

## **Remedial Options for PFC Contaminated Sites: A Review**

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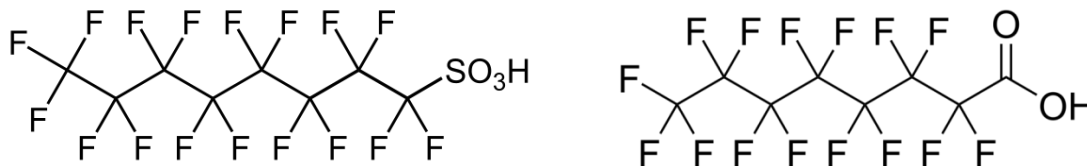
### **Abstract**

The Federal Contaminated Sites Action Plan (FCSAP) program provides funding for the assessment and remediation/risk management of contaminated sites that fall under federal responsibility. Historically used in the firefighting training procedures, perfluorinated compounds (PFCs) present a particular set of challenges. As part of Environment Canada's recent efforts to provide scientific and technical support to improve the understanding of PFC assessment and remediation at some federal contaminated sites, a literature review of studies related to the remediation of PFC contaminated sites has been conducted. Remediation/treatment technologies that were identified and reviewed included both destructive (e.g., biodegradation, oxidation and reduction) and non-destructive (e.g., sorption and filtration). It was found that most of the studies reported were related to perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) found in water. Considerably less information was found on the treatment of PFC contaminated soil. This paper provides a summary of reported effectiveness of the existing treatment techniques. The identified information gaps are also discussed and recommendations for further studies of PFC remediation options for PFC contaminated sites are provided.

### **1 Introduction**

Perfluorinated compounds (PFCs) are a group of man-made chemicals, which consist of carbon chains saturated with fluorine atoms (Shultz et al. 2003). PFCs have been synthesized since the 1960s. Due to their excellent thermal stability and hydrophobic properties, they have been widely used in consumer and industrial products. Perfluorooctanesulfonic acid (PFOS, CAS# 1763-23-1) and perfluorooctanoic acid (PFOA, CAS# 335-67-1) are two of the most common PFCs. The principal global applications for PFOS, its salts and its precursors are water, oil, soil and grease repellents for use on surface and paper-based applications. PFOS, its salts and its precursors also have specialized chemical applications, such as fire-fighting foams, hydraulic fluids, carpet spot removers, mining and oil well surfactants and other specialized chemical formulations (EC, 2006). The PFOS used in aqueous film forming foams (AFFF) reduces the surface tension of water, allowing an aqueous film to spread over the flammable liquid and further acts as a vapour sealant during firefighting. The high thermal stability of PFOS allows foam to last longer in hot environments. It is primarily through this historical use that PFOS has impacted some federal contaminated sites, particularly those with firefighting training centres. For PFOA, its historical uses include applications in industrial processes and in commercial and

consumer products. PFOA and its salts are used as polymerization aids in the production of fluoropolymers and fluoroelastomers (EC and HC, 2012).



**Figure 1. Chemical Structures of PFOS (left) and PFOA (right)**

Figure 1 shows the chemical structures of PFOS and PFOA. PFOS is a chain with molecular formula  $C_8F_{17}O_3S$  and a molecular weight of 500.13 g. PFOA is part of a family of compounds called perfluorinated carboxylic acids (PFCAs) which are substances with the general structure of  $CF_3(CF_2)_nCOOH$ . PFOA is typically a linear chain with molecular formula  $C_8HF_{15}O_2$  and has a molecular weight of 414.07 g. The physiochemical properties of PFCs make them difficult to treat using most conventional methods (Vecitis et al. 2009). This is because they are fully fluorine-substituted compounds. Fluorine atom is much larger than hydrogen and it acts as a shield to prevent the breakage of the carbon chain. The presence of fluorine atoms also contributes to the rigidity of perfluorocarbon chains. The highly polarized carbon-fluorine bond is the strongest of known covalent bonds and fluorination also strengthens the adjacent C-C bonds. This results in thermal stability as well as resistance to acids, bases, oxidants, and reductants. This stability is what causes fluorinated compounds to be environmentally persistent (Moody and Field 2000, Schultz et al. 2003).

Under the *Canadian Environmental Protection Act*, 1999 (CEPA 1999), Environment Canada (EC) and Health Canada (HC) have conducted ecological and human health screening assessments for PFOS and PFOA and their salts and precursors, and Environment Canada conducted an ecological assessment for long-chain (C9-C20) perfluorocarboxylic acids (PFCAs), and their salts and precursors (EC, 2006; EC and HC, 2012; EC, 2012). These assessments concluded that PFOS, PFOA, long-chain PFCAs, and their salts and their precursors are entering or may be entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity.

As part of its recent effort related to the management of PFCs at some federal contaminated sites, EC has determined that there are some science and technology related gaps, including a lack of information on available remediation approaches. To start to address these gaps, Environment Canada compiled 580 publications associated with PFCs. MPunt Environmental Consulting and Velicogna Consulting performed a scan of the 580 articles, and identified and analysed those that related specifically to the remediation of PFC contaminated sites. This paper provides a summary of this analysis, identifies gaps in the available approaches for managing these compounds, and presents recommendations related to the management of federal sites contaminated with PFCs.

## **2 Summary of Literature Reviewed**

### **2.1 General Remediation Technology Reviews**

There have been several general reviews of treatment/remediation technologies published in the last ten years (Shultz et al., 2003; Fujii et al., 2007; ATSDR, 2009; Vecitis et al., 2009;

Schröder, et al., 2010; Hawley et al., 2012). They provide a general picture of the technologies, both conventional and innovative, that are available for PFCs, and their effectiveness. Specifically, the Agency for Toxic Substances and Disease Registry (ATSDR) (2009) in their “Draft Toxicological Profile for Perfluoroalkyls” provides a section on disposal techniques, indicating that while disposal methods specific to PFCs are limited, DuPont (a former manufacturer of PFCs) has presented two preferred disposal options for fluoropolymer dispersions. The first method involves precipitation, decanting, or filtering to separate solids from liquid waste. The dry solids are then disposed of in an approved industrial solid waste landfill while the liquid waste is discharged to a wastewater treatment facility. The second method involves incineration at temperatures greater than 800 °C using a scrubber to remove hydrogen fluoride.

A review performed by Schröder, et al. (2010) of multiple removal techniques for fluorinated surfactants indicated that for artificially prepared wastewater samples containing PFOS and PFOA, a maximum of 70% removal by transformation using oxidation with Fenton’s reagent and a combination of photooxidation and Fenton’s reagent could be obtained. However, polar organic degradation products such as carboxylic and sulfonic acids were found. This study also found that adsorption by activated sludge or granular activated carbon (GAC) and retention by reverse osmosis (RO) led to >78, 99 or 86% removal from the wastewater respectively.

Shultz et al. (2003) performed a review of various techniques and found that both aerobic and anaerobic biodegradation were not effective in degrading PFOS and PFOA. This study also found that up to 98% of perfluorinated surfactants could be removed through adsorption on activated carbon. It was also suggested that once the activated carbon is saturated, the adsorbed fluorinated surfactants could be destroyed by incinerating the activated carbon at 1,200°C for 20 min, burning the gas generated at 1,200°C for 2 s, and treating the burned gas to produce solid  $\text{CaF}_2$ .

Paterson et al. (2008) indicated that many remediation methods utilized to address hydrocarbon contamination at Fire Fighting Training Areas (FFTAs), such as sparging, soil vapour extraction and bioremediation, are ineffective on PFCs due to the low volatility of the compounds and their resistance to microbial degradation. However, sorption of PFCs to GAC and anionic resins has been demonstrated to successfully remove PFCs from contaminated groundwater. GAC and anionic resins will only remove PFCs from contaminated water. For destruction of the PFCs to occur, a tremendous amount of energy is required. Spent activated carbon from water treatment units must be incinerated at temperatures in excess of 1,000°C.

Finally, Vecitis et al. (2009) performed a review of various treatment methods for aqueous PFOS and PFOA and stated that conventional water treatment processes have little effect on PFOS and PFOA. These ineffective technologies include: trickling filtration, activated sludge, anaerobic digestion, and chlorination. The review presented evidence that some tertiary wastewater treatment technologies are moderately successful, such as GAC, ion exchange and RO but that in all these cases, disposal of spent materials must be considered. It also examined the effectiveness of other treatment methods including chemical and photodegradation techniques, sonication and thermal techniques. With regard to thermal treatment, it was found that incineration is feasible for salts of PFOS and solid stabilized materials. In addition, sonolysis appears to be a viable method for the degradation of PFOS and PFOA in groundwater, but this technology is still in developmental stages without any fully tested and sanctioned large scale application.

In addition to the general literature reviews, there were also several publications that presented information on specific PFC treatment technologies. The technologies identified can be categorized as follows:

1) Destructive technologies:

- Bioremediation (aerobic and anaerobic)
- Oxidation/reduction (photodegradation, chemical degradation and sonolysis)

2) Non-destructive technologies

- Physical treatment (adsorption and filtration)

The information found that relates to these technologies is provided in Sections 2.2, 2.3, and 2.4 below.

## **2.2 Bioremediation**

### **2.2.1 Technology Description**

Bioremediation is a process in which indigenous or inoculated micro-organisms (i.e., fungi, bacteria, and other microbes) degrade (metabolize) organic contaminants found in soil and/or ground water (U.S. EPA, 2012; U.S. FRTR, 2007). Aerobic bioremediation is applied with oxygen present. Anaerobic bioremediation is applied in the absence of oxygen or under a reduced oxygen environment.

### **2.2.2 General Information/Combined Techniques**

According to Shultz et al. (2003), aerobic and anaerobic biodegradation was not effective in degrading PFOS and PFOA. However, Meesters et al. (2004) examined the biochemical degradation of PFOS and PFOA under aerobic and anaerobic conditions in a closed-loop laboratory scale system and found that under anaerobic treatment conditions, anionic PFOS and PFOA surfactants could be eliminated successfully, whereas under aerobic treatment, no elimination was observed. In neither case, however, did the researchers find an increase in concentrations of fluoride ions, which calls into question whether biodegradation of the fluorine containing branches of the compounds occurred.

Moody et al. (1999; 2000) presented a general overview of fluorinated surfactants and their use in fire-fighting foams. The paper provides a summary of the literature related to the biodegradation of PFCs and indicates that the extent to which AFFF components and priority pollutants in AFFF wastewater biodegrade is quite varied. In general, these compounds resist biodegradation. The authors point to the evidence of PFCs being detected at fire-fighting training sites years after these products have no longer been used. They cite the example of PFCs found in groundwater at the Tyndall Air Force Base, FL even after nearly a decade since AFFF compounds had been used at the site.

Moody et al. (1999; 2000) indicated that several studies have shown that PFOS does not biodegrade under aerobic or anaerobic conditions, however, partially fluorinated surfactants can be partially degraded both aerobically and under sulphur-limiting conditions. Biodegradation of partially fluorinated surfactants appears to be limited to the non-fluorinated portion of the molecule. The recalcitrant nature of perfluorinated compounds is attributed, in part, to the strength of the carbon-fluorine bond as well as the rigidity of the perfluorocarbon chain. The paper also points out that while some information is available on the biodegradability of individual AFFF components, virtually nothing is known about the biodegradation of this complex mixture under actual subsurface conditions. As such, additional research is required to understand the biodegradation of AFFF compounds as a whole.

Moody et al. (1999; 2000) also suggested that perfluorinated surfactants may have an effect on groundwater microbial populations and their ability to degrade co-contaminants, but that no information exists on this potential impact. However, the ability of a surfactant to promote or inhibit co-contaminant biodegradation also appears structure-specific, and recent studies with hydrocarbon surfactants have indicated that they can either inhibit or promote organic contaminant degradation. This structure-activity relationship has not been established for fluorinated surfactants.

Sáez et al. (2008) performed an evaluation of the bacterial degradation of PFCs under aerobic and anaerobic conditions in municipal sewage sludge. Bacterial communities from sewage sludge were exposed to a mixture of PFCs (PFOS, PFOA, and perfluorooctanesulfonamides (PFOSA)) under aerobic or anaerobic conditions. While the research showed no conclusive evidence for PFC degradation, some reduction in concentrations was observed for some compounds in the sludge under aerobic conditions.

### 2.2.3 Aerobic

The biodegradation of various types of firefighting foams was evaluated by Król et al. (2012). The types of foams tested included synthetic foam concentrates (S), AFFF, protein foam concentrates (P), fluoroprotein foam concentrates (FP), film-forming fluoroprotein foam concentrates (FFFP) and alcohol resistant foam concentrates (AR) and Class A fire fighting chemicals, such as surfactants, organic solvents, aliphatic alcohols and water. The AFFF, FFFP and FP foams contained fluorinated surfactants. The tests indicated that synthetic firefighting foams (i.e., S, AFFF, Class A and AFFF-AR) are usually composed of more easily biodegradable solvents and surfactants. However, the protein-based foaming agents (i.e., FFFP, FP and P) were not readily biodegradable despite the general opinion that these types of firefighting foams are more environmentally friendly. It should be noted that the biodegradation tests performed using the OECD Method 301 F only evaluated the overall biodegradability of the foams, not necessarily the PFCs in them.

Gottschall, et al., (2010) monitored the biodegradation of PFCs in tile drainage and groundwater following the application of liquid and dewatered municipal biosolid to silty-clay loam agricultural field plots. PFOS (max concentration = 17 ng/L) and PFOA (max concentration = 12 ng/L) were found above detectable limits in tile drainage from the application plots indicating that they were not broken down and, therefore, leached to the groundwater.

Key et al. (1998) evaluated the biodegradation of fluorinated compounds including PFOS and 1H,1H,2H,2H-perfluorooctane sulfonate (H-PFOS) using a *Pseudomonas sp.* microbe. The results showed that microbial growth and defluorination were only observed for those compounds containing hydrogen (e.g., H-PFOS). The H-PFOS was partially defluorinated but the PFOS was not degraded. Six volatile degradation products were detected for H-PFOS. All of the volatile products contained oxygen and fluorine, but not sulphur.

### 2.2.4 Anaerobic

Hollingsworth et al. (2005) performed research on the anaerobic biodegradation of PFOS in wastewater in bioreactors inoculated with anaerobic granular sludge. At the concentrations tested, the PFOS was not biodegraded under sulphate reducing or methanogenic anaerobic conditions.

The potential for natural biodegradation of PFOA under anaerobic conditions was also investigated by Liou et al. (2010) who evaluated the anaerobic reductive defluorination potential

of five different microbial environments: sludge from a municipal waste-water treatment plant; industrial site sediment; an agricultural soil; and soils from two fire training areas. It was found that PFOA did not show the potential for anaerobic defluorination and the authors concluded that this compound was environmentally persistent.

## **2.3 Oxidation/Reduction**

### **2.3.1 Technology Description**

Oxidation/reduction (redox) involves the conversion of hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Redox reactions involve the transfer of electrons from one compound to another – oxidation is the process of loss of electrons and reduction is the gain of electrons. Chemical oxidation/reduction is performed using chemicals such as ozone, hydrogen peroxide, persulphate or titanium oxide. Photodegradation is performed in the presence of UV or visible light. Photocatalytic degradation is performed using a combination of an oxidizing or reducing agent.

### **2.3.2 Photodegradation**

Wang et al. (2008) evaluated the combination of ferric ions and photodegradation on PFOA destruction. This research showed that while minimal decomposition of PFOA occurred after irradiation of 254 nm UV light, the addition of trace ferric ion ( $\text{Fe}^{3+}$ ) greatly increased the decomposition and defluorination of PFOA. Specifically, in the presence of 10  $\mu\text{M}$  ferric ion, 47.3% of initial PFOA was decomposed within 4 h and the degradation and defluorination greatly increased, when the ferric ion concentration increased to 80  $\mu\text{M}$ . It was also found that other metal ions like  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  also slightly improved the photochemical decomposition of PFOA under irradiation of 254 nm UV light. Besides fluoride ion, other intermediates formed during PFOA decomposition, including formic acid and five shorter-chain perfluorinated carboxylic acids, were identified and quantified.

The photodegradation of PFOA in water using two types of low-pressure mercury lamps was performed by Chen et al. (2006a). In these tests, one lamp emitting 254 nm and the other emitting both 254 nm and 185 nm were used, combined with potassium persulphate ( $\text{K}_2\text{S}_2\text{O}_8$ ) as an oxidant. Photochemical decomposition of PFOA in the presence of  $\text{K}_2\text{S}_2\text{O}_8$  was conducted with the initial concentration of PFOA (25 mg/L) and  $\text{K}_2\text{S}_2\text{O}_8$  (407 mg/L) under 185 nm or 254 nm light irradiation in the oxygen atmosphere. PFOA was significantly decomposed under irradiation of 185 nm light, while decomposition was very slow and negligible under 254 nm light irradiation.

Chen and his co-workers (2006b) also evaluated the degradation of PFOA using the photocatalyst  $\text{TiO}_2/\text{Ni-Cu}$  and compared the results to those obtained using UV photodegradation. The results found that direct photolysis of PFOA under 254 nm UV light was very slow and negligible. However, PFOA decomposed significantly in the presence of  $\text{TiO}_2/\text{Ni-Cu}$  such that it almost disappeared after 6 h. At that time, fluoride ion was also detected in aqueous solution, and continued to be detected beyond that point, indicating that the fluorinated branch of the compound was broken down. The researchers also performed tests using  $\text{TiO}_2$  powder and sol-gel prepared  $\text{TiO}_2$  film as a photocatalyst. However, no significant decomposition of PFOA was observed from these tests.

Cho et al. (2011) performed research to examine the degradation rate and reduction in toxicity of PFOA in aqueous solutions using  $\text{TiO}_2$  absorption, vacuum UV photolysis (VUV) and combined VUV/ $\text{TiO}_2$ . The results showed that the most effective method to degrade and

defluorinate PFOA was VUV/TiO<sub>2</sub> at pH 4 with perchloric acid (HClO<sub>4</sub>). The results found that the technique was capable of almost complete degradation of PFOA within 360 min and rapid removal of acute microbial toxicity within 60 min. It was also found that with a higher pH (i.e., under basic conditions) oxidation resulted in the formation of short chain carboxylic acids and lower concentrations of fluorine ions indicating less defluorination. The order of efficiency for the applied photochemical treatment methods was VUV/ TiO<sub>2</sub> (pH 4) > VUV/ TiO<sub>2</sub> (pH 10) > VUV photolysis (pH 4) > VUV photolysis (pH 10) > TiO<sub>2</sub> adsorption (pH 4) > TiO<sub>2</sub> adsorption (pH 10).

Titanium dioxide photocatalysis of PFOA was investigated by Panchangam et al. (2009). The tests indicated that after an irradiation time of 7 h with a 16W (254 nm) low-pressure mercury UV-lamp, more than 99% decomposition of a 50 mg/L solution of PFOA occurred with 38% complete mineralization at room temperature and pH < 3.

Hori et al. (2004) compared the degradation of PFOA using UV-visible light irradiation, H<sub>2</sub>O<sub>2</sub> with UV-visible light irradiation, and a tungstic heteropolyacid photocatalyst. The tests used PFOA in the concentrations (0.34–3.35 mM) typical of those in wastewaters after an emulsifying process in fluoropolymer manufacture. It was found that the heteropolyacid photocatalyst combined with irradiation from a 200-W xenon-mercury lamp completely decomposed the PFOA in 24 h. The completeness of the degradation was evident by the formation of fluorine ions and CO<sub>2</sub>. It was also found that there was no degradation of the catalyst, which would allow it to be reused. Direct photolysis (i.e., UV-visible light irradiation alone) proceeded slowly to produce CO<sub>2</sub> and fluorine ions but also some short-chain perfluorocarboxylic acids. By contrast, the tests using H<sub>2</sub>O<sub>2</sub> with UV-visible light irradiation was less effective in PFOA decomposition.

Qu et al. (2010) investigated the use of UV photoreduction, using potassium iodide as the mediator, for the treatment of PFOA contaminated wastewater. In a synthetic solution of PFOA, the PFOA was completely transformed into fluoride, acetic acid, formic acid, and a small amount of CHF<sub>3</sub>. The initial concentration of PFOA and potassium iodide was 0.025 mM and 0.3 mM, respectively. A total of 740 mL was treated for 14 h using a 15W UV light. When the process was tested using PFOA contaminated wastewater, it was found that 96% of the PFOA was removed, however the resulting products could not be determined. The wastewater was treated for 12 h with 0.3 mM of iodide.

Park et al. (2009) also evaluated the effect of iodide catalyzed UV for the reductive defluorination of perfluorinated compounds in water including PFOA and PFOS. However, this study was only interested in elucidating the reaction mechanisms and did not provide any practical remediation data.

The photodegradation of PFOA in water by 185 nm vacuum UV light was examined by Chen et al. (2007). PFOA degraded very slowly under irradiation of 254 nm UV light. However, 61.7% of initial PFOA was degraded by 185 nm UV light within 2 h, and the defluorination ratio (i.e., the removal of fluorine) reached 17.1%. There was evidence of fluoride ion formation in the sample. Four shorter-chain perfluorinated carboxylic acids (PFCAs) (perfluoroheptanoic acid, perfluorohexanoic acid, perfluoropentanoic acid, and perfluorobutanoic acid) were identified as intermediates (i.e., breakdown products) but were further degraded with irradiation time. According to the mass balance calculation, no other by-products were formed.

Giri et al. (2011) also investigated the photodegradation of PFOA using multiple UV wavelengths (combined UV wavelengths (185 nm + 254 nm) and 254 nm) in solutions at three concentration levels (50, 500 and 1000 µg/L). Almost 100% PFOA was degraded by the

combined wavelengths in 4-h reaction period. Formic acid and acetic acid were two tentatively identified intermediates of PFOA photolysis while the former was a major intermediate predominantly controlling solution pH during the oxidation. The study showed that PFOA photolysis by the combined wavelengths in dilute solutions can be sufficiently enhanced with proper design of UV jacket and reactor, which could be an important step for practical application.

Yamamoto et al. (2007) irradiated an alkaline 2-propanol solution containing PFOS (40  $\mu\text{M}$ ) with a low-pressure mercury lamp (254 nm, 32 W) for 1 and 10 days, which respectively resulted in 76 and 92% of PFOS degradation and the formation of short-chain fluorocarbons.

An investigation of the natural attenuation of PFOA in sea water due to sun light and direct photolysis was performed by Vaalgamaa et al. (2011). These tests determined that UV radiation at 254 nm decomposed PFOA to perfluoroheptanoic-, perfluorohexanoic- and perfluoropentanoic acids. Under simulated sunlight (290–800 nm), there was no perceptible degradation.

### 2.3.3 Chemical Degradation

Fuji et al. (2007) presented a review of treatment methods for perfluorinated compounds indicating that some advanced oxidation techniques such as ozonation,  $\text{O}_3$  with  $\text{H}_2\text{O}_2$ , and Fenton's reagent were found to be ineffective. Other advanced oxidation techniques, such as ultrasonic irradiation, were able to degrade PFOS and PFOA to shorter chain PFCAs. Furthermore, advanced oxidation techniques, such as subcritical water catalyzed with zero valent iron were capable of degrading PFOS completely.

As well, a review performed by Schröder, et al., (2010) of multiple removal techniques for fluorinated surfactants indicated that for artificially prepared wastewater samples containing PFOS and PFOA, a maximum of 70% removal by transformation using Fenton and photo-Fenton reagents could be obtained. In terms of degradation products, only small amount of surplus fluoride ions were observed. Fluorinated degradation products (e.g., sulfonic and carboxylic acids) were found.

### 2.3.4 Sonolysis

Sonolysis involves passing ultrasound waves through water containing contaminants. The ultrasound causes molecules to oscillate resulting in the average distance between the molecules to vary about their mean position (Capelo-Martínez, 2009). When the resulting negative pressure is large enough, the distance between the molecules exceeds the minimum molecular distance required to hold the liquid intact, and then the liquid breaks down and voids are created that are called cavitation bubbles. If the intensity of the sonication is enough to increase the size of the bubbles to the point where they collapse this results in localized temperatures of several thousands degrees and pressures higher than one thousand atmospheres. It is these effects that cause the breakdown of contaminants in the water. This also results in the formation of hydroxyl radicals, which can break down organic molecules.

A review of various techniques for the breakdown of PFOS and PFOA by Vecitis et al. (2009) found that sonication is an effective method to breakdown PFOA and PFOS in water. Several other researchers have examined the effect of sonication on PFC degradation and have obtained varying results on its effectiveness. More specifically, in an earlier study, Vecitis et al. (2008) found that sonication with high frequency ultrasound (i.e., sonication at 618 kHz, 250 W/L and  $6.4 \text{ W/cm}^2$  for up to 180 min) of PFOS and PFOA in water was effective in degrading



these compounds over a wide range of concentrations with near complete conversion to CO, CO<sub>2</sub>, F<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>.

Vecitis et al. (2010) also investigated the sonochemical degradation of aqueous dilutions of the AFFF FC-600 (a mixture of hydrocarbon (HC) and fluorochemical components including co-solvents, anionic hydrocarbon surfactants, fluorinated amphiphilic surfactants, anionic fluorinated surfactants, and thickeners such as starch). These tests showed that the primary FC surfactant in FC-600, PFOS, was sonolytically degraded over a range of FC-600 aqueous dilutions, 65 ppb < [PFOS] < 13,100 ppb. The results did not show complete mineralization of the PFOS. Tests were also performed to determine if the presence of the other components in AFFF had an effect on the degradation of the PFOS by comparing these results with those of PFOS in deionized water. It was determined that the PFOS in water alone broke down more completely than the PFOS in the AFFF mixture.

By contrast to Vecitis' work, Moriwaki et al. (2005) did not find that sonication (using 200 W (energy density of 3W/cm<sup>2</sup>) for 60 mL of a 10 or 100 mg/L solution of PFOS or PFOA) resulted in complete breakdown of PFOS and PFOA. In these tests, the half-lives of PFOS and PFOA were 43 and 22 min respectively. As well, evidence provided in this study suggested that PFOS and PFOA degradation occurred mainly as a result of thermal decomposition, rather than sonolysis.

Campbell et al. (2009) investigated ultrasonic degradation for wastewater treatment. The study examined the ultrasonic degradation kinetics of dilute aqueous (<1 µM) solutions of various perfluorochemicals and compared the results to the previously reported sonochemical kinetics of PFOS and PFOA, in order to evaluate the effect that the PFC chain length (C3-C8) and headgroup (-CO<sup>-</sup> vs. -SO<sup>-</sup>) had on kinetics. It was found that sonochemical degradation of perfluoroalkancarboxylates and -sulfonates is influenced by their adsorption behaviour at the air-water interface, mass transfer to the bubble-water interface and the applied acoustic frequency (i.e., the number of cavitation events per unit time).

Cheng et al. (2008) looked specifically at sonication degradation of PFOS and PFOA in actual groundwater samples and evaluated the effect of various organic groundwater constituents on the sonic degradation of PFOS and PFOA. For this study, groundwater was taken from an actual landfill. This water contained volatile organic compounds (VOCs) such as acetone, diisopropyl ether, and 2-butanone at mg/L level, and a moderately high level of bicarbonate and iron and natural organic matter. The concentrations of PFOS and PFOA in the landfill groundwater were 30 and 65 µg/L, respectively. However, for these tests the samples were spiked with PFOS and PFOA to bring the concentration of each to 100 µg/L. The degradation results were also compared with pure water samples also having concentrations of PFOS and PFOA of 100 µg/L each. The results showed that sonication was successful in significantly reducing the concentration of PFOS and PFOA in 600 mL of groundwater. It was also found that volatile organic compounds had a negative effect on the degradation of PFOS and PFOA but that the presence of dissolved natural organic matter did not. As well, tests performed combining ozonation with sonication resulted in an increase in PFOS and PFOA degradation.

As a continuation of their 2008 work, Cheng et al. (2009) further investigated the effect of inorganic materials on the sonic degradation of PFOS and PFOA at concentrations of 100 µg/L each in water. The results showed that anions in the range of 1–10 mM concentration had a detrimental effect on the PFOS and PFOA degradation, however, cations at 5 mM concentration had a negligible effect. It was shown that the degradation rate reduction in the groundwater in

this study is primarily due to the presence of bicarbonate. pH adjustment prior to treatment restored the effectiveness of sonication degradation.

### **2.3.5 Other Oxidation/Reduction Techniques**

Vecitis et al. (2009) reviewed several treatment technologies (i.e., direct photolysis, photocatalytic oxidation, photochemical oxidation, photochemical reduction, thermally induced reduction and sonochemical pyrolysis) for PFOS and PFOA in terms of kinetics, mechanism, energetic cost, and applicability. They pointed out that PFOS is more kinetically susceptible to reductive processes, whereas PFOA is more susceptible to oxidative and photolytic processes. Sonolysis is the only technique that is able to quickly degrade both PFOS and PFOA. Kinetics will be of importance in flowing systems where the aqueous PFCs will only be in the reactor for a finite period. For batch reactor cases, treatment time is not a factor and the kinetics will be relatively unimportant. Thermal methods, such as sonolysis and incineration, have a distinct advantage, while defluorination could yield partially fluorinated species that have long environmental lifetimes (e.g., fluoroform has an atmospheric lifetime of 250–390 y). It was found that direct photolytic and oxidative processes are weakest in terms of degradation products. The authors considered that sonolysis is a viable method for the degradation of PFCs in groundwater. Sonolysis is discussed in detail in Section 2.3.4.

Schroder et al. (2005) evaluated several advanced oxidation processes (AOPs) and their effect on PFOS degradation. The reagents were applied to the anionic and the non-ionic fluorinated surfactants (including PFOS) dissolved in ultrapure water. PFOS in water was not degraded when exposed to each of the following reagents for 120 minutes: (a) ozone alone; (b) ozone combined with ultraviolet light; (c) ozone combined with hydrogen peroxide; and (d) Fenton's Reagent. While no elimination of PFOS was observed, N-ethyl-N-(perfluoroalkyl)-sulfonyl-glycinic acid (HFOSA-glycinic acid) (HFOSA-glycinic acid) and AOP treated non-ionic surfactants were eliminated by oxidation. PFOS was found during HFOSA-glycinic acid oxidation as a degradation product.

## **2.4 Physical Treatment**

### **2.4.1 Technology Description**

This category includes treatment techniques that can be used to physically separate PFCs from liquid and solid matrices. Two main types of such techniques are adsorption and filtration.

Adsorption methods are generally categorized as either physical adsorption, chemisorption, or electrostatic adsorption. Weak molecular forces, such as Van der Waals forces, provide the driving force for physical adsorption, while a chemical reaction forms a chemical bond between the compound and the surface of the solid in chemisorption. Electrostatic adsorption involves the adsorption of ions through Coulombic forces, and is normally referred to as ion exchange.

Filtration typically uses a physical means (usually filters or membranes) to separate contaminants from waters. Specifically, reverse osmosis involves the use of pressure to force water through a membrane while contaminants cannot pass through in order to separate the contaminants.

### **2.4.2 General Information**

The Agency for Toxic Substances and Disease Registry (ATSDR) (2009) in their *Draft Toxicological Profile for Perfluoroalkyls* indicates that one of the preferred methods for PFC

treatment is to use precipitation, decanting, or filtering to separate solids from liquid waste and then dispose of the resulting solids in an approved industrial solid waste landfill and treat the liquid waste through a wastewater treatment facility.

### 2.4.3 Adsorption

Shultz et al. (2003) performed a review that found that up to 98% of perfluorinated surfactants could be removed through adsorption on activated carbon. Schröder et al. (2010) found that adsorption by activated sludge removed greater than >78% of PFOS and PFOA and that granular activated carbon removed 99% of these compounds.

Hansen et al. (2010) determined PFC absorption coefficients of granular activated carbon (GAC) and powdered activated carbon (PAC) in a waste stream. Activated carbon was shown to be effective in removing PFCs from water at the low concentrations (ng/L to µg/L range) used in the tests.

Yu et al. (2009) also studied the feasibility of using powdered and granular activated carbons but also investigated the use of anion-exchange resin (AI400) to remove PFOS and PFOA from water. Of the three, it was found that granular activated carbon had the lowest adsorption capacity.

Paterson et al. (2008) described the use of an in-situ vacuum-enhanced multiphase extraction (VEMPE) system that was installed in 2005 at a former FFTA in the British Columbia Interior where GAC was used to remove PFCs from the extracted groundwater. The system configuration in 2005 included two 110 kg GAC vessels, which was expanded to include an additional three 225 kg GAC vessels in the spring of 2008. While the actual extraction of the PFCs by VEMPE was deemed to be ineffective, the tests that were performed on the water extracted indicated 99% PFC removal was generally measured through the GAC units in 2008.

Deng et al. (2010) performed a more extensive review of anion exchange resins using PFOS in simulated wastewater. This work investigated the sorption rates and capacities of six different anion exchange resins and found that the sorption capacities were up to 5 mmol/g and the resins could be easily regenerated with a mixture of NaCl and methanol. Solutions containing initial concentrations of 200 mg/L PFOS were used and equilibrium was reached between 48 and 168 h, depending on the resin.

The removal of PFC surfactants (including PFOS and PFOA) from aqueous solutions by sorption onto various types of GAC was also investigated by Ochoa-Herrera et al. (2008) and compared with the sorptive capacity of zeolites (i.e., aluminosilicates) and sludge. The results showed that the sorption of PFOS onto activated carbon was stronger than PFOA, suggesting that the length of the fluorocarbon chain and the nature of the functional group influenced sorption of the anionic surfactants. Among all adsorbents evaluated in this study, activated carbon showed the highest affinity for PFOS at low aqueous equilibrium concentrations, followed by the hydrophobic, high-silica zeolite, and anaerobic sludge. Activated carbon also displayed a superior sorptive capacity at high soluble concentrations of the surfactant (up to 80 mg/L). These findings indicate that activated carbon adsorption is a promising treatment technique for the removal of PFOS from dilute aqueous streams. The results obtained in evaluating sludge clearly demonstrate that biosorption of PFOS is effective and that the type of the sludge strongly influences the degree of PFOS sorption and suggest that characteristics other than organic matter content must contribute to controlling sorption of PFOS onto wastewater treatment sludge.

The use of precipitation for the removal of PFOA was evaluated by Deng et al. (2011). In these tests polyaluminum chloride (PACl) was used to treat wastewater with initial concentrations of between 0.3 to 3 mg/L of PFOA. The results showed that the PFOA adsorbed readily to the suspended solids in the solution and could subsequently be removed. It was further found that the addition of PAC before precipitation increased the removal efficiency of PFOA, whereby the PFOA concentrations were reduced to 1 ug/L with the addition of 1 to 16 mg/L of PAC followed by precipitation.

The use of three non-ion-exchange polymers (DowV493, DowL493 and AmbXAD4), two ion-exchange polymers (DowMarathonA and AmbIRA400) and one GAC (Filtersorb400) were tested by Senevirathna et al. (2010) using PFOS in water. The results showed that the adsorption capacities achieved were dependent on the initial concentration of PFOS. At concentrations between 10 µg/L and 100 µg/L, the order of sorption capacities was: ion-exchange polymers > non-ion-exchange polymers > GAC. However, at 100 ng/L, the non-ionic exchange materials performed best.

Wang et al. (2011) studied the effect of adsorption of PFOS and PFOA onto alumina. The sorption isotherms show the maximum adsorption was 0.252 mg/m<sup>2</sup> and 0.157 mg/m<sup>2</sup>, for PFOS and PFOA respectively.

Other researchers also evaluated less conventional sorption media. Chen et al. (2011) performed tests on maize straw char and willow derived chars, maize straw ash, and three different carbon nanotubes to determine their ability to sorb PFOS. The results showed that both single-walled carbon nanotubes and maize-straw-origin ash had high sorption capacities (over 700 mg/g), while the two chars had low sorption capacities (below 170 mg/g) caused by their small surface area. In the case of the ash, the high sorption capacity was attributed to its positively charged surface and the formation of hemi-micelles. The results also found that the nanotubes reached equilibrium much faster than the ash or the chars, however from an economic aspect, the ash was considered the best candidate for the sorption of PFOS from water.

Li et al. (2011) also examined the removal of PFOA and PFOS from water by adsorption to multi-walled carbon nanotubes using electrochemically assisted adsorption, which involves imposing an electrical field across a slurry of the nanotubes suspended between a titanium and platinum electrode. The results found that electrochemical sorption was able to improve the adsorption rates and adsorption capacity of PFOA and PFOS. In this study 100 µg/L of each of PFOA and PFOS in 20 mL was treated under an electrical potential of 0.6 V at 25°C and equilibrium was reached after 1.5 h. Removal rates of 90% for 100 µg/L solutions of PFOS and PFOA were achieved. The system also had the advantage that the nanotubes were recoverable and could be regenerated for reuse.

The adsorption of PFOS onto goethite and silica was studied by Tang et al. (2010) and it was found that PFOS uptake by goethite was increased as pH decreased and calcium concentration increased. However, the adsorption onto silica was only marginally affected by pH, ionic strength, and calcium concentration, likely due to the dominance of non-electrostatic interactions.

While not specifically a remediation technique, Pan et al. (2009) investigated the effect of two different surfactants on the sorption of PFOS to sediment. It was found that the cationic surfactant, cetyltrimethylammonium bromide (CTAB) increased the sorption of PFOS to sediments. The anionic surfactant, sodium dodecylbenzene sulfonate (SDBS), above a threshold concentration, reduced the sorption of PFOS to sediments.

#### 2.4.4 Filtration

Tang et al. (2006) investigated the feasibility of using RO membranes for treating semiconductor wastewater containing PFOS. These tests used four commercial RO membranes. The tests found that over a wide range of feed concentrations (0.5–1,600 ppm), the membranes generally rejected 99% or more of the PFOS. For concentrations >1 ppm, rejection exceeded 99% for all membrane types. Rejection increased at higher PFOS concentrations, except at a feed concentration of 1,600 ppm (which is above the aqueous solubility of PFOS of 570 ppm) when 5% isopropyl alcohol was also present. Isopropyl alcohol, present in some semiconductor wastewaters, had a detrimental effect on membrane flux, which led to the recommendation that it be removed from the wastewater prior to using RO membranes.

### 3 Conclusions

This literature review shows that the majority of the research evaluated methods for the treatment of PFOS or PFOA (or the two together) in water with a focus on wastewater treatment. It is worthy to note that the majority of the research described in these papers was performed at the laboratory scale and primarily using synthetic water samples (i.e., pure water spiked with specific concentrations of the desired chemical), rather than actual groundwater samples from contaminated sites. Considerably less information is available on the treatment of PFC contaminated soil. The effectiveness of the reported technologies is summarized in Table 1. Among destructive technologies, sonochemical treatment of PFOS and PFOA shows promise. Non-destructive adsorption and RO membrane filtration also seem to be promising. Based on the findings of this literature review, recommendations for future work are as follows:

- Perform an additional information review related to adsorptive technologies for PFC removal from water;
- Compile further information related to how other co-contaminants and fire fighting foam components may affect the fate, behaviour and remediation of PFCs;
- Perform technology feasibility studies for remediation of PFC contaminated sites;

**Table 1. Summary of PFC Treatment Technology Effectiveness**

Technology Type	Summary of Technology Effectiveness
Bioremediation	<ul style="list-style-type: none"><li>• Aerobic biodegradation – minimal evidence of effectiveness.</li><li>• Anaerobic biodegradation – limited evidence of effectiveness and evidence of intermediate formation.</li></ul>
Oxidation/Reduction	<ul style="list-style-type: none"><li>• UV light combined with heteropolyacid photocatalyst, ferric ion or liquid CO<sub>2</sub>/persulphate (under pressure) showed some effectiveness with minimal intermediate formation.</li><li>• Photooxidation alone, titanium oxide alone or UV light</li></ul>

Technology Type	Summary of Technology Effectiveness
	<p>with persulphate or iodide catalyst showed some evidence of effectiveness but also evidence of intermediates formation.</p> <ul style="list-style-type: none"> <li>• Some evidence of successful PFOS and PFOA destruction by sonolysis but complete mineralization was not always obtained.</li> </ul>
Physical Treatment	<ul style="list-style-type: none"> <li>• Effective sorbents for PFCs include: <ul style="list-style-type: none"> <li>○ Powdered activated carbon (low concentrations)</li> <li>○ Granular activated carbon (low concentrations)</li> <li>○ Carbon nanotubes</li> <li>○ Maize-straw ash</li> <li>○ Electrochemical sorption</li> <li>○ Hydrophobic, high-silica zeolite</li> <li>○ Anaerobic sludge</li> <li>○ Ion-exchange, and non-ion exchange polymers</li> <li>○ Anion-exchange resin</li> </ul> </li> <li>• Reverse osmosis membranes generally rejected 99% or more of PFOS.</li> </ul>

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