). Predicted pKa values of the PFCs listed range from -3.57 to 0.52 (Table 3.4), meaning that the selected PFCs are strong acids that are predominantly present in their anionic carboxylate and sulfonate forms over the pH range evaluated in this study (5.5 to 8.5). As indicated in Table 3.4, the PCAs will be referred to as C4-C10 and the PSAs as PFBS, PFHS, and PFOS.

Table 3.4
Chemical properties of PFCs studied

Compound	Formula	CAS #	MW	pK _a (25°C)
Perfluorobutanoic acid (C4)	C ₄ HF ₇ O ₂	375-22-4	214.0	0.37 ^a , 0.39 ^b
Perfluoropentanoic acid (C5)	C ₅ HF ₉ O ₂	2706-90-3	264.1	0.40 ^a , 0.57 ^b
Perfluorohexanoic acid (C6)	C ₆ HF ₁₁ O ₂	307-24-4	314.1	0.42 ^a , 0.84 ^b
Perfluoroheptanoic acid (C7)	C ₇ HF ₁₃ O ₂	375-85-9	364.1	0.47 ^a
Perfluorooctanoic acid (C8, PFOA)	C ₈ HF ₁₅ O ₂	335-67-1	414.1	0.50 ^a , 1.01-2.80 ^b
Perfluorononanoic acid (C9)	C ₉ HF ₁₇ O ₂	375-95-1	464.1	0.52 ^a , 2.58 ^b
Perfluorodecanoic acid (C10)	C ₁₀ HF ₁₉ O ₂	335-76-2	514.1	0.52 ^a , 2.61 ^b
Perfluorobutane sulfonate (PFBS)	C ₄ HF ₉ SO ₃	375-73-5	300.1	-3.57 ^a
Perfluorohexane sulfonate (PFHS)	C ₆ HF ₁₃ SO ₃	355-46-4	400.1	-3.34 ^a
Perfluorooctane sulfonate (PFOS)	C ₈ HF ₁₇ SO ₃	1763-23-1	500.2	-3.27 ^a

^a SciFinder Scholar (values were calculated with Advanced Chemistry Development (ACD/Labs) Software)

^b Experimental values (Ding and Peijnenburg 2013)

^c Measured values (Kauck and Diesslin 1951)

^d Based on OECD 105, OPPTS 830.7840 (OECD 2002)

Separate stock solutions for calibration curves and spiking of reactor contents were prepared from neat PFC standards (Wellington Labs, Guelph, ON, Canada). Neat standards were weighed to produce individual PFC stocks of 10,000 ng/ μ L in methanol. A combined PFC stock of 1,000 ng/ μ L for each PFC was prepared by combining 1 mL of each individual 10,000 ng/ μ L PFC stock. Dilutions of the combined stock produced calibration stocks with individual PFC concentrations of 0.01 ng/ μ L and 0.1 ng/ μ L in methanol and a reactor dosing stock containing 10 ng/ μ L in methanol. The stocks made from neat compounds were compared to a purchased PFC mixture containing 5 μ g/mL of each of the ten PFCs in methanol (Wellington Labs, Guelph, ON, Canada) to confirm concentrations. Six internal standards [mass labeled C4 (MC4), mass labeled C6 (MC6), mass labeled C8 (MC8), mass labeled C10 (MC10), mass labeled PFHS (MPFHxS), and mass labeled PFOS (MPFOS)] were purchased from Wellington Labs each at a concentration of 50 μ g/mL. A 20 μ L aliquot of each internal standard was added to 10 mL of methanol to produce an internal standard stock of 0.1 ng/ μ L.

Batch kinetic tests

Kinetic tests were conducted in 2 L acrylic jars using a jar tester. Jars were filled with 1 L of water, and reactor contents were spiked to a targeted concentration of 500 ng/L for each PFC. After PFC spiking, jars were mixed at 100 rpm with the jar tester paddle (Rokicki and Boyer 2011; Walker and Boyer 2011). The resin was dosed at concentrations of 1, 5 and 10 mL/L, and the resin dose was measured in 10-mL graduated cylinders (Rokicki and Boyer 2011; Walker and Boyer 2011). Following addition of the resin, samples were taken after

contact times of 5, 15, 30, 60, and 120 minutes and analyzed for PFC concentrations. An initial sample was taken prior to resin addition (time 0 sample). Prior to analysis, each sample was filtered through a 0.45- μm glass microfiber membrane filter to remove resin and other particulate matter.

Batch kinetic tests were also performed to evaluate the effect of competing anions on PFC removal. The experimental matrix for these experiments is shown in Table 3.5.

Table 3.5
Experimental design to evaluate the effect of competing anions on PFC removal by anion exchange processes

Ion	Charge Concentration (eq/L)	Anion Concentration (mol/L)	pH
Bicarbonate (NaHCO₃)	0.001	0.001	8.3
	0.005	0.005	8.4
	0.01	0.01	8.4
	0.02	0.02	8.3
Chloride (NaCl)	0.001	0.001	7.0
	0.005	0.005	7.2
	0.01	0.01	7.3 ⁺
	0.02	0.02	7.2 ⁺
Nitrate (NaNO₃)	0.001	0.001	7.3
	0.005	0.005	7.0 ⁺
	0.01	0.01	7.0
	0.02	0.02	7.0 ⁺
Sulfate (Na₂SO₄)	0.001	0.0005	6.9 ⁺
	0.005	0.0025	7.1
	0.01	0.005	6.8
	0.02	0.01	6.7

⁺ The pH was adjusted using a 0.1 N NaOH solution

Analytical method for determining PFC concentration

PFC concentrations were measured by liquid chromatography tandem mass spectrometry (LC-MS/MS) at the National Exposure Research Laboratory of the United States Environmental Protection Agency (USEPA) in Research Triangle Park, NC. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC/MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (FlouroFlash, Flourous Technologies Inc. or Kinetex C18 5 μ m 100Å, Phenomenex Inc.) was used for PFC separation. The gradient method shown in Table 3.6 was used to elute PFCs from the HPLC column for the majority of the analyses. Mobile phase A was 2 mM ammonium acetate in DI water with 5% methanol. Mobile Phase B was 2 mM ammonium acetate in methanol with 5% DI water. Seven months prior to the end of the study, the gradient method was changed to reduce background noise (Table 3.7). Mobile phase A was maintained the same while Mobile phase B was changed to 2 mM ammonium acetate in acetonitrile with 5% DI water.

Table 3.6
LC Gradient Method for PFC Analysis

Time (min)	Mobile Phase A % (v/v)	Mobile Phase B % (v/v)	Flow Rate (mL/min)
0 – 1	95	5	0.9
1 – 1.1	95	5	0.5
1.1 – 5	95 → 10	5 → 90	0.5
5 – 9	10	90	0.5
9 – 9.1	10 → 95	90 → 5	0.5
9.1 – 15	95	5	0.5

Table 3.7
Updated LC Gradient Method for PFC Analysis

Time (min)	Mobile Phase A % (v/v)	Mobile Phase B % (v/v)	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mass spectrometer transitions for PFC analytes and internal standards used are shown in Appendix A.

Calibration curves were generated by analyzing standards with concentrations of 10, 25, 50, 100, 250, 500, and 750 ng/L. The limit of quantitation (LOQ) for all compounds was 10 ng/L for all PFCs except C10 and PFOS, for which the LOQ was 25 ng/L. Calibration standards were analyzed at the beginning and end of LC runs and averaged to account for instrument drift.

All samples and calibration standards were filtered through a 0.45- μ m glass fiber syringe filter into a 15-mL Becton-Dickinson polypropylene vial. After filtration, samples and standards were spiked with 25 μ L of the internal standard mixture and 8 μ L formic acid, which was used to lower the pH to below 2. A blank with no PFCs added was also prepared with the calibration standards and plotted as a calibration curve point.

PFC levels were quantitated by calculating the response factor from the areas of the analyte and the matching mass-labeled IS. For compounds without matching IS (C5, C7, C9, PFBS), response factors were calculated using the areas of the analyte and mass labeled C6 (MC6) for C5 and C7, mass labeled C8 (MC8) for C9, and mass labeled PFHS (MPFHxS)

for PFBS. Chromatograms for each of the ten PFCs and six internal standards are presented in Appendix B. Representative calibration curves for each PFC are shown in Appendix C.

Background Water Matrix

The total organic carbon (TOC) concentration was measured by high-temperature combustion (Shimadzu TOC-VCSN) according to Standard Method 5310B. The UV-absorbing organic matter concentration was measured at a wavelength of 254 nm according to Standard Method 5910. A Thermo Scientific Orion 3-star pH meter was used to measure the pH of solutions. Total alkalinity was determined by titrating samples with 0.02 N sulfuric acid according to Standard Method 2320 B, and bicarbonate concentrations were calculated from alkalinity and pH data. The remaining anion concentrations were measured by ion chromatography. Hardness was determined by titration with EDTA, according to Standard Method 2340 C, and conductivity was measured using an HM Digital Water Tester (AP-2).

RESULTS AND DISCUSSION

Effect of PFC type on uptake by anion exchange resin

Using a resin dose of 5 mL/L, a batch kinetic test was conducted in CCR water to determine the resin effectiveness for removing each of the ten PFCs. After a contact time of 2 hours, removals ranged from 68% for C4 to >95% for PFOS. PFC uptake increased with increasing perfluorinated carbon-chain length of the carboxylates and sulfonates (Figure 3.1). Also, removal of the three sulfonates generally exceeded that of any of the seven tested carboxylates (Figure 3.1).

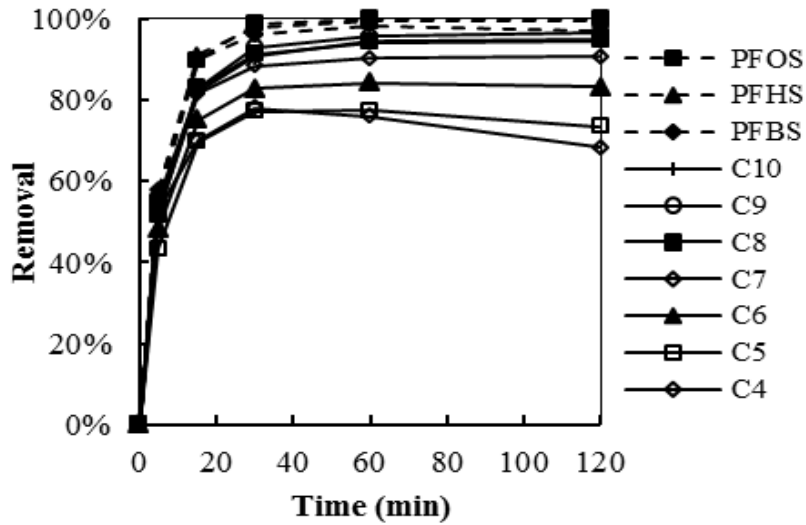


Figure 3.1 PFC removal kinetics in CCR water. Resin dose: 5 mL/L.

Differences in uptake among the 10 studied PFCs can be explained by the mechanisms involved when organic anions interact with anion exchange resins (e.g., Li and Sengupta 1998). First, electrostatic or Coulombic interactions between the anionic functional group of the PFC and the cationic functional group of the anion exchange resin (quaternary amine for resin 1) contribute to the overall interaction of PFCs with the anion exchange resin. Second, the non-polar moiety (NPM) of the PFCs, i.e., the perfluorinated carbon chain, sorbs to the resin matrix via non-specific van der Waals interactions. On the basis of these two interaction mechanisms, it can be postulated that the strength of the overall interaction is influenced both by the selectivity of the anion exchange resin for the charged functional group of the PFC (carboxylate, sulfonate) and the hydrophobicity of the NPM (length of the perfluorinated carbon chain).

The latter mechanism likely explains why PFC removal increases with increasing length of the perfluorinated carbon chain. The behavior of the sorptive interaction would ideally be studied with a non-functionalized resin that has the same polymeric matrix as resin 1. In the absence of such data, activated carbon adsorption data from can be used to help interpret how the strength of sorptive interactions varies with PFC characteristics. PFC adsorption data for carboxylates and sulfonates with equal perfluorinated carbon chain lengths (C5 and PFBS, C7 and PFHS, C9 and PFOS) illustrate that the adsorptive uptake of the sulfonate was always greater than that of the corresponding carboxylate (Dudley et al. 2014). These results suggest that sulfonates of a given perfluorinated carbon chain length are more hydrophobic than the corresponding carboxylate.

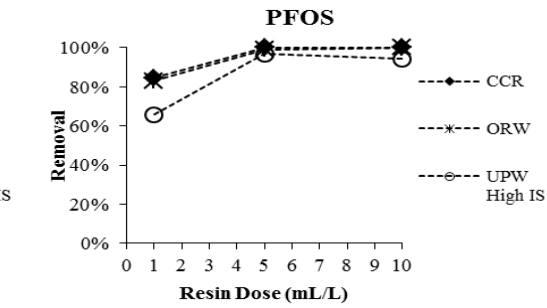
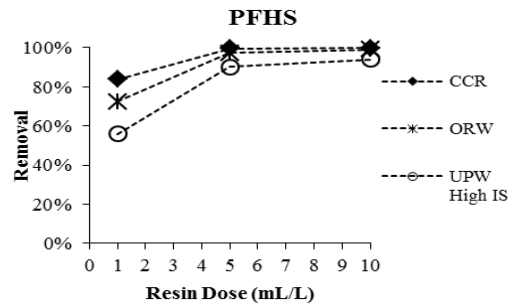
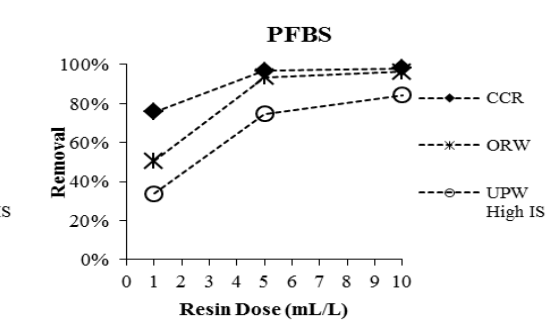
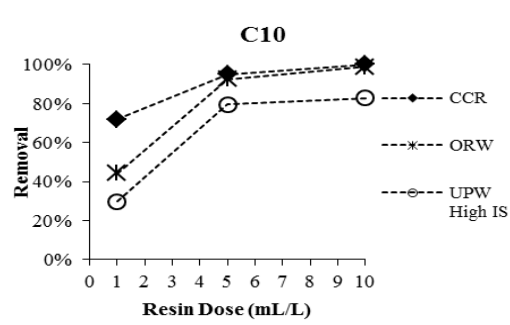
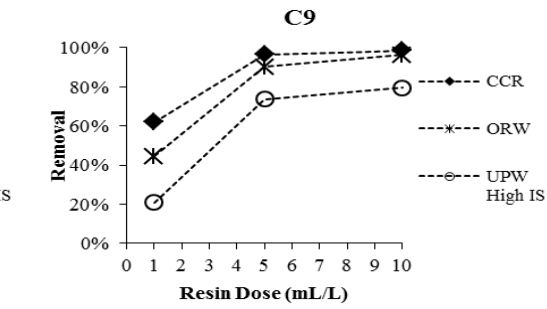
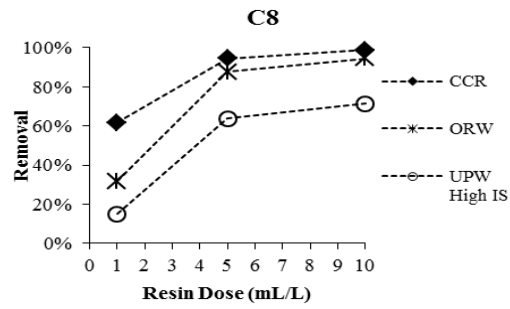
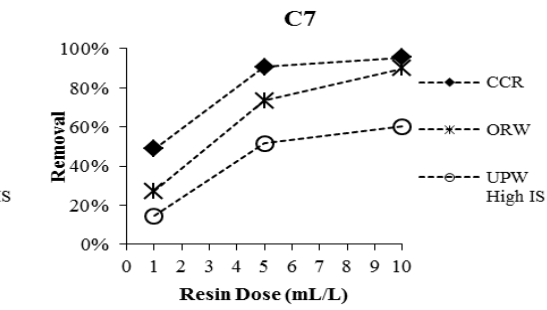
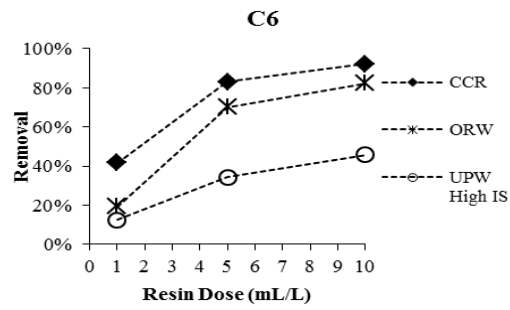
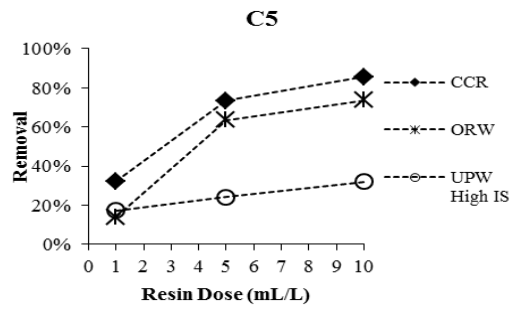
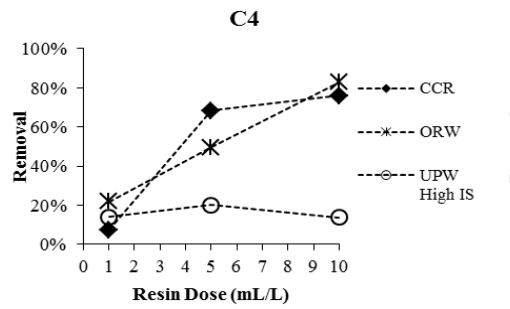
If sorption were the only mechanism contributing to PFC uptake, it would be reasonable to postulate that PFC uptake data by the ion exchange resin studied here would follow trends similar to those observed with activated carbon. However, the affinity of sulfonates for the ion exchange resin was substantially greater than what can be expected based on adsorption alone; e.g., PFBS removal exceeded that of C9 on the ion exchange resin but not on activated carbon. A likely explanation for the difference in PFC uptake behavior is that the ion exchange resin exhibits a higher selectivity for the sulfonate group than for the carboxylate group. No literature data was found to corroborate this hypothesis for the studied resin. Shukla et al. (2000) showed, however, that benzene sulfonate is a more effective displacer in anion exchange chromatography than benzoate. The functional group on the anion exchange column of Shukla et al. (2000) was a quaternary amine group, which is also the case for resin studied here.

Effect of resin dose

To assess the effect of resin dose and background water matrix, PFC removal percentages after a contact time of 2 hours were compared at resin doses of 1, 5, and 10 mL/L, and in CCR water, ORW, and high IS UPW (Figure 3.2). The results in Figure 3.2 illustrate that an increase in resin dose from 1 to 5 mL/L led to a substantial increase in PFC removal, except for C4 and C5 in UPW High IS water. For the latter, increasing the resin dose from 1 to 5 mL/L increased removal only by 6 and 7% for C4 and C5, respectively. Increasing the resin dose from 5 to 10 mL/L generally led to smaller improvements in PFC removal. In some instances, no measurable improvement was observed because the remaining aqueous phase PFC concentrations were at or close to the method reporting limit. However, results for the high IS UPW suggest that an increase in resin dose from 5-10 mL/L resulted in <12% increases in PFC removal. An exception is the C4 data obtained in ORW for which a 33% increase was measured.

Results in Figure 3.2 also illustrate that removal of smaller carboxylates (C4-C6) was most strongly affected by the presence of competing anions in the salt-amended UPW (IS = 0.02) such that <50% removal was achieved even at the highest resin dose of 10 mL/L. Also, PFC removal from ORW was more challenging than from CCR even though CCR has a higher DOM concentration. Overall, the results in Figure 3.2 suggest that ionic strength has a more pronounced effect on PFC removal by anion exchange resins than the presence of DOM.

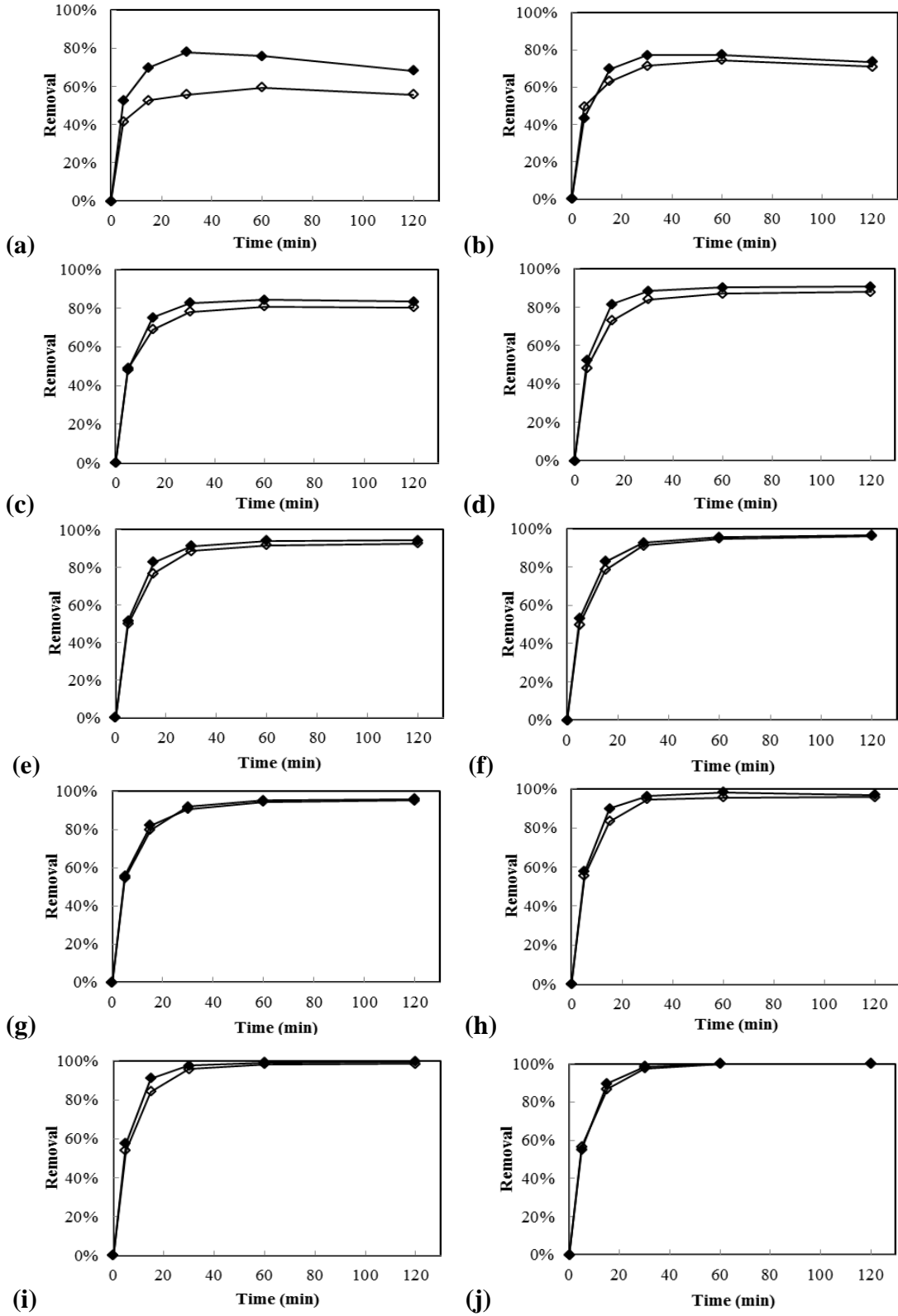
Figure 3.2 Effect of resin dose on PFC removal from CCR water, ORW, and high IS UPW. Contact time: 2 hours.



Effect of solution pH

To assess the effect of solution pH on PFC removal, batch kinetic tests were conducted in CCR water at ambient pH (7.5) and after adjusting the pH to 5.5 with HCl. The PFC removal results in Figure 3.3 illustrate that solution pH had a negligible effect on the removal of all PFCs except C4. After a contact time of 2 hours, C4 removal at pH 5.5 was 56% while it was 68% at pH 7.5.

Figure 3.3 Effect of solution pH on PFC removal. Filled series represent CCR water (pH 7.5), open series represent CCR water adjusted to a pH of 5.5: (a) C4 (b) C5 (c) C6 (d) C7 (e) C8 (f) C9 (g) C10 (h) PFBS (i) PFHS (j) PFOS. Resin dose: 5 mL/L.



Effect of background water matrix

To assess how background water quality affects PFC removal, batch kinetic tests were conducted with 5 mL/L of resin in the following waters:

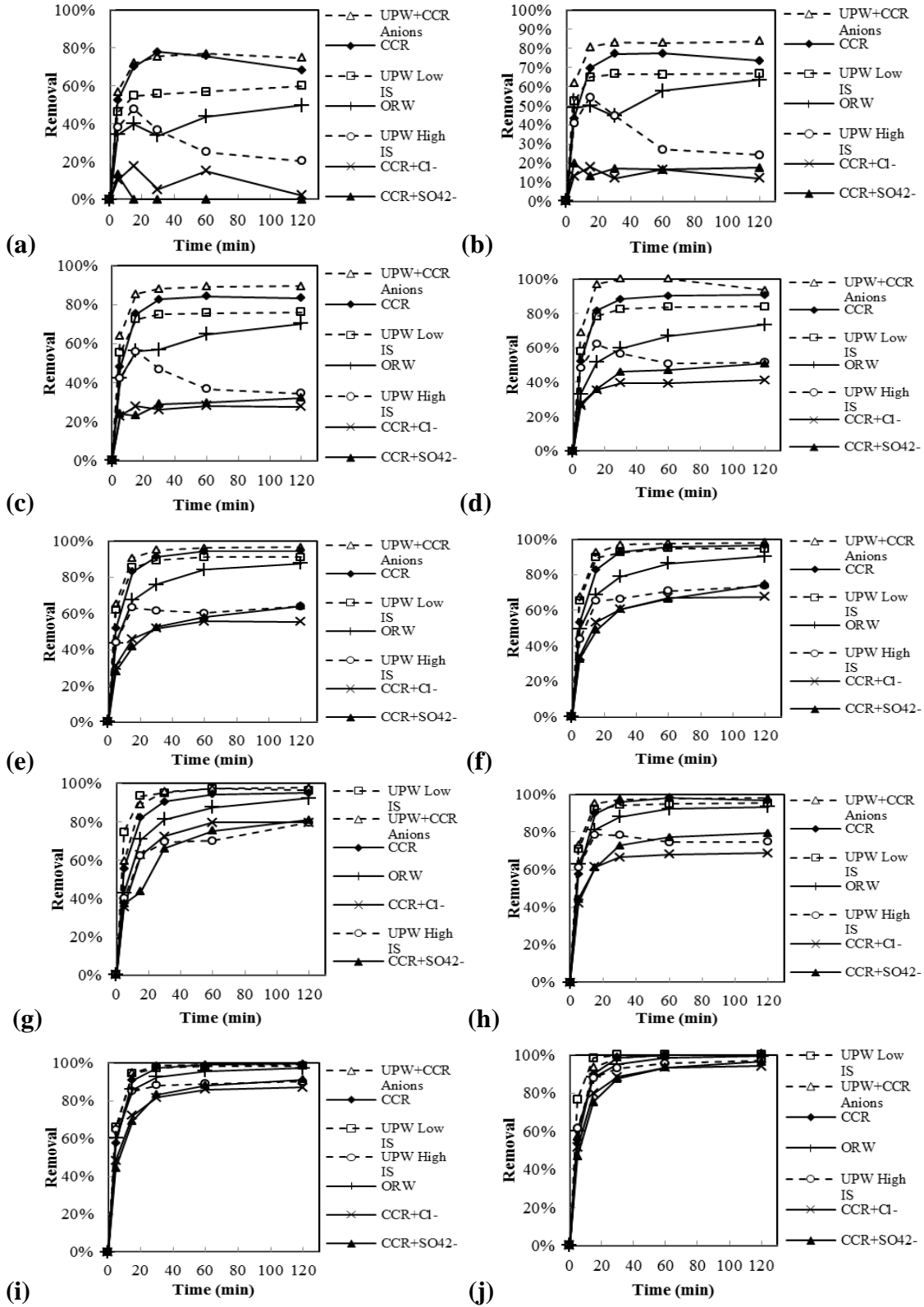
1. CCR
2. ORW
3. Ultrapure water with an IS of 0.002 (UPW Low IS)
4. Ultrapure water with an IS of 0.02 (UPW High IS)
5. UPW amended with sodium salts to match the anion composition of CCR water shown in Table 3.1 (UPW+CCR Anions)
6. CCR amended with sodium chloride (CCR+Cl⁻) to an IS of 0.02 to match UPW high IS
7. CCR amended with sodium sulfate (CCR+SO₄²⁻) to obtain a sulfate concentration of 200 mg/L (upper end of what can be expected in fresh water).

The panels in Figure 3.4 summarize the kinetic data separately for each of the ten PFCs while the results in Figure 3.5 provide a summary of PFC removals that were obtained after a contact time of 2 hours. A comparison of the CCR and UPW+CCR anions data permits an assessment of the effect of DOM on PFC removal. Comparisons after a contact time of 2 hours suggest that DOM decreased the removal percentage of the smaller carboxylic acids (C4-C6) by about 10% but had a negligible effect on the larger carboxylic acids and on the tested sulfonates. Another comparison can be made at a higher ionic strength of 0.02 (UPW High IS and CCR+Chloride data sets). The results in Figure 3.4 and Figure 3.5

show a more pronounced effect of DOM as follows: (1) in the absence of DOM, removal of smaller carboxylic acids (C4-C8) and PFBS increased and subsequently decreased (most likely, PFCs were displaced by chloride), but such a behavior was not observed in the presence of DOM, and (2) removal after 2 hours was adversely affected by DOM for a wider range of PFCs (C4-C9 and PFBS). The effect of DOM was most pronounced for C4 and C5.

While the effect of DOM on PFC removal was relatively small after a contact time of 2 hours, the results in Figure 3.4 and Figure 3.5 illustrate that PFC removal decreased considerably with increasing ionic strength (IS was 0.0017 for CCR and UPW+CCR Anions; 0.002 for UPW Low IS; 0.0057 for ORW; and 0.02 for UPW High IS and CCR+Chloride). The IS of the CCR+Sulfate water was 0.008, but this background matrix affected PFC removal in a manner similar to what was observed in waters with an IS of 0.02, suggesting that sulfate competed more strongly with anion exchange sites for PFC removal than chloride.

Figure 3.4 Effect of background water characteristics on PFC removal: (a) C4 (b) C5 (c) C6 (d) C7 (e) C8 (f) C9 (g) C10 (h) PFBS (i) PFHS (j) PFOS. Resin dose: 5 mL/L.



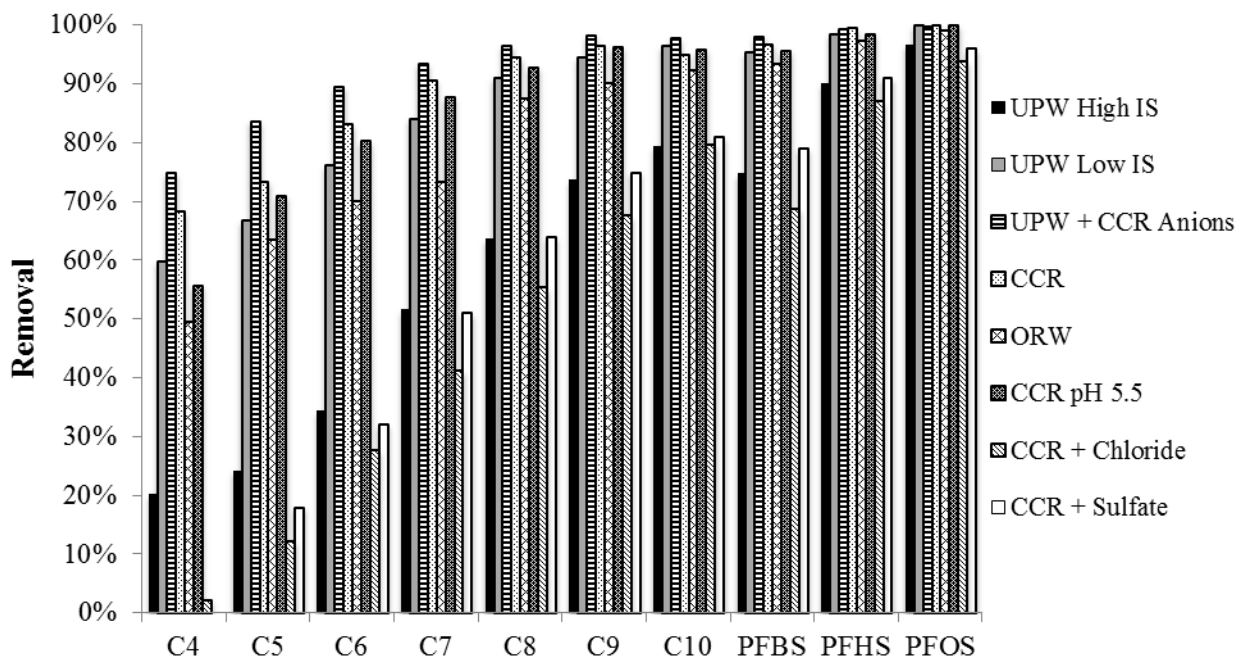


Figure 3.5 Effect of background water characteristics on PFC removal after a contact time of 2 hours. Resin dose: 5 mL/L.

To assess the effect of individual anions (bicarbonate, chloride, sulfate, and nitrate) at equivalent concentrations on PFC removal, additional batch kinetic tests were conducted. Anions were added as sodium salts to UPW. The concentration effect of each competing anion on PFC removal after a contact time of 1 hour is compared in Figure 3.6. As expected, PFC removal decreased with increasing anion concentration. For example, C8 removal after a contact time of 1 hour was 96% in the presence of 0.001 eq/L sulfate and 52% in the presence of 0.02 eq/L sulfate. The effect of increasing anion concentration was stronger for carboxylates than for sulfonates, and it became more pronounced as the perfluorinated carbon chain length decreased. Among the tested ions, bicarbonate was generally the least competitive and nitrate the most competitive anion (Figure 3.7). For carboxylates, sulfate

exerted a larger competitive effect than chloride at a given normality. In contrast, chloride and sulfate had similar effects, at equivalent concentrations, on the removal of sulfonates.

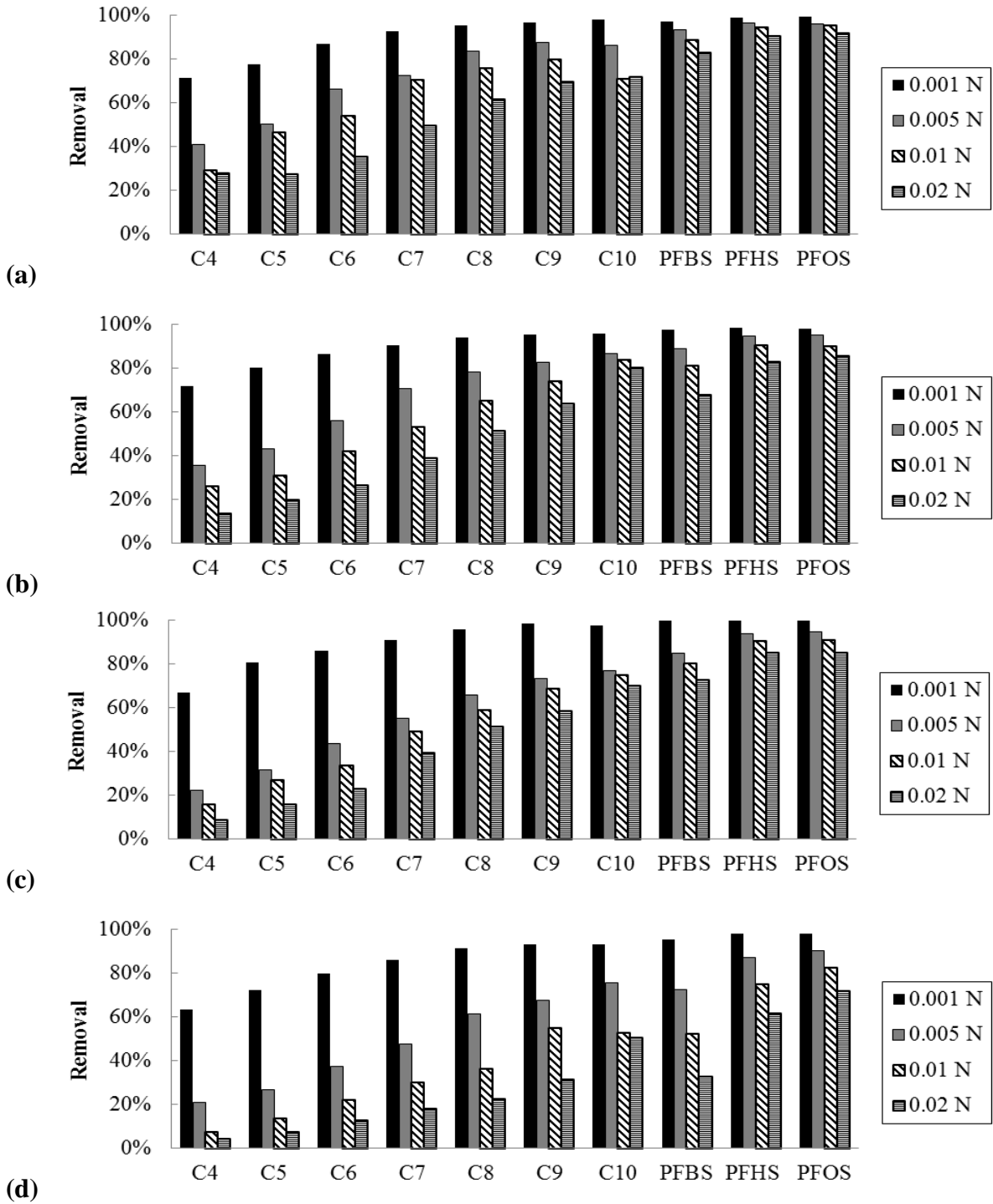


Figure 3.6 Effect of concentration of four competing anions on PFC removal: (a) bicarbonate (b) chloride (c) sulfate (d) nitrate. Resin dose: 5 mL/L. Contact time: 1 hour.

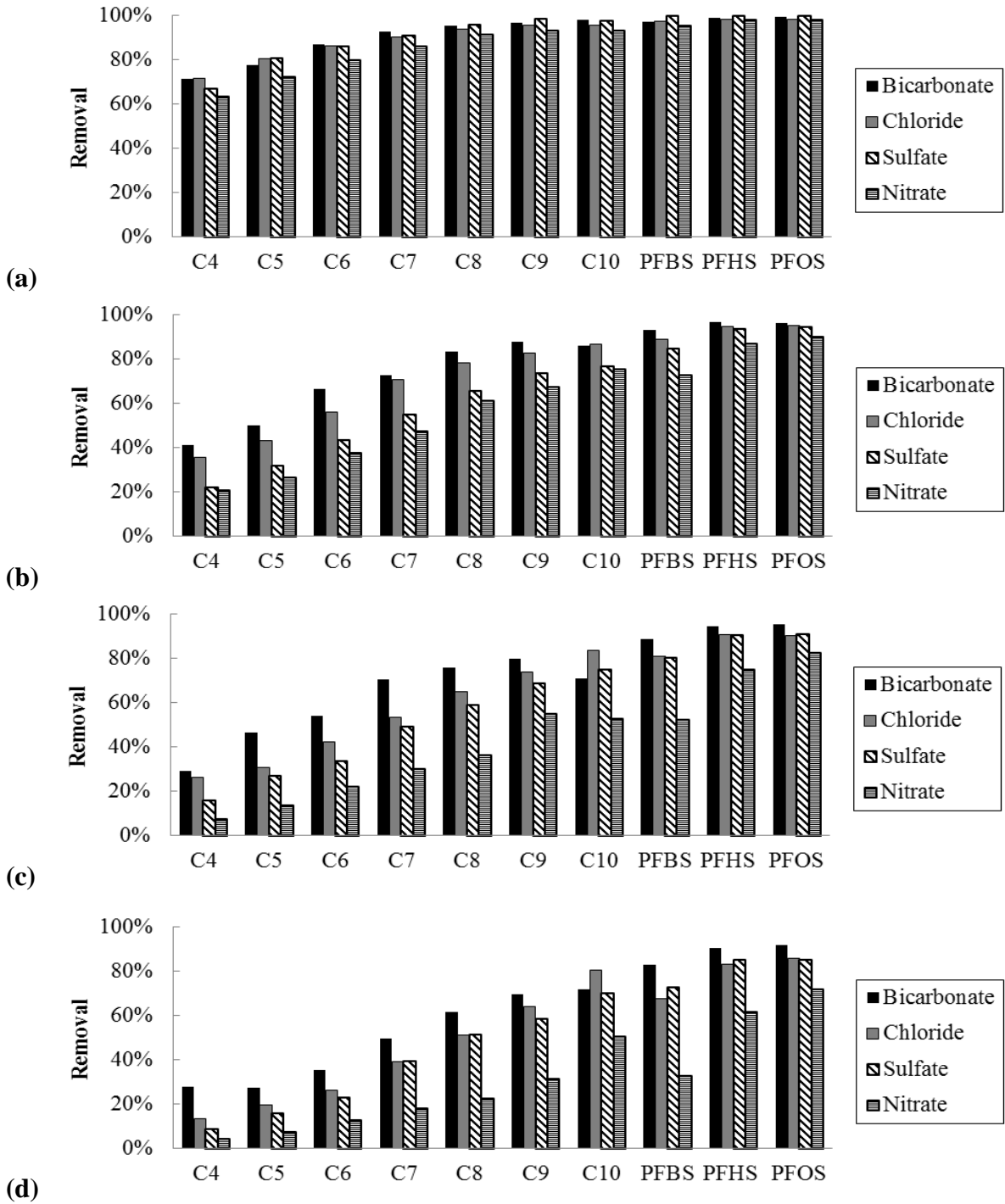


Figure 3.7 Effect of competing anion type at four concentrations on PFC removal: (a) 0.001 N (b) 0.005 N (c) 0.01 N (d) 0.02 N. Resin dose: 5 mL/L. Contact time: 1 hour.

CONCLUSIONS

Results from batch kinetic tests suggest that anion exchange is a promising approach for the removal of PFCs. PFC uptake by the selected anion exchange resin increased with increasing length of the perfluorinated carbon-chain, and sulfonates were more readily removed than carboxylates. Natural organic matter had a small adverse effect on PFC removal for the more weakly removed PFCs (e.g. C4 and C5) but had a negligible effect on more strongly removed PFCs (e.g. C10 and PFOS). In contrast, PFC removal decreased considerably with increasing ionic strength. Among the tested anions, bicarbonate had the smallest and nitrate the largest effect on PFC uptake.

ACKNOWLEDGEMENTS

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CHAPTER 4 : REGENERATION OF ANION EXCHANGE RESINS USED IN THE REMOVAL OF PERFLUORINATED COMPOUNDS

ABSTRACT

Perfluorinated compounds (PFC) such as perfluorooctanoic acid (C8) and perfluorooctane sulfonate (PFOS) are of concern because of their toxicity, persistence, and long half-lives in humans. In this study, the regeneration and reusability of a polyacrylic strong base anion (SBA) resin used for the removal of ten PFCs (seven perfluorocarboxylic acids: C4-C10, and three perfluorinated sulfonic acids: PFBS, PFHS, and PFOS) was studied. Regeneration strategies were evaluated by varying regenerant composition (pH, anion type, solvent matrix) and regenerant batch volume (3 and 30 bed volumes per batch). Using four regeneration strategies, the PFC removal effectiveness of the resin was evaluated over six loading/regeneration cycles. Results from cyclic loading tests and associated mass balances showed that complete PFC removal was obtained when regenerating the resin with four 30-bed volume batches of 0.76 M NaCl in a methanol/water mixture (50/50). Based on PFC 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 PFC removal. Longer-term studies are required to optimize resin regeneration strategies (e.g. aqueous NaCl solutions for routine regenerations interspersed with NaCl solutions in methanol/water for targeted PFC removal).

INTRODUCTION

Perfluorinated compounds (PFCs) are organic compounds in which all carbon-hydrogen bonds are replaced with carbon-fluorine bonds. PFCs are used in the production of stain repellants, non-stick coatings, water-repellent fabrics, and firefighting materials. They are compounds of concern because of their toxicity and their persistence in the environment and the human body. Perfluorooctanoic acid (C8) and perfluorooctane sulfonate (PFOS) have been detected globally in humans and wildlife. For example, measurable PFOS concentrations were found in the black-footed albatross in remote oceanic locations (Giesy and Kannan 2002). In addition, PFCs have been measured in human blood serum collected from both fluorochemical industry workers and the general population (Lau et al. 2007; Steenland and Woskie 2012). In terms of human health effects, a variety of adverse health conditions have been putatively associated with PFC exposure. Among them are cancer, decreased birth weight in newborns, immunotoxicity, thyroid disease, chronic kidney disease, and decreased sperm count (Barry, Winqvist, and Steenland 2013; Fei et al. 2007; Melzer et al. 2010; Shankar, Xiao, and Ducatman 2011; Joensen et al. 2009).

As drinking water is one important exposure route, the USEPA has issued a drinking water Provisional Health Advisory (PHA) for C8 and PFOS at 0.4 and 0.2 µg/L, respectively (US Environmental Protection Agency 2009). In New Jersey, a health-based C8 guideline of 0.04 µg/L was developed as a protective measure against lifetime C8 exposure. In addition, the USEPA is seeking occurrence data for six PFCs [C8, PFOS, perfluoroheptanoic acid (C7), perfluorononanoic acid (C9), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHS)] in U.S. drinking waters as part of the third Unregulated Contaminant

Monitoring Rule (UCMR3). As more information about PFC occurrence and the effects of PFCs on human health becomes available, it is important to concurrently identify treatment methods that are capable of protecting human health by limiting PFC exposure through drinking water.

Multiple studies have shown that conventional water treatment processes are ineffective for PFC removal (Vecitis et al. 2009; Quiñones and Snyder 2009; Appleman et al. 2013b). Oxidation processes such as chlorination, ozonation, and advanced oxidation (AOP) are also ineffective. However, ion exchange resins have shown promise. For example, PFOS was effectively removed by macroporous styrene-divinylbenzene (DVB) resins in column tests (Senevirathna et al. 2010) and by gel-type polystyrene DVB resins in batch experiments (Chularueangaksorn et al. 2013). Polyacrylic quaternary amine SBA resin at a dose of ~1.7 g/L achieved >95% removal of PFOS and PFBS in four hours (Carter and Farrell 2010).

An important consideration with respect to anion exchange removal is the regeneration and reusability of the resin. Several authors have investigated strategies to regenerate anion exchange resins. Rokicki and Boyer (2011) demonstrated that a sodium bicarbonate solution was as effective as the typically used sodium chloride solution, for the regeneration of a polyacrylic macroporous anion exchange resin loaded with dissolved organic carbon (DOC). Furthermore, Chularueangaksorn et al. (2013) confirmed the efficacy of 1% and 5% NaCl in MeOH/deionized water (7:3) regenerant solution for PFOS removal and the reusability of the tested resin over six cycles. Similarly, a mixture of 1% NaCl and 70% methanol solution was successfully used to regenerate more than 90% of both polyacrylic gel and macroporous resins that had been previously loaded with PFOS (Deng et

al. 2010). However, none of these studies considered the regeneration of resins loaded with PFCs of varying carbon chain length, or faced the challenges associated with environmentally relevant PFC concentrations. Therefore, the objective of this study was to identify regeneration conditions that restore the PFC removal capacity of an anion exchange resin loaded with ten PFCs, and to measure the PFC removal effectiveness over multiple loading/regeneration cycles.

MATERIALS AND METHODS

Materials

Sequential loading tests were conducted in either Cane Creek Reservoir (CCR) water (Carrboro, NC), or in a 50%/50% v/v CCR water:University Lake water blend. Both waters serve as drinking water sources for the Orange Water and Sewer Authority (OWASA). Water quality parameters are summarized in Table 4.1.

Table 4.1
Water quality parameters for drinking water sources

	CCR	50%/50% v/v University Lake:CCR
pH	7.5	7.2
TOC (mg/L)	4.5	5.7
UV₂₅₄	0.150	0.185
Alkalinity (mg/L as CaCO₃)	37	32
Hardness (mg/L as CaCO₃)	35	NM
Turbidity (NTU)	30	3.34
Specific conductivity (μS/cm)	106	102
Ionic strength*	0.0017	0.0016

NM: not measured

*Ionic strength= 1.6×10^{-5} x specific conductivity (μS/cm) (Snoeyink 1980)

Experiments were conducted using a strong base anion (SBA) resin that is NSF-certified for use in drinking water treatment. The resin was tested in the chloride form. Prior to experiments, the resin was prepared by rinsing with at least 20 bed volumes of deionized water in a column. Rinsed resin was stored at room temperature in deionized water until use. Resin properties are presented in Table 4.2.

Table 4.2
Resin properties

Matrix		Functional Group	Anion Exchange Capacity (eq/L)	Dry Resin Bed Density (mg/mL)	Mean Diameter (µm)
Polyacrylic	Macroporous	Quaternary amine (strong base)	0.52	213	180

Ten PFCs were chosen based on occurrence and the availability of an analytical method (Table 4.3). Predicted pKa values of the PFCs range from -3.57 to 0.52 (Table 4.3), meaning that the PFCs were present in their anionic carboxylate and sulfonate forms over the pH range evaluated in this study (5.5 to 8.5). Carboxylic acids will be referred to as C4-C10 and the sulfonates will be referred to by the abbreviations PFBS, PFHS, and PFOS.

Table 4.3
Chemical properties of PFCs studied

Compound	Formula	CAS #	MW	pK _a (25°C)	Solubility at pH 7 (g/L)
Perfluorobutanoic acid (C4)	C ₄ HF ₇ O ₂	375-22-4	214.0	0.37 ^a , 0.39 ^b	1000 ^a
Perfluoropentanoic acid (C5)	C ₅ HF ₉ O ₂	2706-90-3	264.1	0.40 ^a , 0.57 ^b	1000 ^a
Perfluorohexanoic acid (C6)	C ₆ HF ₁₁ O ₂	307-24-4	314.1	0.42 ^a , 0.84 ^b	260 ^a
Perfluoroheptanoic acid (C7)	C ₇ HF ₁₃ O ₂	375-85-9	364.1	0.47 ^a	58 ^a
Perfluorooctanoic acid (C8, PFOA)	C ₈ HF ₁₅ O ₂	335-67-1	414.1	0.50 ^a , 1.01-2.80 ^b	13 ^a , 9.5 ^c
Perfluorononanoic acid (C9)	C ₉ HF ₁₇ O ₂	375-95-1	464.1	0.52 ^a , 2.58 ^b	3 ^a
Perfluorodecanoic acid (C10)	C ₁₀ HF ₁₉ O ₂	335-76-2	514.1	0.52 ^a , 2.61 ^b	0.67 ^a
Perfluorobutane sulfonate (PFBS)	C ₄ HF ₉ SO ₃	375-73-5	300.1	-3.57 ^a	999 ^a
Perfluorohexane sulfonate (PFHS)	C ₆ HF ₁₃ SO ₃	355-46-4	400.1	-3.34 ^a	150 ^a
Perfluorooctane sulfonate (PFOS)	C ₈ HF ₁₇ SO ₃	1763-23-1	500.2	-3.27 ^a	7.5 ^a , 0.68 ^d

^a SciFinder Scholar (values were calculated with Advanced Chemistry Development (ACD/Labs) Software)

^b Experimental values (Ding and Peijnenburg 2013)

^c Measured values (Kauck and Diesslin 1951)

^d Based on OECD 105, OPPTS 830.7840 (OECD 2002)

Stock solutions for calibration curves and spiking of reactor contents were prepared from neat PFC standards (Wellington Labs, Ontario, Canada). Neat standards were weighed to produce individual PFC stocks of 10,000 ng/μL in methanol. A combined PFC stock of 1,000 ng/uL for each PFC was prepared by combining 1 mL of each individual 10,000 ng/μL PFC stock. Dilutions of the combined stock produced calibration stocks with individual PFC concentrations of 0.01 ng/μL and 0.1 ng/μL in methanol and a reactor dosing stock containing 10 ng/μL in methanol. The stocks made from neat compounds were compared to a purchased PFC mixture (5 μg/mL, Wellington Labs) to confirm concentrations. Six internal standards [mass labeled C4 (MC4), mass labeled C6 (MC6), mass labeled C8 (MC8), mass

labeled C10 (MC10), mass labeled PFHS (MPFHxS), and mass labeled PFOS (MPFOS)] were purchased from Wellington Labs each at a concentration of 50 µg/mL. A 20 µL aliquot of each internal standard was added to 10 mL of methanol to produce an internal standard stock of 0.1 ng/µL.

Sequential loading tests

To relate percent PFC removal to bed volumes of water treated, sequential loading tests were conducted in a jar test apparatus. Briefly, to 20 mL of freshly regenerated resin, 2-L batches of PFC-spiked water were added, stirred for 15 minutes and decanted. In some instances, this procedure was conducted with resin volumes of 5 or 10 mL, in which case the volume of water in each batch was adjusted to 500 or 1,000 mL such that 100 bed volumes were treated in each batch.

Regenerant Compositions

To identify resin regeneration conditions that effectively restore the PFC uptake capacity, several regeneration strategies were evaluated. Factors considered included regenerant composition (chloride versus sulfate, acidic pH versus ambient pH), regenerant batch volume (3 and 30 BV per batch), and number of sequential regenerant batches (up to 10). Samples from strategies 1, 2, 3, and 6 were analyzed by LC-MS/MS using a dilution factor of 100, and a dilution factor of 50 was used for the remaining regeneration strategies. The regeneration strategies evaluated are shown in Table 4.4, along with the corresponding reporting limits (ng of PFC removed from resin per batch).

Table 4.4
Screening regeneration strategies

Strategy ID	Regenerant		Volume (mL)	pH	Batches	Bed Volumes per batch	Reporting Limit (ng)
	Salt content	Solvent					
1	6M NaCl	DI water	15	6.15	1	3	15 ^a
2	6M NaCl	DI water	15	2.12	1	3	15 ^a
3	6M NaCl	DI water	15	8.80	10	3	15 ^a
4	6M NaCl	DI water	150	8.80	1	30	75 ^b
5	6M NaCl	DI water	150	2.50	1	30	75 ^b
6	3M Na ₂ SO ₄	DI water	15	4.70	1	3	15 ^a
7	3M Na ₂ SO ₄	DI water	150	4.70	1	30	75 ^b
8	3M Na ₂ SO ₄	DI water	150	2.50	1	30	75 ^b

^a 37.5 ng for C10, and PFOS

^b 187.5 ng for C10, and PFOS

Prior to regeneration, the resin was loaded in sequential loading tests with 1,000 bed volumes of CCR water into which 500 ng/L of each PFC was spiked. Subsequently, regeneration strategies 1-8 were evaluated by regenerating 5 mL of the PFC-loaded resin. The resin was added to 15 or 150 mL of regenerant (3 or 30 BV, respectively). The container was shaken for one hour on a mechanical shaker after which time a sample was taken for PFC analysis. The regenerant was decanted and, if additional batches were tested (strategy 3), another batch of regenerant (3 BV) was added into the vial containing the resin. The vial was shaken for another hour and another sample was taken for PFC analysis. Considering the reporting limits for each strategy (Table 4.4), the lowest percentages of PFC release that we could confidently consider are shown in Table 4.5 (note: percentages for a given compound vary because of (1) different reporting limits for the different regeneration strategies (different batch volumes and dilution factors) and (2) differences in PFC loading that was

achieved at the end of different sequential loading tests, which served as the starting point for the mass balance calculations).

Table 4.5
Reporting limits for the PFCs for the different strategies (% of loaded PFC)

Strategy #	C4	C5	C6	C7	C8	C9	C10	PFBS	PFHS	PFOS
1	1.4	1.4	0.9	0.7	0.6	0.6	1.2	0.5	0.5	1.2
2	1.4	1.4	0.9	0.7	0.6	0.6	1.2	0.5	0.5	1.2
3	1.6	1.4	0.9	0.8	0.7	0.6	1.3	0.7	0.6	1.3
4	7.9	7.0	4.6	4.1	3.4	2.9	6.6	3.4	3.0	6.3
5	7.9	7.0	4.6	4.1	3.4	2.9	6.6	3.4	3.0	6.3
6	3.1	2.1	1.1	0.9	0.8	0.7	1.3	0.7	0.6	1.3
7	15.3	10.3	5.4	4.5	3.8	3.4	6.5	3.3	3.0	6.7
8	7.9	7.0	4.6	4.1	3.4	2.9	6.6	3.4	3.0	6.3

Cyclic loading tests

A series of six cyclic loading tests was performed to evaluate the performance of the resin over multiple loading/regeneration cycles, and four regeneration strategies were evaluated (Strategies A, B, C, and D in Table 4.6). Prior to the first sequential loading test, 100 mL of resin were regenerated with four 1.5-L batches of 0.76M NaCl in 50%/50% v/v MeOH:DI water. Each batch was mixed for 20 minutes; and, after the regeneration, the resin was rinsed with four 1.5-L batches of DI water. Then, 1,000 bed volumes of CCR water were treated in a sequential loading test with 20-mL of the regenerated resin. Every 100 bed volumes, a sample from the composited treated water was taken for PFC analysis. These results correspond to Cycle I.

Following the first cycle, the resin was divided into four 5-mL groups (Group 1, Group 2, Group 3, and Group 4), and each group was regenerated with one of the four regeneration strategies considered (Table 4.6). In each regeneration batch, resin was mixed with regenerant for 20 minutes and settled for 5 minutes. Subsequently, the resin was rinsed with four 0.15-L batches of DI water, mixing for 10 minutes and settling for 5 minutes. PFC samples were taken for each regeneration and rinse batch. Sequential loading tests for the following five loading/regeneration cycles were completed separately for the four 5-mL groups of resin. The regenerated resin was stored in DI water between cycles.

Table 4.6
Resin regeneration strategies

Strategy ID	Regenerant		Volume (mL)	pH	Batches	Bed Volumes per batch
	Salt content	Solvent				
A (Group 1)	0.76M NaCl	DI water	15	6.75-7.26*	4	3
B (Group 2)	0.76M NaCl	DI water	150	6.75-7.26*	4	30
C (Group 3)	0.76M NaCl	50%/50% v/v MeOH/water	15	6.84-7.00*	4	3
D (Group 4)	0.76M NaCl	50%/50% v/v MeOH/water	150	6.84-7.00*	4	30

*The pH was adjusted using 0.1N NaOH or 2N HCl, as needed

Due to the high amount of salt present in the regenerant, samples were diluted prior to LC-MS/MS analysis (solid-phase extraction was extensively evaluated as a sample clean-up option but was eventually dropped for several reasons, including precipitate formation in

methanol extracts with SPE cartridges suitable for capturing all 10 PFCs, and inability to capture all 10 PFCs with SPE cartridges suitable for desalting purposes). The reporting limits (ng of PFC removed from resin per batch) corresponding to the different regeneration strategies are shown in Appendix D.

Mass Balance

A mass balance was conducted using the loading and regeneration data. The mass balance included the mass of each PFC retained by the resin (Equation 4.1), calculated by subtracting the PFC mass present in the liquid phase after 1000 bed volumes (Equation 4.3) from the initial PFC mass (Equation 4.2), and adding the PFC mass that was not recovered from the resin during the previous cycle. The percentage of PFC released during each regeneration batch was calculated (Equation 4.4) as well as the percentage of PFC recovered during the rinsing step (Equation 4.5). Mass balances were developed for each cycle and compound.

$$\text{PFC mass retained by the resin} = (\text{Initial PFC mass} - \text{PFC mass after 1000 BV}) + \text{PFC mass not recovered in previous cycle}$$

Equation 4.1

$$\text{Initial PFC mass} = \text{Initial PFC concentration} \times 5 \text{ Liters}$$

Equation 4.2

$$\text{PFC mass after 1000 BV} = \text{PFC concentration measured after 1000 BV} \times 5 \text{ Liters}$$

Equation 4.3

$$\% \text{ PFC released} = \frac{\text{Concentration measured after regeneration} \times (0.15 \text{ L or } 0.015 \text{ L})}{\text{PFC mass retained in resin (Eq.4.1)}}$$

Equation 4.4

$$\% \text{ PFC released in rinse} = \frac{\text{PFC concentration measured after rinse} \times 0.15 \text{ L}}{\text{PFC mass retained by resin (Eq.4.1)}}$$

Equation 4.5

Analytical method for determining PFC concentrations

PFC concentrations were measured by liquid chromatography tandem mass spectrometry (LC-MS/MS) at the National Exposure Research Laboratory of the United States Environmental Protection Agency (USEPA) in Research Triangle Park, NC. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC/MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5 μ m 100Å, Phenomenex Inc.) was used for PFC separation. The gradient method shown in Table 4.7 was used to elute PFCs from the HPLC column for the majority of the analyses. Mobile phase A was 2 mM ammonium

acetate in DI water with 5% methanol. Mobile phase B was changed to 2 mM ammonium acetate in acetonitrile with 5% DI water.

Table 4.7
LC Gradient Method for PFC Analysis

Time (min)	Mobile Phase A % (v/v)	Mobile Phase B % (v/v)	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mass spectrometer transitions for PFC analytes and internal standards used are shown in Appendix A.

Calibration curves were generated by analyzing standards with concentrations of 10, 25, 50, 100, 250, 500, and 750 ng/L. The limit of quantitation (LOQ) for all compounds was 10 ng/L for all PFCs except C10, for which the LOQ was 25 ng/L. Calibration standards were analyzed at the beginning and end of LC runs and averaged to account for possible instrument drift.

All samples and calibration standards were filtered through a 0.45- μ m glass fiber syringe filter into a 15-mL Becton-Dickinson polypropylene vial. After filtration, samples and standards were spiked with 25 μ L of the internal standard mixture and 8 μ L formic acid, which was used to lower the pH to below 2. A blank with no PFCs added was also prepared with the calibration standards and plotted as a calibration curve point.

PFC levels were quantitated by calculating the response factor from the areas of the analyte and the matching mass-labeled IS. For compounds without matching IS (C5, C7, C9, PFBS), response factors were calculated using the areas of the analyte and mass labeled C6 (MC6) for C5 and C7, mass labeled C8 (MC8) for C9, and mass labeled PFHS (MPFHxS) for PFBS. Chromatograms for each of the ten PFCs and six internal standards are presented in Appendix B. Representative calibration curves for each PFC are shown in Appendix C.

Background Water Matrix

The total organic carbon (TOC) concentration was measured by high-temperature combustion (Shimadzu TOC-VCSN) according to Standard Method 5310B. The UV-absorbing organic matter concentration was measured at a wavelength of 254 nm according to Standard Method 5910. A Thermo Scientific Orion 3-star pH meter was used to measure the pH of solutions. Total alkalinity was determined by titrating samples with 0.02 N sulfuric acid according to Standard Method 2320 B. Hardness was determined by titration with EDTA, according to Standard Method 2340 C.

RESULTS AND DISCUSSION

Sequential loading tests

To relate percent PFC removal to bed volumes of water treated, sequential loading tests were conducted. The selected bench-scale testing approach followed a protocol designed to mimic the full-scale TOC removal performance of the resin. Full-scale systems

employing the studied resin for TOC removal are typically operated at conditions equivalent to treating between 500 to 1,000 bed volumes (BV).

Raw CCR water was used in the sequential loading tests, and the resin was tested in its chloride form. Four sequential loading tests were performed, and reproducibility of the resulting breakthrough curves was good, as illustrated by the representative error bars shown for C6 (Figure 4.1).

The breakthrough curves shown in Figure 4.1 illustrate that (1) for both the perfluorinated carboxylate and sulfonate compound classes, removal effectiveness increased with increasing carbon chain length and (2) all three perfluorinated sulfonates were more effectively removed than any of the tested perfluorinated carboxylates. Among the tested PFCs, removal of C4 was the most difficult. At 100 BV, C4 removal was 82%, but this percentage decreased to 57% at 500 BV and to 30% at 1,000 BV. Removal of C5 was slightly better, but also decreased rapidly with increasing BV (86% removal at 100 BV, 37% removal at 1,000 BV). For PFCs with longer carbon chains, the performance degradation with increasing BV was not as large. For example, C8 removal at 100 BV was approximately 95% and decreased to 77% at 1,000 BV. For the most effectively removed compound among the tested PFCs, PFOS, the performance of the resin remained almost constant (97.3% removal at 100 BV, 95.9% at 1,000 BV).

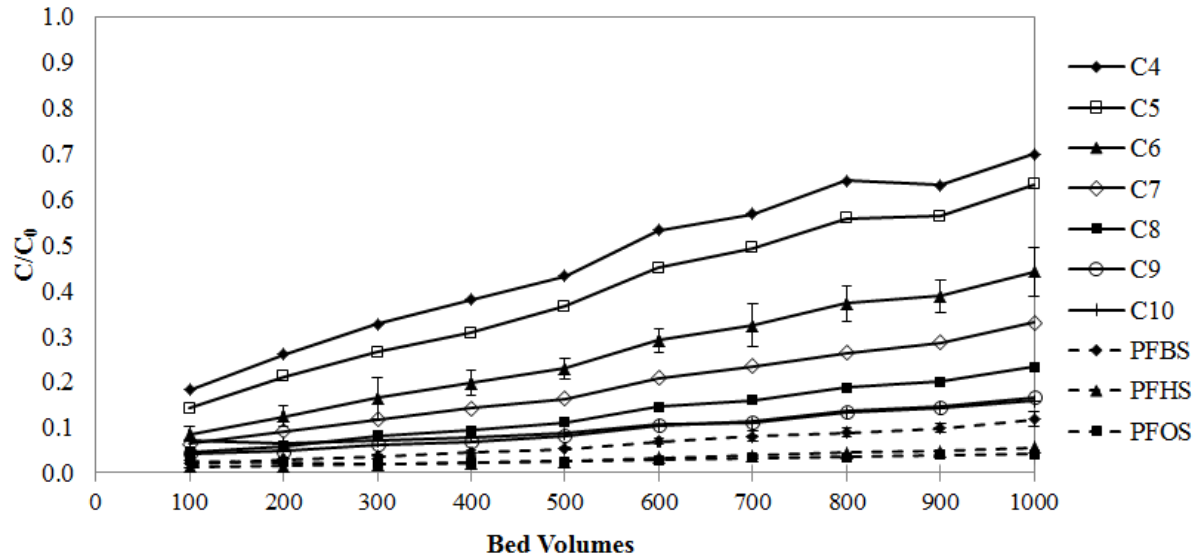


Figure 4.1 PFC breakthrough curves resulting from sequential loading tests. Water: CCR. Results are averages of four replicate tests. Error bars indicating one standard deviation are shown for C6 and PFBS but are omitted for other PFCs for clarity.

Regeneration strategies

PFC release results for the 8 regeneration strategies shown in Table 4.4 are summarized in Table 4.8. The regeneration efficiency was typically highest for C4 and C5, the two PFCs that exhibited the weakest uptake capacity. With strategy 3, for example, 69 and 78% of the loaded C4 and C5 was recovered, respectively, after the resin had been contacted with 10 three-bed volume batches of 6 M NaCl solution at pH 8.8. In contrast, only negligible amounts of C8, C9, and PFHS were released. A comparison of regeneration results obtained with strategy 3 (10 three-bed volume batches of 6 M NaCl) matched those obtained with regeneration strategy 4 (one 30-bed volume batch of 6 M NaCl) fairly well. Among the tested regeneration alternatives, only strategy 5 (6M NaCl, pH 2.50, 30 bed volumes) yielded PFC recoveries that were higher than those obtained with strategies 3 and 4. The data for

strategy 5 suggest that lowering the regenerant pH to 2.5 and adding a large volume of regenerant (30 BV) improves PFC recovery. Possible explanations include (1) partial conversion of PFCs from the anionic to the neutral form such that electrostatic interactions between the PFCs and the resin were interrupted and (2) maintenance of a larger concentration gradient with the larger regenerant volume promoted PFC desorption. Furthermore, the data for strategy 5 indicate that recoveries of several PFCs exceeded 100%, a result that may be attributable to the fact that the resin employed in this study had been previously used and was regenerated using conditions designed to recover its TOC removal capacity. The results shown in Table 4.8 illustrate that regeneration with 3M Na₂SO₄ was less effective than regeneration with 6M NaCl both at pH 4.7 and 2.5. Recognizing that strategies 1-8 were either not effective for releasing PFCs that strongly interact with the resin or required a large volume of acidic regenerant, additional regeneration strategies were explored. The rationale for developing such a strategy is discussed below.

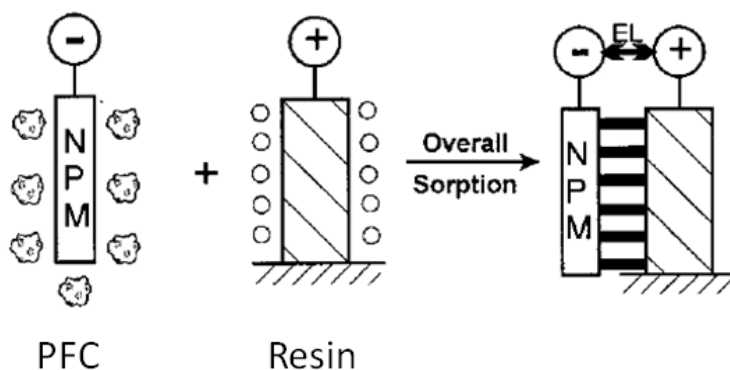
Table 4.8
Percentage of loaded PFCs released with eight regeneration alternatives

Strategy #	Batch	PFCs released (%)									
		C4	C5	C6	C7	C8	C9	C10	PFBS	PFHS	PFOS
1	1	32.8	29.7	15.3	8.9	2.3	<0.6	<1.2	3.9	0.6	<1.2
2	1	31.1	28.4	13.8	6.5	1.7	<0.6	<1.2	3.6	<0.5	<1.2
3	1	37.9	31.6	15.3	7.3	2.1	<0.6	<0.5	4.6	0.7	<0.5
	2	11.8	10.3	4.1	2.2	<0.7	<0.6	<0.5	1.5	<0.6	<0.5
	3	8.9	9.0	4.0	1.6	<0.7	<0.6	0.7	1.8	<0.6	<0.5
	4	4.1	5.4	2.6	1.1	<0.7	<0.6	0.7	1.2	<0.6	<0.5
	5	3.4	5.5	2.8	1.2	<0.7	<0.6	1.8	1.4	<0.6	<0.5
	6	2.5	4.8	2.7	0.9	<0.7	<0.6	1.8	1.3	<0.6	<0.5
	7	1.6	3.4	2.2	1.1	<0.7	<0.6	1.6	1.3	<0.6	<0.5
	8	<1.6	2.8	2.2	1.1	<0.7	<0.6	1.4	1.3	<0.6	<0.5
	9	<1.6	2.5	1.9	0.9	<0.7	<0.6	1.8	1.3	<0.6	<0.5
	10	<1.6	2.6	2.6	1.1	<0.7	<0.6	1.8	1.7	<0.6	<0.5
	TOTAL	68.6	77.9	40.3	18.5	2.1	<0.6	11.7	17.4	0.7	<0.5
4	1	79.2	95.3	34.4	15.4	4.3	<2.9	<6.6	14.6	2.8	<6.3
5	1	230.7	252.5	129.3	92.0	309.6	91.8	112.1	81.1	43.63	84.9
6	1	14.3	3.9	1.1	1.2	<0.8	<0.7	<0.5	<0.7	<0.6	<0.5
7	1	25.9	8.0	<5.4	<4.5	<3.8	<3.4	3.83	<3.3	<3.0	2.72
8	1	19.7	8.6	<4.6	<4.1	<3.4	<2.9	7.5	<3.4	<3.0	<2.5

Removal mechanisms of PFCs by anion exchange resins and rationale for selecting additional regeneration conditions

As shown in Figure 4.1, perfluorinated carboxylates were more poorly removed than sulfonates in sequential loading tests. This result can be explained by a number of factors. A review of the literature shows that two mechanisms contribute to the removal of organic anions by anion exchange resins (Li and Sengupta 1998). First, electrostatic or Coulombic interactions between the anionic functional group of the PFC and the cationic functional group of the anion exchange resin (quaternary amine for the selected resin) contribute to the

overall interaction of PFCs with the anion exchange resin. Second, the non-polar moiety (NPM) of the PFCs, i.e., the perfluorinated carbon chain, sorbs to the resin matrix via non-specific van der Waals interactions. The two interaction mechanisms between PFCs and the anion exchange resins are illustrated in Figure 4.2.



Source: Adapted from (Li and Sengupta 1998)

Figure 4.2 PFC uptake mechanisms on anion exchange resins (NPM: non-polar moiety = perfluorinated carbon chain length; EL: electrostatic interaction).

On the basis of these two interaction mechanisms, it can be postulated that the strength of the overall interaction is influenced both by the selectivity of the anion exchange resin for the charged functional group of the PFC (carboxylate, sulfonate) and the hydrophobicity of the NPM (length of the perfluorinated carbon chain). Therefore, both sorption and ion exchange processes contribute to PFC uptake by the selected resin. As a result, an effective regenerant needs to address both uptake mechanisms. As shown by Li and Sengupta (1998), neither a concentrated NaCl solution alone nor methanol alone was

effective for the regeneration of an anion exchange resin loaded with pentachlorophenol ($pK_a = 4.8$). However, a 50%/50% v/v MeOH/water mixture containing 5% NaCl was an effective regenerant because (1) the high concentration of chloride ions was able to restore the ion exchange capacity of the resin and (2) the presence of MeOH enhanced interactions between the NPM of pentachlorophenol, i.e. the chlorinated aromatic ring, and the regenerant, such that the NPM effectively desorbed from the resin matrix. The latter phenomenon can be explained by a decrease in the dielectric constant of the regenerant when MeOH is added.

Based on the above analysis, an additional regeneration strategy was evaluated: a 50%/50% v/v MeOH:H₂O mixture containing 0.76M NaCl.

Cyclic loading/regeneration tests

The objective of the cyclic loading/regeneration tests was to assess the PFC removal effectiveness of the resin over six loading/regeneration cycles. Briefly, 20 mL of regenerated resin (see Materials and Methods) was loaded in a sequential loading test with 1,000 bed volumes of PFC spiked water for the first loading cycle, and subsequently, the resin was divided into four 5-mL groups. Each group was regenerated as shown in Table 4.6.

Following regeneration of the Group 4 resin, mass balances indicated that PFC recovery was complete (average recoveries over the 6 loading cycles ranged from 100-132% for C4-C9, PFBS and PFHS; for C10 and PFOS, recoveries of 206 and 186%, respectively, were obtained, and it is unclear whether these values were influenced by the prior history of the resin). Consequently, PFC removal results obtained with the Group 4 resin were taken as a baseline case, to which the performance of the Group 1-3 resins was compared. The

performance of the Group 4 resin over the 6 loading/regeneration cycles did not vary in a systematic manner, and the average PFC fraction remaining was plotted as a function of bed volumes as shown in Figure 4.3.

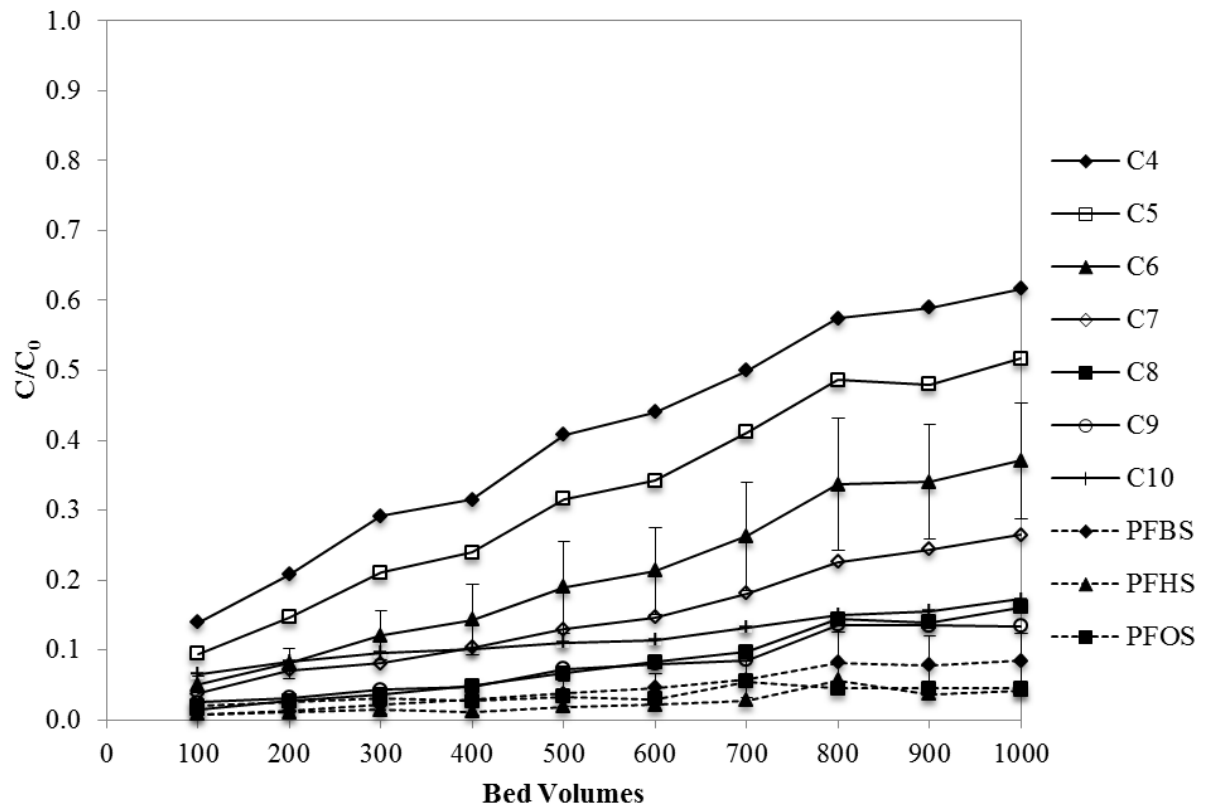


Figure 4.3 Performance of Group 4 resin over 6 loading/regeneration cycles. Error bars indicating one standard deviation are shown for C6 and PFBS but are omitted for other PFCs for clarity.

PFC removal obtained with resins in Groups 1-3 was compared to that obtained with the Group 4 resin as follows:

$$\left(\frac{(C/C_0)_{\text{Group } i}}{(C/C_0)_{\text{Group } 4}} \right)_{\text{average}} = \frac{1}{10} \sum_{BV/100=1}^{10} \left(\frac{(C/C_0)_{\text{Group } i}}{(C/C_0)_{\text{Group } 4}} \right)_{BV/100} \quad \text{where } i = 1, 2, \text{ or } 3$$

The performance of Group 1-3 resins relative to that of the Group 4 resin is summarized in Figure 4.4. For regeneration strategies that did not include methanol (Group 1 and Group 2), the results in Figure 4.4 show that C4 and C5 removals matched those obtained with the Group 4 resin. However, removal of larger carboxylates and the sulfonates by the Group 1 and 2 resins was lower. Relative to the Group 4 resin, C/C₀ values for the Group 1 resin were up to 5.4 times higher, while those for the Group 2 resin were up to 3.2 times higher. The largest performance degradation was observed for C8, C9, and PFHS (note: ratios for PFHS and PFOS could not be calculated for loading cycles 5 and 6 because non-detectable aqueous phase concentrations were obtained for the Group 4 resin). The smaller performance degradation of the Group 2 resin relative to the Group 1 resin illustrates that regeneration with four 30-bed volume batches of aqueous NaCl regenerant was more effective than regeneration with four 3-bed volume batches, a result that is corroborated by the mass balances shown in Figure 4.5 (panels a and b). Although incomplete regeneration of Group 1 and 2 resins can explain the performance differences of these resins relative to the Group 4 resin, the results in Figure 4.4 (panels a and b) suggest that PFC removal did not degrade measurably over the 6 loading/regeneration cycles.

Results for the Group 3 resin suggest that its performance relative to the Group 4 resin was similar. Therefore, regeneration with four 3-bed volume batches of 0.76 M NaCl in a 50/50 methanol/water mixture effectively restored the PFC removal capacity of the resin. While the PFC removal data suggest that the regeneration strategy for the Group 3 resin more effectively restored its PFC removal capacity than the regeneration strategy for the Group 2 resin, the mass balance data do not corroborate this interpretation (Figure 4.5, panels b and c). Because large dilution factors were required for the analysis of the regenerant solutions, it is possible that the uncertainty associated with the measurements masks the trends observed during the PFC uptake phase (Figure 4.4). For completeness, mass balance results for the Group 4 resin are shown in Figure 4.5. As explained above, mass balance closure was reasonable (100-132%) for all PFCs except C10 and PFOS, for which recoveries were approximately 200%.

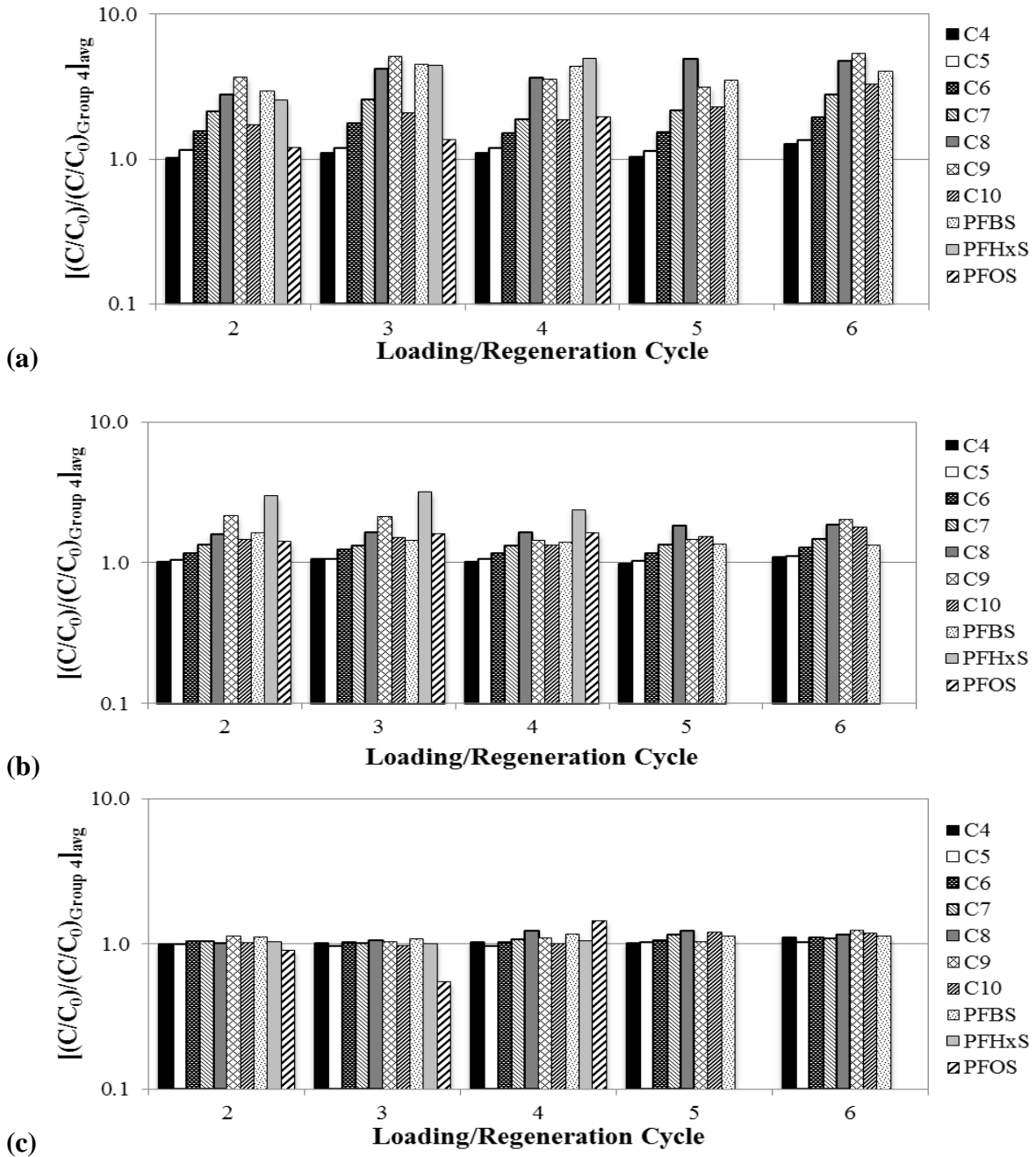


Figure 4.4 Performance of the resin over multiple loading/regeneration cycles: (a) Group 1, (b) Group 2, (c) Group 3. Performance of each group is normalized to that measured for Group 4. PFHS and PFOS results not shown for cycles 5 and 6 because Group 4 results were below detection.

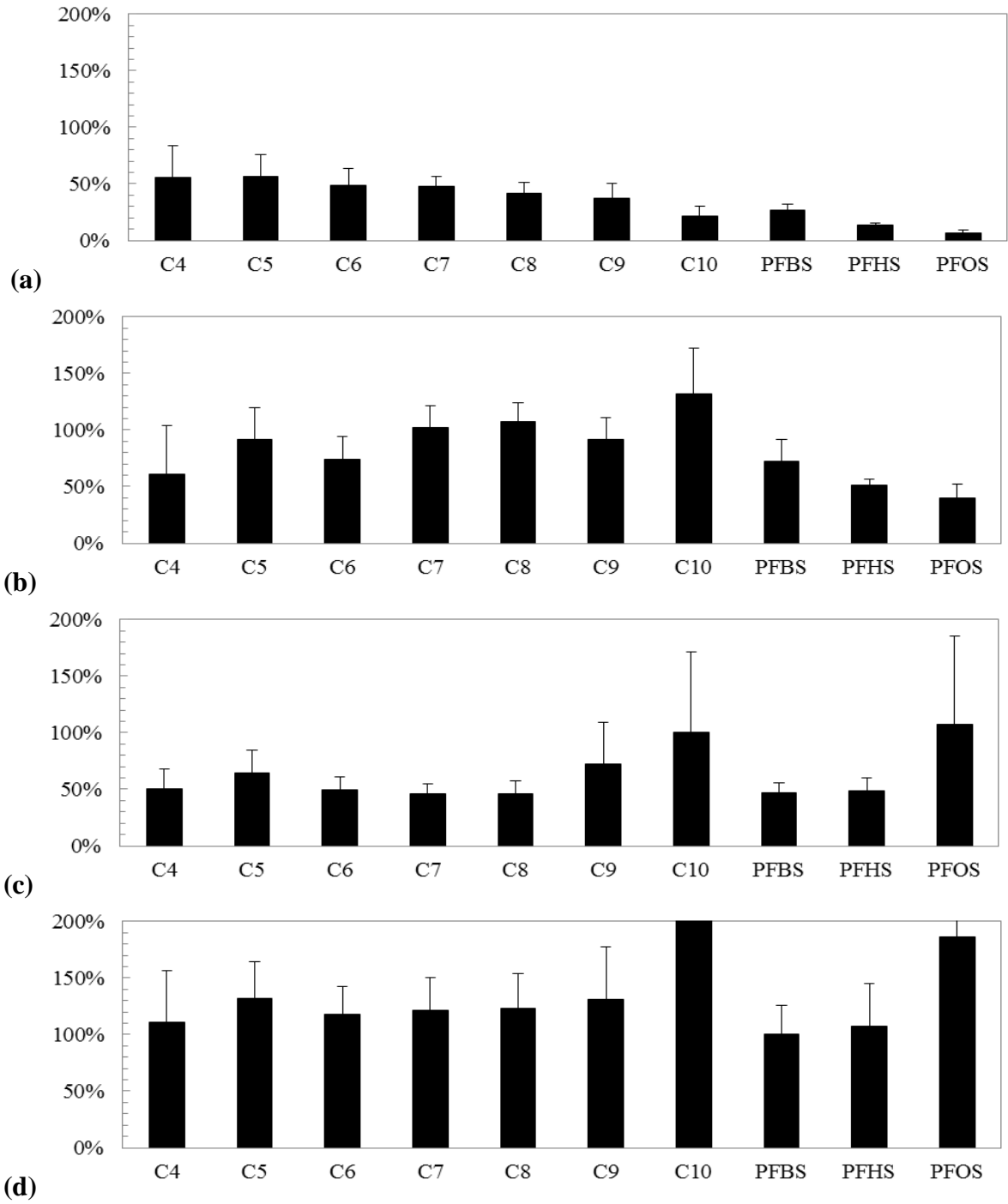


Figure 4.5 PFC mass balances for (a) Group 1 (b) Group 2 (c) Group 3 (d) Group 4

Overall, the results of the cyclic loading/regeneration experiments illustrate that regeneration with four 3-bed volume batches of a 0.76 M NaCl solution in 50/50 water/methanol may be sufficient to maintain the PFC removal capacity of the resin. In addition, it may be sufficient to regenerate the resin with an aqueous NaCl brine for several loading/regeneration cycles as little performance degradation was observed for the Group 1 resin over 6 loading/regeneration cycles. A targeted PFC removal regeneration step may therefore only be necessary on a periodic basis.

CONCLUSIONS

Anion exchange processes show promise for PFC removal, provided that resins are regenerated in a manner that restores the PFC removal capacity of the resin. During sequential loading tests, the performance degradation of the resin, with increasing bed volumes of water treated, was larger for C4 and C5 and smallest for PFHS and PFOS. Results from cyclic loading tests and associated mass balances showed that complete PFC recovery was obtained when regenerating the resin with four 30-BV batches of 0.76 M NaCl in a methanol/water mixture (50/50). Therefore, this regeneration strategy may be at least periodically, required to restore the PFC uptake capacity of the resin. Alternatively, the regenerant volume may be reduced by 90% to four 3-bed volume batches of the same regenerant without degrading PFC removal. Longer-term studies are needed to optimize regeneration protocols for a given water source and resin.

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CHAPTER 5 : CONCLUSIONS AND RECOMMENDED FUTURE WORK

The main objective of this research was to assess the performance of anion exchange processes for the removal of ten PFCs from drinking water sources. Experiments were conducted with a commercially available anion exchange resin in salt-amended ultrapure water and in two drinking water sources.

Removal of PFCs by anion exchange and background water matrix effects

Batch kinetic tests were conducted to evaluate PFC removal and the effect of background water quality on PFC removal by anion exchange. Experiments were conducted in UPW, CCR, and ORW.

- PFC uptake by the tested anion exchange resin increased with increasing perfluorinated carbon-chain length of the carboxylates and sulfonates, and the removal of the three sulfonates exceeded that of any of the seven tested carboxylates.
- An increase in resin dose from 1 to 5 mL/L led to a substantial increase in the removal of most PFCs. However, less than 10% additional removal of longer carbon chain carboxylates and sulfonates was achieved when the resin dose was increased from 5 to 10 mL/L.
- Solution pH had a negligible effect on the removal of all PFCs, except for C4.
- Ionic strength has a more pronounced effect on PFC removal by anion exchange resins than the presence of DOM.

- PFC removal decreased with increasing anion concentration. The effect was stronger for carboxylates than for sulfonates, and it became more pronounced as the perfluorinated carbon chain length decreased.
- Among the tested ions, bicarbonate was generally the least competitive and nitrate the most competitive anion.

Regeneration of anion exchange resins

Anion exchange processes show promise for PFC removal, provided that resins are regenerated in a manner that restores, at least periodically, the PFC removal capacity of the resin. Sequential loading tests were conducted to relate percent PFC removal to bed volumes of water treated; and cyclic loading/regeneration tests were conducted to identify regeneration conditions that restore the PFC removal capacity of anion exchange resins, and to measure the PFC removal effectiveness of an anion exchange resin over multiple loading/regeneration cycles.

- In sequential loading tests, it was confirmed that for both the perfluorinated carboxylate and sulfonate compound classes, removal effectiveness increased with increasing carbon chain length.
- Removal of C4 and C5 was difficult during sequential loading tests. However, for PFCs with longer carbon chains, the performance degradation with increasing BV of water treated was not as large. PFOS was the most effectively removed compound among the tested PFCs.

- When regeneration strategies with aqueous regenerants were evaluated, regeneration efficiency was typically highest for C4 and C5, the two PFCs that exhibited the weakest uptake capacity. Apart from regeneration with 30 BV of 6M NaCl at pH 2.5, strategies involving aqueous regenerants were not effective for releasing PFCs that strongly interact with the resin.
- Complete PFC recovery was obtained when regenerating the resin with four 30-bed volume batches of a 0.76 M NaCl in a methanol/water mixture (50/50). The regenerant volume may be reduced by 90% to four 3-bed volume batches of the same regenerant without degrading PFC removal.
- For each of the four regeneration strategies evaluated in cyclic loading/regeneration tests, PFC removal did not degrade measurably over the 6 loading/regeneration cycles.

Overall, the results of this research illustrate that PFC removal from drinking water sources presents a costly challenge. As a result, PFC introduction into the aquatic environment should be prevented at the source.

Future work

To improve our understanding of PFC uptake mechanisms as well as the feasibility of the ion exchange process, further research is needed.

Equilibrium isotherm tests need to be conducted to determine the PFC uptake capacities for ion exchange resins with different resin matrices (e.g. polyacrylic, polystyrene,

gel, macroporous) and functional groups. Also, longer-term studies are needed to optimize regeneration strategies for a given water source and resin.

The evaluation of a hybrid adsorption/anion exchange treatment approach is also recommended. In this treatment approach, more strongly adsorbing PFCs are initially removed by activated carbon and more weakly adsorbing PFCs subsequently by anion exchange. Several authors have observed the effectiveness of activated carbon for the removal of PFCs and the preference for the removal of longer carbon chain compounds (Appleman et al. 2013b; Hansen et al. 2010; Dudley 2012). This hybrid approach may facilitate resin regeneration, which is more readily accomplished if only PFCs that interact more weakly with the resin need to be removed.

Finally, research is needed to develop effective treatment strategies for the resin regeneration waste stream. As has been mentioned in this thesis, PFCs are persistent, stable, non oxidizable, and non-biodegradable; so, other potentially important routes of transformation need to be investigated, such as reductive defluorination with catalysts and electrode-based processes.

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APPENDICES

APPENDIX A: MASS TRANSITIONS FOR PFCs AND INTERNAL STANDARDS

Table A.1
Mass transitions for PFCs and internal standards

Analyte or Internal Standard	MS/MS Transition	Declustering Potential (V)	Focusing Potential (V)	Collision Energy	Collision cell exiting potential (V)
C4	212.8 > 168.8	-21	-150	-14	-15
C5	262.9 > 218.8	-21	-150	-14	-15
C6	313.6 > 268.8	-21	-150	-14	-15
C7	362.9 > 318.8	-21	-160	-14	-7
C8	413.0 > 368.8	-21	-140	-14	-9
C9	463.0 > 418.8	-31	-210	-16	-11
C10	513.1 > 468.8	-21	-200	-16	-13
PFBS	299.1 > 98.8	-51	-260	-44	-3
PFHS	399.1 > 98.8	-71	-340	-56	-3
PFOS	498.9 > 98.8	-61	-200	-100	-1
Perfluoro-n-[1,2,3,4-¹³C₄]butanoic acid (MC4)	217.0 > 172	-21	-150	-14	-15
Perfluoro-n-[1,2-¹³C₂]hexanoic acid (MC6)	315.1 > 269.8	-21	-150	-14	-15
Perfluoro-n-[1,2-¹³C₂]octanoic acid (MC8)	415.0 > 369.8	-21	-140	-14	-9
Perfluoro-n-[1,2-¹³C₂]decanoic acid (MC10)	515.1 > 469.8	-21	-200	-16	-13
Sodium perfluoro-1-hexane[¹⁸O₂]sulfonate (MPFHxS)	403.1 > 83.8	-71	-340	-76	-1
Sodium perfluoro-1-[1,2,3,4-¹³C₄]octane sulfonate (MPFOS)	502.9 > 79.9	-31	-200	-100	-1

APPENDIX B: REPRESENTATIVE LC-MS/MS CHROMATOGRAMS

Representative chromatograms for the carboxylates and sulfonates are shown in Figures B.1 and B.2, respectively. Representative chromatograms for the internal standards are shown in Figure B.3.

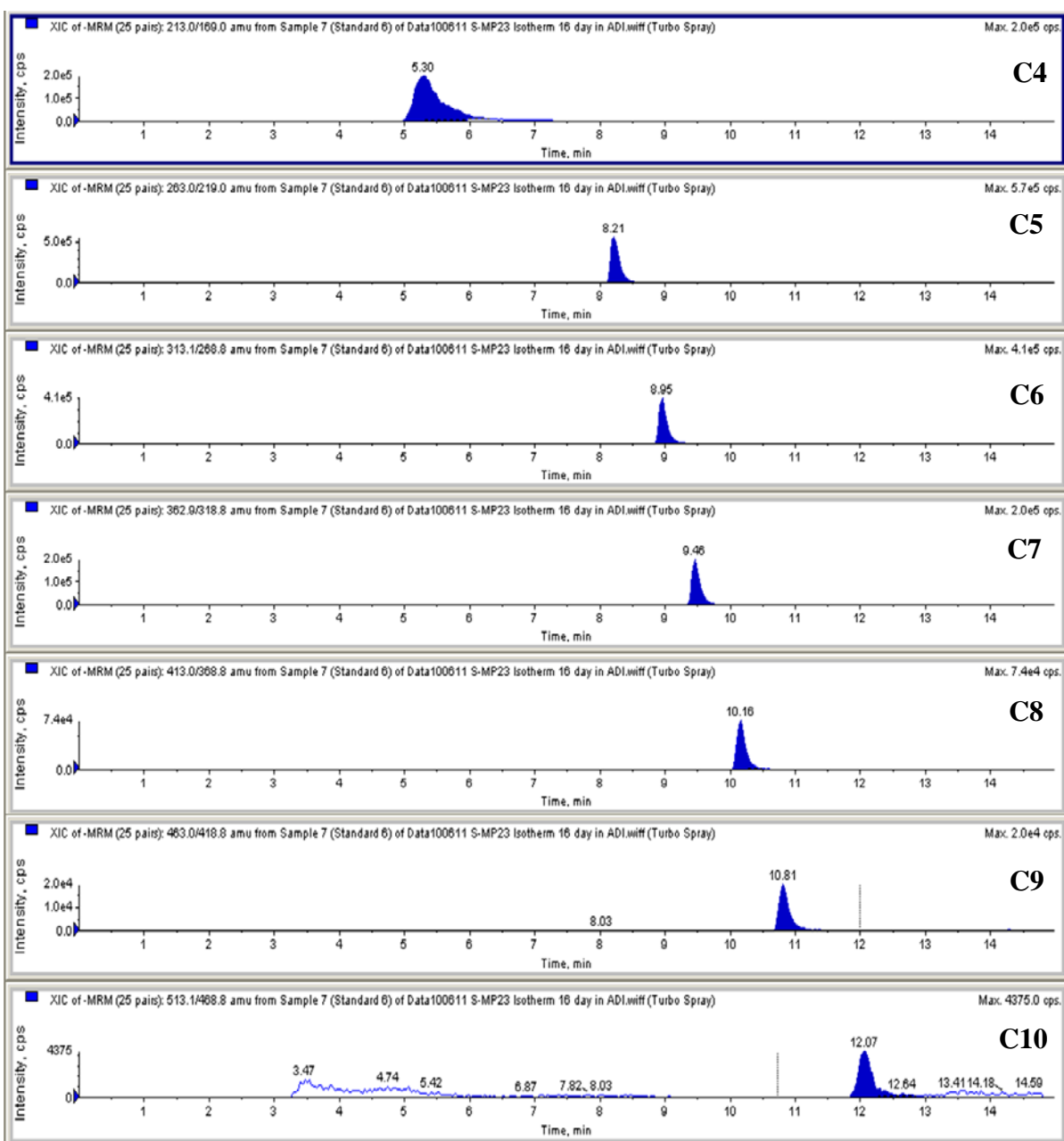


Figure B.1 Chromatograms for carboxylates C4 – C10

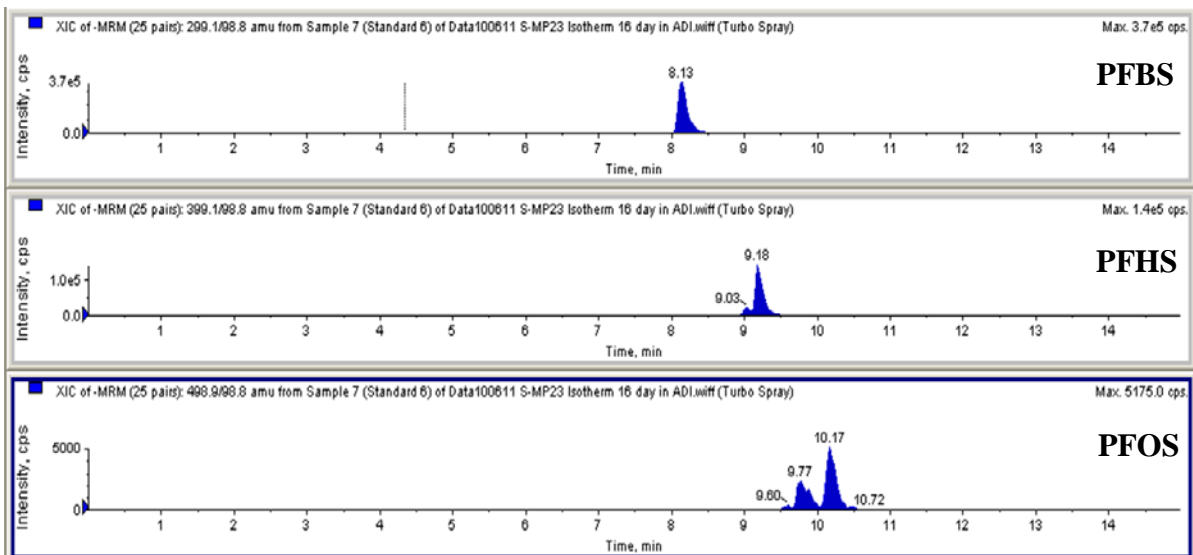


Figure B.2 Chromatograms for the sulfonates PFBS, PFHS, and PFOS

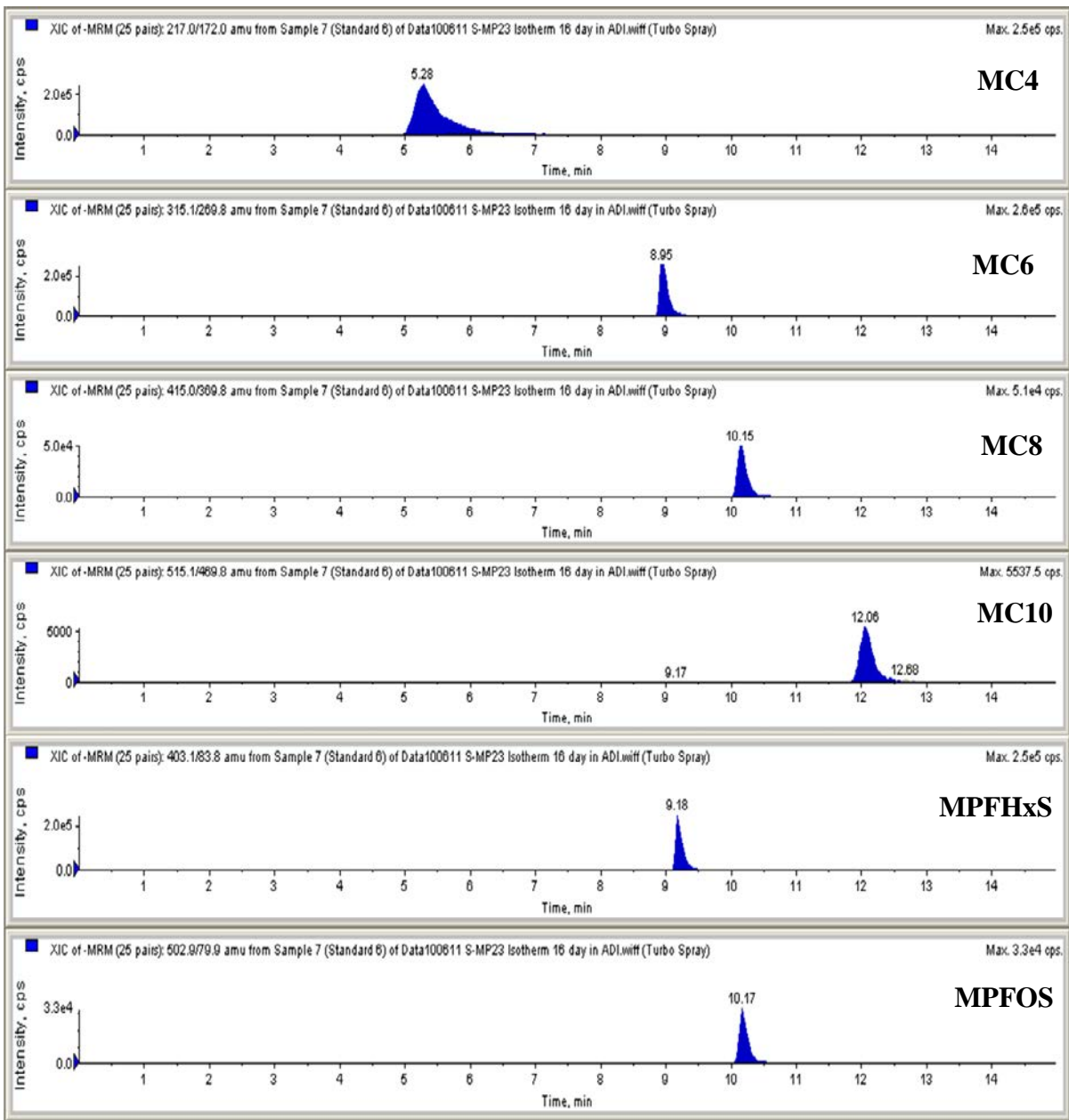


Figure B.3 Chromatograms for internal standards

APPENDIX C: REPRESENTATIVE CALIBRATION CURVES FROM PFC ANALYSIS

Calibration curves for all ten PFCs are shown in Figure C.1. The calibration curves were well described by second order polynomial regression equations. Calibration curves were prepared for every LC-MS/MS sample set. The two points for each concentration represent the calibration curve run at the beginning and end of the sample set. The response factor was used to quantitate the results, and to account for any loss of analyte during sample handling.

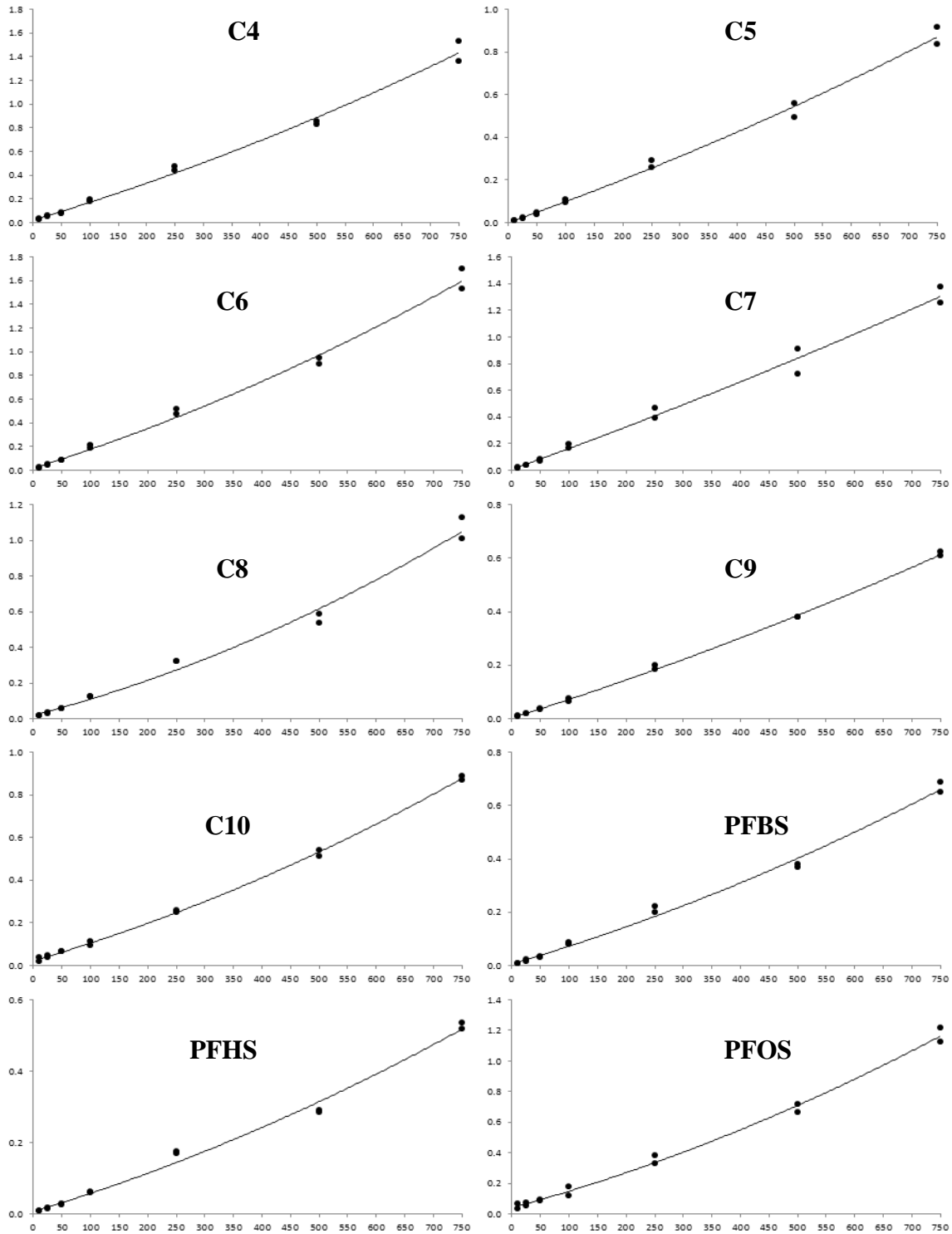


Figure C.1 Calibration curves for ten PFCs. The response factor (y-axis) is plotted against the known standard concentration in ng/L (x-axis).

APPENDIX D: REPORTING LIMITS FOR CYCLIC LOADING TESTS

The reporting limits (ng of PFC removed from resin per batch) corresponding to the different regeneration strategies used in the cyclic loading tests are presented; as well as, the lowest percentages of PFC release that we could confidently consider.

Table D.1
Reporting limits for regeneration strategy A

Cycle	Batch	DF	Reporting Limit (ng/L)		Reporting Limit (ng)	
			C10, PFOS	Other PFCs	C10, PFOS	Other PFCs
I	1-4	10	250	100	3.75	1.5
II	1-4	50	1250	500	18.75	7.5
III, IV, V, VI	1-2	100	2500	1000	37.5	15
	3-4	50	1250	500	18.75	7.5

Table D.2
Reporting limits for regeneration strategy A (lowest percentages of PFC release)

Cycle	Batch	PFC (%)									
		C4	C5	C6	C7	C8	C9	C10	PFBS	PFHS	PFOS
I	1-4	0.15	0.10	0.06	0.05	0.04	0.04	0.07	0.04	0.04	0.07
	Rinse	0.01	0.01	0.01	0.005	0.004	0.004	0.01	0.004	0.004	0.01
II	1-4	0.52	0.36	0.23	0.19	0.15	0.12	0.23	0.13	0.10	0.21
	Rinse	0.01	0.01	0.005	0.004	0.003	0.002	0.005	0.003	0.002	0.004
III	1-2	1.21	0.98	0.62	0.48	0.36	0.28	0.47	0.26	0.18	0.36
	3-4	0.60	0.49	0.31	0.24	0.18	0.14	0.23	0.13	0.09	0.18
	Rinse	0.01	0.01	0.01	0.005	0.004	0.003	0.005	0.003	0.002	0.004
IV	1-2	1.10	0.86	0.62	0.52	0.38	0.31	0.48	0.26	0.18	0.31
	3-4	0.55	0.43	0.31	0.26	0.19	0.16	0.24	0.13	0.09	0.16
	Rinse	0.01	0.01	0.01	0.01	0.004	0.003	0.005	0.003	0.002	0.003
V	1-2	0.73	0.63	0.50	0.41	0.34	0.30	0.45	0.24	0.16	0.28
	3-4	0.37	0.32	0.25	0.21	0.17	0.15	0.22	0.12	0.08	0.14
	Rinse	0.01	0.01	0.01	0.004	0.003	0.003	0.004	0.002	0.002	0.003
VI	1-2	1.10	1.05	0.66	0.52	0.44	0.36	0.47	0.25	0.16	0.27
	3-4	0.55	0.53	0.33	0.26	0.22	0.18	0.23	0.13	0.08	0.13
	Rinse	0.01	0.01	0.01	0.01	0.004	0.004	0.005	0.003	0.002	0.003

Table D.3
Reporting limits for regeneration strategy B

Cycle	Batch	DF	Reporting Limit (ng/L)		Reporting Limit (ng)	
			C10, PFOS	Other PFCs	C10, PFOS	Other PFCs
I	1-4	10	250	100	37.5	15
II, III, IV, V,	1	50	1250	500	187.5	75
VI	2-4	10	250	100	37.5	15

Table D.4
Reporting limits for regeneration strategy B (lowest percentages of PFC release)

Cycle	Batch	PFC (%)									
		C4	C5	C6	C7	C8	C9	C10	PFBS	PFHS	PFOS
I	1-4	1.48	1.00	0.61	0.48	0.44	0.40	0.73	0.40	0.38	0.70
	Rinse	0.15	0.10	0.06	0.05	0.04	0.04	0.07	0.04	0.04	0.07
II	1	0.49	0.41	0.28	0.24	0.22	0.17	0.33	0.21	0.14	0.24
	2-4	0.10	0.08	0.06	0.05	0.04	0.03	0.07	0.04	0.03	0.05
III	Rinse	0.10	0.08	0.06	0.05	0.04	0.03	0.07	0.04	0.03	0.05
	1	0.56	0.84	0.42	0.47	0.38	0.27	0.94	0.27	0.16	0.27
	2-4	0.11	0.17	0.08	0.09	0.08	0.05	0.19	0.05	0.03	0.05
IV	Rinse	0.11	0.17	0.08	0.09	0.08	0.05	0.19	0.05	0.03	0.05
	1	0.52	0.74	0.43	0.54	0.46	0.33	1.10	0.29	0.18	0.27
	2-4	0.10	0.15	0.09	0.11	0.09	0.07	0.22	0.06	0.04	0.05
V	Rinse	0.10	0.15	0.09	0.11	0.09	0.07	0.22	0.06	0.04	0.05
	1	0.34	0.42	0.33	0.37	0.39	0.37	0.89	0.25	0.18	0.29
	2-4	0.07	0.08	0.07	0.07	0.08	0.07	0.18	0.05	0.04	0.06
VI	Rinse	0.07	0.08	0.07	0.07	0.08	0.07	0.18	0.05	0.04	0.06
	1	0.42	0.64	0.43	0.52	0.47	0.40	0.87	0.26	0.19	0.32
	2-4	0.08	0.13	0.09	0.10	0.09	0.08	0.17	0.05	0.04	0.06
	Rinse	0.08	0.13	0.09	0.10	0.09	0.08	0.17	0.05	0.04	0.06

Table D.5
Reporting limits for regeneration strategy C

Cycle	Batch	DF	Reporting Limit (ng/L)		Reporting Limit (ng)		
			C10, PFOS	Other PFCs	C10, PFOS	Other PFCs	
I	1-4	10	250	100	3.75	1.5	
II, III	1-2	100	2500	1000	37.5	15	
	3-4	50	1250	500	18.75	7.5	
IV	1-3	100	2500	1000	37.5	15	
	4	50	1250	500	18.75	7.5	
V	1	100 ^a	2500	1000	37.5	15	
		200 ^b	5000	2000	75	30	
	2	100 ^c	2500	1000	37.5	15	
		200 ^d	5000	2000	75	30	
	3	100	2500	1000	37.5	15	
	4	50	1250	500	18.75	7.5	
	VI	1	100 ^e	2500	1000	37.5	15
			200 ^f	5000	2000	75	30
2		100 ^g	2500	1000	37.5	15	
		200 ^h	5000	2000	75	30	
3	100	2500	1000	37.5	15		
4	50	1250	500	18.75	7.5		

^a C4, C5, C6, PFBS, PFHS, PFOS

^b C7, C8, C9, C10

^c C4, C5, C6, C7, C8, PFBS

^d C9, C10, PFHS, PFOS

^e C4, C5, C6, PFBS, PFHS

^f C7, C8, C9, C10, PFOS

^g C4, C5, C6, C7, C8, C9, PFBS, PFHS

^h C10, PFOS

Table D.6
Reporting limits for regeneration strategy C (lowest percentages of PFC release)

Cycle	Batch	PFC (%)									
		C4	C5	C6	C7	C8	C9	C10	PFBS	PFHS	PFOS
I	1-4	0.15	0.10	0.06	0.05	0.04	0.04	0.07	0.04	0.04	0.07
	Rinse	0.01	0.01	0.01	0.005	0.004	0.004	0.01	0.004	0.004	0.01
II	1-2	0.98	0.60	0.38	0.29	0.26	0.24	0.52	0.25	0.23	0.51
	3-4	0.49	0.30	0.19	0.14	0.13	0.12	0.26	0.13	0.12	0.26
	Rinse	0.01	0.01	0.004	0.003	0.003	0.002	0.01	0.003	0.002	0.01
III	1-2	1.03	0.81	0.47	0.34	0.30	0.29	0.75	0.28	0.27	0.79
	3-4	0.51	0.40	0.23	0.17	0.15	0.15	0.38	0.14	0.14	0.40
	Rinse	0.01	0.01	0.005	0.003	0.003	0.003	0.01	0.003	0.003	0.01
IV	1-3	0.91	0.78	0.49	0.36	0.31	0.36	0.89	0.29	0.28	0.87
	4	0.46	0.39	0.25	0.18	0.16	0.18	0.44	0.15	0.14	0.43
	Rinse	0.01	0.01	0.005	0.004	0.003	0.004	0.01	0.003	0.003	0.01
V	1	0.70	0.66	0.47	0.70	0.63	0.88	2.50	0.32	0.31	1.29
	2	0.70	0.66	0.47	0.35	0.31	0.88	2.50	0.32	0.62	2.59
	3	0.70	0.66	0.47	0.35	0.31	0.44	1.25	0.32	0.31	1.29
	4	0.35	0.33	0.23	0.18	0.16	0.22	0.63	0.16	0.16	0.65
	Rinse	0.01	0.01	0.005	0.004	0.003	0.004	0.01	0.003	0.003	0.01
VI	1	1.05	1.26	0.65	0.94	0.84	1.52	3.37	0.39	0.39	1.70
	2	1.05	1.26	0.65	0.47	0.42	0.76	3.37	0.39	0.39	3.39
	3	1.05	1.26	0.65	0.47	0.42	0.76	1.69	0.39	0.39	1.70
	4	0.52	0.63	0.33	0.24	0.21	0.38	0.84	0.19	0.20	0.85
	Rinse	0.01	0.01	0.01	0.005	0.004	0.01	0.02	0.004	0.004	0.02

Table D.7
Reporting limits for regeneration strategy D

Cycle	Batch	DF	Reporting Limit (ng/L)		Reporting Limit (ng)	
			C10, PFOS	Other PFCs	C10, PFOS	Other PFCs
I	1-4	10	250	100	37.5	15
II, III	1	50	1250	500	187.5	75
	2-4	10	250	100	37.5	15
IV, V, VI	1-2	50	1250	500	187.5	75
	3	10	250	100	37.5	15
	4	5	125	50	18.75	7.5

Table D.8
Reporting limits for regeneration strategy D (lowest percentages of PFC release)

Cycle	Batch	PFC (%)									
		C4	C5	C6	C7	C8	C9	C10	PFBS	PFHS	PFOS
I	1-4	1.48	1.00	0.61	0.48	0.44	0.40	0.73	0.40	0.38	0.70
	Rinse	0.15	0.10	0.06	0.05	0.04	0.04	0.07	0.04	0.04	0.07
II	1	0.74	0.44	0.30	0.25	0.21	0.20	0.49	0.19	0.17	0.44
	2-4	0.15	0.09	0.06	0.05	0.04	0.04	0.10	0.04	0.03	0.09
III	Rinse	0.15	0.09	0.06	0.05	0.04	0.04	0.10	0.04	0.03	0.09
	1	0.88	0.87	0.56	0.44	0.40	0.34	0.82	0.27	0.27	0.89
	2-4	0.18	0.17	0.11	0.09	0.08	0.07	0.16	0.05	0.05	0.18
IV	Rinse	0.18	0.17	0.11	0.09	0.08	0.07	0.16	0.05	0.05	0.18
	1-2	0.89	0.74	0.59	0.44	0.41	0.40	1.00	0.27	0.26	0.72
	3	0.18	0.15	0.12	0.09	0.08	0.08	0.20	0.05	0.05	0.14
	4	0.09	0.07	0.06	0.04	0.04	0.04	0.10	0.03	0.03	0.07
V	Rinse	0.38	0.18	0.12	0.08	0.07	0.05	0.10	0.07	0.07	0.10
	1-2	0.54	0.58	0.53	0.40	0.38	0.37	0.81	0.35	0.40	0.85
	3	0.11	0.12	0.11	0.08	0.08	0.07	0.16	0.07	0.08	0.17
	4	0.05	0.06	0.05	0.04	0.04	0.04	0.08	0.03	0.04	0.09
VI	Rinse	0.11	0.12	0.11	0.08	0.08	0.07	0.16	0.07	0.08	0.17
	1-2	1.18	0.97	0.67	0.52	0.45	0.37	0.82	0.44	0.41	0.80
	3	0.24	0.19	0.13	0.10	0.09	0.07	0.16	0.09	0.08	0.16
	4	0.12	0.10	0.07	0.05	0.05	0.04	0.08	0.04	0.04	0.08
	Rinse	0.24	0.19	0.13	0.10	0.09	0.07	0.16	0.09	0.08	0.16