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(54) **Title:** REMOVAL OF AQUEOUS POLY AND PERFLUOROALKYL SUBSTANCES BY COVALENT TRANSFORMATION TO INSOLUBLE FLUORINATED ESTER

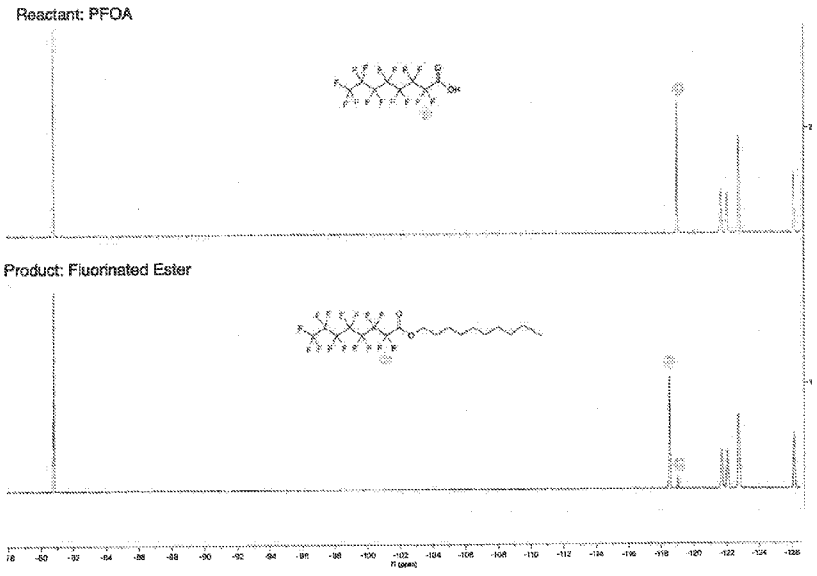

Fig. 1

(57) **Abstract:** Poly arid perfluoroalkyl substances (PFAS) are toxic, ubiquitous contaminants in the environment along with drinking and waste water systems. Current treatment approaches struggle to effectively treat PEAS molecules without generating large amounts of toxic waste or requiring large energy and/or material inputs. With addition of alcohol such as decanol alone, PFAS such as water-soluble perfluorooctanoic acid (PFOA), can be transformed into a water-insoluble, fluorinated ester(s) that precipitate out of solution, facilitating self-removal. Highly hydrophobic fluorinated tails allow for esterification to proceed in water without the addition of any surfactant.

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REMOVAL OF AQUEOUS POLY AND PERFLUOROALKYL SUBSTANCES BY COVALENT TRANSFORMATION TO INSOLUBLE FLUORINATED ESTER

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present invention claims the benefit of U.S. Provisional Application Serial No. 63/472,871, filed on June 14, 2023, the subject matter of which is herein incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates generally to the treatment and removal of poly and perfluoroalkyl substances (PFAS) from contaminated water by efficiently covalently transforming PFAS into fluorinated esters, which precipitate for subsequent low-energy removal, concentration, and disposal.

BACKGROUND OF THE INVENTION

[0003] Poly and perfluoroalkyl substances (PFAS) are a class of over 12,000 fluorinated chemicals known for their amphiphilic properties. PFAS are used in industrial applications and are found in consumer goods such as clothing, food packaging, cookware, cosmetics, and carpet as well as fire-fighting foams. PFAS compounds are common choices for water-repellant, fire-fighting, and surfactant applications because of the properties afforded by their hydrophilic head groups and hydrophobic fluorinated tails. These substances have served many purposes in industrial and consumer product applications and have been utilized for their ability to repel oil and water and long-term stability.

[0004] PFAS are very stable in the environment. Because they are designed for long-term stability, PFAS do not easily break down and are difficult to destroy. Not only are they slow to degrade, but they can form degradation by-products that also present toxicity concerns. Their presence has been measured in water, soil, air, food and even human blood. The half-life of PFAS in the human body can range from four months to over nine years. Increased exposure to high concentrations of PFAS has been shown to cause negative health effects in laboratory animals, such as abnormal endocrine activity, tumors, organ damage, reduced immune system function and reproductive and developmental problems. Individuals may be exposed to PFAS by consuming contaminated water and food, breathing in dust containing PFAS, and by contact with

consumer products that contain PFAS. Sources of contamination include not only industrial and manufacturing facilities, but landfills where PFAS have leached into groundwater, and places where PFAS-based firefighting foam has been used.

[0005] Perfluorooctanoic acid and perfluorooctanoate sulfonate are of primary concern to drinking water utilities and regulators since they are present at increased concentrations in source waters and have public health implications. Furthermore, exposure to even very low levels of PFAS is associated with many health risks, including, for example, kidney cancer, thyroid disease, and high cholesterol. In the United States alone, over 200 million people are expected to receive drinking water with PFAS levels over 1 ng/L, so the health risks linked to PFAS exposure pose a serious threat. Given the widespread presence of this toxic and persistent chemical, removal of PFAS from drinking waters, including drinking water, is of the utmost importance.

[0006] PFAS removal from water is made challenging by the unique molecular properties and typically low environmental concentrations of PFAS molecules. PFAS molecules are highly water soluble. A suite of technologies are available for PFAS removal, including membrane technologies (e.g., reverse osmosis and nanofiltration), sorption, ion exchange resins, advanced oxidation, chlorination, and sonolysis. High removal efficiency in these processes is thwarted by the amphiphilic properties of PFAS compounds. In addition, these traditional PFAS treatment technologies generate massive amounts of toxic waste, causing further disposal concerns.

[0007] There remains a need in the art for an improved process for removing PFAS from contaminated water, which overcomes the deficiencies of the prior art.

SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to provide a process for removing PFAS from contaminated water.

[0009] It is another object of the present invention to provide a process for removing PFAS from contaminated water that contains low concentrations of PFAS.

[0010] It is another object of the present invention to provide a process for removing perfluoroalkyl carboxylic acids (PFCAs) including perfluorooctanoic acid (PFOA), from contaminated water.

[0011] It is another object of the present invention to provide a process for removing PFAS from contaminated water by physicochemical modification of PFAS.

[0012] It is another object of the present invention to provide a process for removing PFAS from contaminated water that reduces the amount of toxic waste generated in the process.

[0013] It is another object of the present invention to demonstrate that aqueous fisher esterification chemistry is feasible for PFCAs.

[0014] It is another object of the present invention to demonstrate that esterification of PFCAs can proceed without the addition of a surfactant.

[0015] It is another object of the present invention to demonstrate that esterification of PFCAs can proceed without the use of DBSA.

[0016] In one embodiment, the present invention relates generally to a method of treating a source of water contaminated with poly and perfluoroalkyl substances (PFAS) to transform the PFAS into a fluorinated ester precipitate, the method comprising the steps of:

a) providing a volume of the source of water contaminated with the PFAS;
b) optionally, adjusting a concentration of PFAS in the volume of source of water;
c) adding at least one alcohol to the volume of the source of water for a period of time and under process conditions to esterify the PFAS in the volume of the source of water into a fluorinated ester; and
d) separating the fluorinated ester from the volume of the source of water.

BRIEF DESCRIPTION OF THE FIGURES

[0017] Fig. 1 depicts ^{19}F NMR in $CDCl_3$ of starting material PFOA and esterification reaction product.

[0018] Fig, 2 depicts ^{1}H NMR spectra of starting materials (decanol and PFOA) and esterification reaction product in $CDCl_3$.

[0019] Fig. 3 depicts ^{19}F-^{13}C NMR of fluorinated ester.

[0020] Fig. 4 depicts ^{13}C NMR of unreacted decanol and esterification reaction product.

[0021] Fig. 5 depicts ^{1}H-^{1}H NMR of fluorinated ester.

[0022] Fig. 6 depicts FTIR spectra of reaction starting materials (PFOA and decanol) and reaction product (decyl pentadecafluorooctanoate).

[0023] Fig. 7 depicts ^{19}F NMR in $CDCl_3$ of ester product after stirring with additional acid (HCl, 2 molar equivalencies to ester concentration) for ten days.

[0024] Fig. 8 depicts ^{1}H NMR spectra for monitoring the behavior of octanoic acid (nonfluorinated) in the reaction system.

[0025] Fig. 9 depicts In-situ ^{19}F NMR spectra of the esterification reaction in H_2O scaled-down to 5 and 2.5 mM PFOA concentrations.

[0026] Fig. 10 depicts In-situ ^{19}F NMR spectra of the esterification reaction in H_2O at an initial PFOA concentration of 5 mM, with and without DBSA.

[0027] Figs. 11A and 11B depict ^{1}H (Fig. 11A) and ^{19}F (Fig. 11B) NMR comparison of products of reactions run in H_2O (Fig. 11A) and D_2O (Fig. 11B).

[0028] Fig. 12 depicts ^{19}F NMR spectra of PFOA in H_2O alone (a) and after the addition of decanol (b) and decanol and DBSA (c).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0029] As described above, PFAS have been found in increased concentrations in water sources, including public drinking waters. In addition, PFAS are also found in industrial waste water streams in various concentrations.

[0030] As used herein, the term "contaminated water" is used to refer to a water source that contains a measurable concentration of PFAS for which treatment is desired.

[0031] As used herein, "a," "an," and "the" refer to both singular and plural referents unless the context clearly dictates otherwise.

[0032] As used herein, the term "about" refers to a measurable value such as a parameter, an amount, a temporal duration, and the like and is meant to include variations of +/-15% or less, preferably variations of +/-10% or less, more preferably variations of +/-5% or less, even more preferably variations of +/-1% or less, and still more preferably variations of +/-0.1% or less of and from the particularly recited value, in so far as such variations are appropriate to perform in the invention described herein. Furthermore, it is also to be understood that the value to which the modifier " about" refers is itself specifically disclosed herein.

[0033] As used herein, spatially relative terms, such as "beneath," "below," "lower," "above," "upper" and the like, are used for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. Spatially relative terms may be intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures.

[0034] As used herein, the terms "comprises" and/or "comprising," specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0035] As used herein the term "substantially-free" or "essentially-free" if not otherwise defined herein for a particular element or compound means that a given element or compound is not detectable by ordinary analytical means that are well known to those skilled in the art of metal plating for bath analysis. Such methods typically include atomic absorption spectrometry, titration, UV-Vis analysis, secondary ion mass spectrometry, and other commonly available analytically methods.

[0036] Given that PFAS compounds can be present in water at extremely low levels, the inventors of the present invention have developed a process by which the physicochemical properties of the molecules themselves can be altered so that the molecules could be precipitated out of solution. What remains is a small (by industry standards) volume of toxic waste.

[0037] Perfluoroalkyl carboxylic acids (PFCAs) are a large class of PFAS molecules commonly found in industry and in the environment. Among PFCAs, perfluorooctanoic acid is (PFOA) is of particular concern. Physicochemical modification of PFOA is realized by transformation from a soluble carboxylic acid into an insoluble ester.

[0038] In going from a perfluorinated carboxylate to a fluorinated ester, a hydrogen bond donor is lost, and a long alkyl chain (and extreme steric hindrance) is introduced, dramatically increasing partition coefficient log K_{ow} and reducing aqueous solubility (C_{iw}^{sat}) by a factor of nearly 50,000.

[0039] As shown below, the inventors sought to predict the physicochemical changes of PFOA after esterification via computational estimators of octanol-water partitioning coefficient K_{OW}. Two programs were utilized: Marvin (via ChemAxon) and KOWWIN (via EPISuite), as both of these programs give K_{OW} values for both charged (PFO^-) and uncharged species (fluorinated ester). K_{OW} was then utilized to estimate aqueous solubility C_{iw} via formula (1) below:

$$\log K_{OW} = -a * \log C_{iw} + b$$

[0040] The results are shown in Table 1 below:

Table 1.

	PFO⁻	PFOA	Fluorinated Ester	Solubility Reduction in Going from PFOA to Fluorinated Ester
ChemAxon Marvin (Method: Consensus)	$\log K_{OW} = 1.58$	$\log K_{OW} = 5.11$	$\log K_{OW} = 9.25$	99.9%
	$C_{iW} = 8.34 \times 10^{4}$ mg/L	$C_{iW} = .639$ mg/L	$C_{iW} = 7.16 \times 10^{-4}$ mg/L	
ChemAxon Marvin (Method: ChemAxon)	$\log K_{OW} = 2.09$	$\log K_{OW} = 5.95$	$\log K_{OW} = 9.57$	99.1%
	$C_{iW} = 1.52 \times 10^{4}$ mg/L	$C_{iW} = .0387$ mg/L	$C_{iW} = 3.40 \times 10^{-4}$ mg/L	
EPISuite KOWWIN	$\log K_{OW} = 1$	$\log K_{OW} = 4.81$	$\log K_{OW} = 9.52$	99.9%
	$C_{iW} = 5.78 \times 10^{5}$ mg/L	$C_{iW} = 1.739$ mg/L	$C_{iW} = 3.81 \times 10^{-4}$ mg/L	
Average	**$\log K_{OW} = 1.56$**	**$\log K_{OW} = 5.29$**	**$\log K_{OW} = 9.45$**	**99.7%**

[0041] Such a transformation forces the generated esters to precipitate out of solution, enabling easy separation via centrifugation (for faster removal) or settling (for slower but lower-energy removal).

[0042] This technique shares similarity with coagulation, a straightforward water treatment technique wherein addition of inorganic aluminum or iron salts facilitates the combination of small particles into larger flocs that are easily separated from aqueous solution.

[0043] Here, though, instead of driving flocculation by adsorption, electrostatic interactions or, destabilization, we present flocculation by transformation of the small molecules *themselves,* where chemical modification is stabilized by a novel covalent bond.

[0044] While classic fisher esterification is typically prohibited by the presence of water, previous studies showed that direct esterification of carboxylic acids in water can be achieved using catalytic amounts of dodecylbenzenesulfonic acid (DBSA). DBSA is a surfactant-type Bronsted acid that can form hydrophobic emulsions in water, inside which esterification proceeds under mild conditions. In an aqueous solution of DBSA (catalytic levels) and water, long-chained carboxylic acids and alcohols partition into the DBSA emulsions and react to generate long-chained fatty acid esters. DBSA-catalyzed aqueous esterification reactions have been utilized in the past for sustainable biofuel synthesis but have not been explored as a PFOA treatment option. In addition, the generation of long-chained fatty acid esters in the absence of surfactants such as DBSA has also not been explored as a PFOA treatment option.

[0045] In one embodiment, the present invention relates generally to the use of an alcohol to transform PFAS in contaminated water into an insoluble ester for subsequent removal by precipitation. This method has been found to generate an extremely low amount of toxic waste as compared with conventional treatment methods.

[0046] In one embodiment, the present invention relates generally to a method of treating a source of water contaminated with poly and perfluoroalkyl substances (PFAS) to transform the PFAS into a fluorinated ester precipitate, the method comprising the steps of:

a) providing a volume of the source of water contaminated with the PFAS;
b) optionally, adjusting a concentration of PFAS in the volume of source of water;
c) adding at least one alcohol to the volume of the source of water for a period of time and under process conditions to esterify the PFAS in the volume of the source of water into a fluorinated ester; and
d) separating the fluorinated ester from the volume of the source of water.

[0047] As shown herein, an intramolecular physicochemical transformation from a soluble molecule to an insoluble molecule has the potential to transform 100 liters of water contaminated with 2,000 ppm (2,000 mg/L) PFOA into 100 liters of clean water and only 268 grams of toxic fluorinated ester. Compared to traditional treatment methods using granular activated carbon, PFOA removal via precipitation are believed to be capable of yielding a 74% decrease in mass of toxic waste as shown below in Table 2 as compared with the total waste generated by using a granular activated carbon (GAC) sorbent.

Table 2.

Treatment of 100 L of 2,000 ppm PFOA			
Using GAC		Using precipitation method	
Mass of PFOA sorbed (g)	200	Mass of PFOA reacted (g)	200
Mass of sorbent required[a] (g)	844	Mass conversion factor[b] of PFOA (414 g/mol) to ester (554 g/mol)	1.34
Total waste generated from GAC sorption of PFOA (g)	1044	Total waste generated from precipitation of PFOA (g)	268
Percent decrease of toxic waste from GAC to precipitation		74.4%	

[a]Assuming no regeneration of GAC
[b]Assuming 100% conversion of PFOA to ester

[0048] In one embodiment, the present invention relates generally to a method of treating water contaminated with PFAS to transform the PFAS into a fluorinated ester precipitate that can be removed for subsequent disposal. The water may comprise, for example, drinking water, municipal wastewater, industrial wastewater, ground water, other industrial waste streams or any other source of water that is contaminated with PFAS and/or contains a measurable concentration of PFAS and for which treatment is desired.

[0049] In one embodiment, the PFAS in the source of water comprises perfluoroalkyl carboxylic acids (PFCAs), preferably wherein the PFCAs comprise perfluorooctanoic acid (PFOA).

[0050] In one embodiment, the contaminated water is treated by adding a volume of at least one alcohol to a volume of the contaminated water under appropriate process conditions (i.e., temperature, pH) for a sufficient period of time to allow the PFAS to transform into long-chain fluorinated esters that can be precipitated from the source of water for subsequent disposal, leaving behind a treated water source that has a significantly reduced PFAS concentration, including, for example, a PFAS concentration that is at least about 60% reduced, more preferably at least about 70% reduced or at least about 80% reduced or at least about 90% reduced or even at least about 95% reduced as compared with the initial concentration of PFAS in the water source.

[0051] Various alcohols and combinations of alcohols may be used so long as they are able to generate a hydrophobic emulsion in solution. Examples of such alcohols include fatty alcohols having a chain length of C6 to C20. In addition, combinations of alcohols may be used, including combinations having a smaller chain length so long as at least a portion of the combination is capable of generating a hydrophobic emulsion. One example of a suitable alcohol that is usable in the practice of the invention is decanol, which may be used alone or in combination with other acids.

[0052] The concentration of the alcohol that is added to the volume of contaminated water is preferably within a range of about 1 to 3 times the concentration of PFAS in the contaminated waste stream, more preferably within the range of about 1.5 to about 2.5 times the concentration of PFAS in the contaminated waste stream, most preferably within the range of about 1.8 to about 2.2 times the concentration of PFAS in the contaminated waste stream, most preferably about 1.9 to about 2.1 times the concentration of PFAS in the contaminated waste stream.

Therefore, prior to treatment, the process described herein may include a step of measuring the concentration of PFAS in the volume of contaminated water so that a suitable amount of alcohol can be added. In one embodiment, the concentration of PFAS in the volume of contaminated water is measured by ^{19}F NMR, advanced chromatographic, or other mass spectrometric techniques.

[0053] In addition, the inventors of the present invention have also determined that a preferred concentration of the PFAS in the wastewater that can be treated by the process described herein is within the range of about 2 mmol to about 75 mmol, more preferably about 5 mmol to about 50 mmol. Therefore, if the concentration of the PFAS is outside this range, the waste stream may be adjusted (i.e., concentrated or diluted) as necessary so that the concentration of the PFAS falls within this range.

[0054] Thus, as a pretreatment step, the contaminated water is preferably adjusted (i.e., concentrated) to a range that can be treated by the process described herein using suitable means, such as a reverse osmosis (RO) membrane or a sorbent such as activated carbon. Other suitable means that can be used to adjust the concentration of the contaminated water so as to exhibit a concentration of PFAS with the preferred range would be known to those skilled in the art.

[0055] As described herein, in one embodiment the PFAS is a PFAS that has a fluorinated tail and a carboxylic acid head group. In one embodiment, the PFAS comprises PFOA. The PFAS to be treated is preferably at least a C4 chain PFAS, more preferably at least a C6 chain PFAS, even more preferably at least an C8 chain or higher (i.e., larger carbon chain) PFAS. Mixed chain PFAS, including PFAS containing a mixture of C4+ carbon chains) may also be treated using the process described herein. In one embodiment, an alcohol is added to a volume of water contaminated with PFAS and is mixed for a suitable period of time to produce the insoluble ester that can be precipitated out of the solution and subsequently removed. In addition, in one embodiment, once the insoluble ester precipitates it may be separated from the solution by centrifugation (for faster removal) or settling (for slower but lower-energy removal).

[0056] The system generally operates at a low pH, preferably a very low pH which may be within the range of less than 7 or less than 6 or less than 5 or less than 4 or less than 3 or less than 2 or within a range of 1 to 2.

[0057] The temperature at which the esterification takes place is generally within the range of room temperature (i.e., about 25°C) to about 100°C, more preferably between about 30 and about 60°C, more preferably within the range of 35 to 45°C.

[0058] In one embodiment, the solution is mixed for a period of time that is at least 1 hour or at least 2 hours or at least 4 hours or at least 8 hours or at least 12 hours or at least 24 hours or at least 48 hours or at least 72 hours to esterify the PFAS in the volume of the source of water into a fluorinated ester precipitate. In one embodiment the solution is stirred to make the solution more homogeneous.

[0059] In addition, it is noted that longer chain PFAS have been banned in many jurisdictions, which has led to the use of shorter chain PFAS, which can be more difficult to treat.

[0060] The inventors of the present invention have determined that waste streams containing PFAS that have a chain length of at least 6 carbon atoms or a chain length of at least 8 carbon atoms may be treated using an alcohol without the use of a surfactant. In this instance, the treatment step proceeds in the absence of a surfactant and a surfactant is not used in the process. This contributes to the process being an environmentally friendly process as certain surfactants may be hazardous.

[0061] On the other hand, when shorter chain PFAS contaminated waters are treated, it may be necessary to also add a surfactant to the contaminated water to be treated.

[0062] Therefore, in one embodiment, a surfactant is added to the volume of contaminated water at the same time that the alcohol is added. If used, the concentration of surfactant added may be in the range of about 1 to about 20%, more preferably within a range of about 8 to about 15% of the concentration of the PFAS in the contaminated water. The concentration of the surfactant may depend in part on the concentration and type of PFAS in the waste stream and on the particular surfactant being used. Therefore, one skilled in the art would be able to determine a suitable concentration of surfactant to achieve the desired result of producing a fluorinated ester precipitate that can be separated and removed for subsequent disposal.

[0063] Examples of suitable surfactants include, but are not limited to, dodecylbenzene sulfonic acid (DBSA), octyl benzene sulfonic acid, sodium lauryl sulfoacetate, ammonium lauryl ether sulfate, sodium lauryl ether sulfate, ammonium lauryl sulfate, potassium octanoate, sodium allylsulfonate, sodium stearate, sodium lauroylsarcosinate, sodium myreth sulfate, and sodium pareth sulfate, tridecylbenzene sulfonic acid, sorbitan monooleate, a commercial product of

which is available under the tradename Span™ 80 from Croda Industrial Specialties, polyethylene glycol sorbitan monolaurate, a commercial product of which is available under the tradename Tween® 20 from Fischer Scientific, polyethylene glycol tert-octylphenyl ether, a commercial product of which is available under the tradename Triton™ X-100 from Sigma-Aldrich, itaconic acid 1-dodecyl ester, sodium dodecyl sulfate, ethylene glycol, rhamnolipid biosurfactants, cocamidopropyl betaine, saponin, lecithin, and combinations of one or more of the foregoing. In one embodiment, the surfactant comprises DBSA.

[0064] The invention will now be illustrated with reference to the following non-limiting examples:

Examples:

Experimental

Materials and reagents

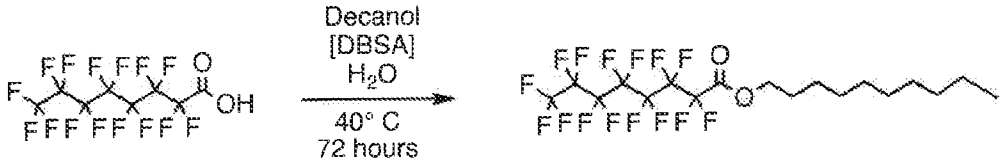
[0065] Perfluorooctanoic acid (PFOA, 96%, Sigma Aldrich), octanoic acid (98%, Thermo Scientific), 1-Decanol (99%, Sigma Aldrich) and dodecylbenzenesulfonic acid (DBSA, 95%, Sigma Aldrich) were used as reagents for esterification. Deuterated water (D_2O, 99.8%, TCI America) and deuterated chloroform ($CDCl_3$, 99.8%, Thermo Scientific) were used as reaction solvent (D_2O only) and NMR solvents. 4-Fluorobenzoic acid (99%, Thomas Scientific), and 2,4-Dichlorobenzotrifluoride (98%, Santa Cruz Biotechnology) were used as internal standards for NMR. Milli-Q water (greater than 18.2 MΩ·cm) was used during all experiments.

Instruments:

[0066] Proton nuclear magnetic resonance (^1H NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded at 25 °C on a 400 MHz Bruker Avance III HD Nanobay equipped with a BBFO Smart probe w/Z-Gradient (unless stated otherwise). Fluorinedecoupled carbon nuclear magnetic resonance (^{13}C NMR) spectra and two-dimensional C-F spectra were recorded on a Bruker Neo 600 MHz system with a QCI-F cryoprobe w/Z-Gradient. Quantitative^{13}C NMR spectra were recorded on a Bruker Avance III 500 MHz system equipped with a 5mm DCH CryoProbe w/Z-Gradient using a 40 second DI delay. Other spectra were recorded on a Bruker Avance III 600 MHz with a BBFO Smart Probe w/Z Z-Gradient. Experiments used pulse programs adapted from standard Bruker pulses library.

Synthesis parameters

[0067] All reactions were carried out under ambient atmosphere. Reaction heating was performed using an aluminum heating block and temperature controller with probe. All reagents were used as received.



[0068] 50 mM PFOA esterification was carried out by sequentially adding PFOA (0.25 mmol), DBSA [when indicated] (0.025 mmol), and decanol (0.5 mmol) to water (5 mL, H_2O or D_2O).

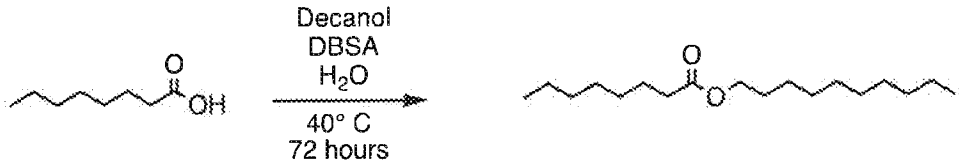
[0069] Figures 11A and 11B depict ^1H NMR (Fig. 11A) and ^{19}F NMR (Fig. 11B) comparison of products of reactions run in H_2O (Fig. 11A) and D_2O (Fig. 11B). Matching spectra indicates that D_2O is an appropriate substitution for H_2O. Reactions were run under identical conditions (5mM PFOA, 72 hours). After 72 hours, reaction contents were centrifuged, aqueous layers were removed, and product was air-dried. After drying, product was re-dissolved in $CDCl_3$.

[0070] Before addition of decanol and DBSA, pH of the solution of PFOA in H_2O was 1.2. Reaction mixtures were stirred at 40° C for 72 hours and then removed from heat. Reaction was monitored and quantified via taking aliquots from the reaction at different time points (see method below). Product was characterized by centrifuging reaction contents (25 minutes, 10,000 rpm, 40° C), decanting the aqueous layer, air-drying the resulting oil in a fume hood for at least 24 hours, and redissolving oil in $CDCl_3$ for NMR.

[0071] ^1H NMR (400 MHz, $CDCl3_3$) δ 4.36 (t, J = 6.6 Hz, 2H), 1.71 (dt, J = 8.2, 6.5 Hz, 2H), 1.43 – 1.07 (m, 21H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.36, 117.05, 110.71, 110.61, 110.22, 108.36, 107.97, 68.71, 31.81, 29.38, 29.32, 29.20, 28.94, 28.04, 25.39, 22.61, 14.01. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.91, -118.62, -121.82, -122.14, -122.82, -126.25.

[0072] Scale-down reactions: 5 mM PFOA esterification was carried out by sequentially adding PFOA (0.025 mmol), DBSA [when indicated] (0.0025 mmol), and decanol (0.05 mmol) to water (5 mL, H_2O). pH of the 5 mM solution of PFOA in H_2O before addition of decanol and DBSA was 1.6. 2.5 mM PFOA esterification was carried out by sequentially adding PFOA (0.0125 mmol), DBSA [when indicated] (0.00125 mmol), and decanol (0.025 mmol) to water (5 mL,

H_2O). Reaction mixtures were stirred at 40° C for 72 hours and then removed from heat. Reaction was monitored via taking aliquots from the reaction after 72 hours.



50 mM octanoic acid esterification was carried out by sequentially adding PFOA (0.25 mmol), DBSA (0.025 mmol), and decanol (0.5 mmol) to water (5 mL, D_2O). Reaction mixtures were stirred at 40° C for 24 hours and then removed from heat. Reaction was monitored in-situ by taking a 400 uL aliquot at the end of the reaction, transferring the aliquot to an NMR tube, and evaluating product formation via ^1H NMR (400 MHz, D_2O). Ester production was tracked using peak at 3.86 ppm (t, J = 6.7 Hz, 2H).

Reaction monitoring and quantification via in-situ F NMR

[0073] To gather quantitative and scale-down data, 5 400 uL aliquots were taken from each reaction. Aliquots were transferred to NMR tubes. To each tube, internal standard (trifluoroacetic acid) was added, as well as 10% D_2O (only for reactions run in H_2O). Samples were analyzed via ^{19}F NMR (for peak quantitation) and ^1H NMR (for peak confirmation). PFOA content was determined by integrating the F NMR peaks at -117.76 ppm (PFOA shift before partitioning to decanol) and -119.96 ppm (PFOA shift after partitioning to decanol), and ester content was determined by integrating the ^{19}F NMR peak at -119.79 ppm.

[0074] Figure 12 depicts ^{19}F NMR spectra of PFOA in H_2O alone (a) and after the addition of decanol (b) and decanol and DBSA (c). All spectra were obtained by adding PFOA to H_2O at 40° C, stirring for 15 minutes to allow full dissolution, and then sampling 400 uL (a) or adding decanol (b) or decanol and DBSA (c), letting the reaction stir for 30 seconds, and then taking a 400 uL sample. 400 uL samples were transferred to clean NMR tubes, into which 50 uL of D_2O (for NMR lock) and internal standard (trifluoroacetic acid) were also added. ^{19}F NMR spectra demonstrate that when PFOA is alone in H_2O (a), it is sparingly soluble and the peak at -117.76 ppm fails to integrate to match the concentration of internal standard TFA. As soon as decanol is added to solution (b), the PFOA ^{19}F NMR shift moves from -117.76 ppm to -119.96 ppm. When DBSA and decanol are both added to solution and a sample is taken after 30 seconds, a small

amount of ester is generated due to DBSA quickening the esterification reaction, corresponding to the ester peak at -119.79 ppm. Unreacted PFOA can be observed via the peak at -119.96 ppm.

[0075] Given the proximity of the PFOA and ester peaks, quantitative ^{19}F NMR was verified with ^{1}H NMR data: Relative integration of the ester peak at 4.08 ppm compared to the decanol peak at 3.38 was used to confirm that ^{19}F NMR peaks were properly assigned.

[0076] For each set of 5 replicate aliquots, the three measurements of closest values were utilized to take averages and standard deviations. ^{19}F NMR spectra were recorded on a 400 MHz spectrometer and are reported in ppm using trifluoroacetic acid as an internal standard (-75.52 ppm). TFA was added to NMR tubes at equal molar concentrations as initial PFOA content to confirm that total fluorine content was correct and concentrations were not misinterpreted due to insolubility. ^{1}H NMR spectra (for peak confirmation) were recorded on a 400 MHz spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). 16 scans were used for samples from 50 mM reactions and 256 scans were used for samples from 5 mM and 2.5 mM reactions.

Ester characterization

[0077] ^{1}H NMR spectra were recorded on a 400 MHz spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). ^{1}H-^{1}H coupled NMR spectra were recorded on a 400 MHz spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). ^{19}F NMR spectra were recorded on a 400 MHz spectrometer and are reported in ppm using 2,4-dichlorobenzotrifluoride as an internal standard (-62.54 ppm). Carbon-fluorine coupled ^{13}C-^{19}F NMR spectra were recorded on a 400 MHz spectrometer and are reported in ppm. To prepare ester for analysis, esterification reaction products were centrifuged, aqueous layer was decanted, and resulting oil was air-dried in a fume hood for at least 72 hours. Qualitative measurements to confirm ester identity were carried out by dissolving ester in pure $CDCl_3$.

Example 1:

[0078] The investigations into aqueous PFOA transformation began by carrying out the esterification reaction.

[0079] Esterification was initiated by sequentially adding DBSA (5 mM) and decanol (100 mM) to a solution of PFOA in water (50 mM). The reaction was stirred for 72 hours at 40° C, the

contents of the reaction vessel were centrifuged, and then the aqueous layer (now with reduced PFOA concentration) was decanted from the dense pellet of insoluble fluorinated ester.

[0080] Even without centrifugation, ester formation and consequent settling is visible to the human eye, as a solution with 50 mM PFOA goes from having full miscibility/no visible separation to clear separation.

[0081] The identification of the fluorinated ester was confirmed via NMR (^{1}H, ^{19}F, ^{1}H-^{1}H, and ^{19}F-^{13}C), which showed formation of the ester bond via two new proton NMR signals at 4.36 ppm and 1.71 ppm, as well as a new fluorine NMR signal at -118.62 ppm as shown in Figures 1-5.

[0082] Figure 1 depicts ^{19}F NMR in $CDCl_3$ of starting material PFOA and esterification reaction product. Ester generation is identified via new peak at -118.62 ppm and diminished PFOA peak at -119.11 ppm. Peak assignment is based off assignments outlined in U.S. Pat. Application No. 18/696,742 to Dichtel et al., the subject matter of which is herein incorporated by reference in its entirety.

[0083] Figure 2 depicts ^{1}H NMR spectra of starting materials (decanol and PFOA) and esterification reaction product in $CDCl_3$. Ester generation is identified via new peaks at 4.36 and 1.71 ppm. Decanol and ester are tracked via triplet peaks at 3.61 ppm and 4.36 ppm, respectively.

[0084] Figure 3 depicts ^{19}F-^{13}C NMR of fluorinated ester. ^{19}F-^{13}C NMR allows for identification of carbon signals bonded to fluorine atoms (the fluorocarbon tail of the fluorinated ester), which are challenging to detect in 1D ^{13}C NMR spectra.

[0085] Figure 4 depicts ^{13}C NMR of unreacted decanol and esterification reaction product. ^{13}C NMR allows for identification of carbon atoms bonded to hydrogen atoms (the hydrocarbon tail of the fluorinated ester).

[0086] Finally, Figure 5 depicts ^{1}H-^{1}H NMR of fluorinated ester. Couplings at 4.36 ppm and 1.71 ppm indicate that the two new ester peaks are connected to one another.

[0087] Product identity was confirmed via FTIR, which showed loss of the hydroxyl group, retention of an alkyl chain, and a slightly shifted carbonyl peak. Figure 6 depicts FTIR spectra of reaction starting materials (PFOA and decanol) and reaction product (decyl pentadecafluorooctanoate). Spectra demonstrate that as the reaction proceeds, an -OH group is lost, an alkyl stretch is retained, and the carbonyl peak slightly shifts. Ester products remained

stable following the end of the reaction, and even retained product identity after stirring with additional acid (HCl, 2 molar equivalencies to ester concentration) for ten days as shown in Figure 7. Figure 7 is an ^{19}F NMR in $CDCl_3$ of ester product after stirring with additional acid (HCl, 2 molar equivalencies to ester concentration) for ten days. Retention of ester peak at -118.62 ppm demonstrates that the ester is stable after the end of the reaction and under acidic conditions.

[0088] In order to determine the rate at which PFOA is transformed into fluorinated ester, periodic aliquots were taken from the reaction flask and utilized in-situ ^{19}F NMR to determine relative concentrations of fluorinated species, PFOA and ester. It was found that conversion reached its highest rate after 24 hours (90% conversion of PFOA to ester), after which no yield increases were observed, although esterification of PFOA happened at a faster rate (24 hours for maximum yield of fluorinated ester versus 72 hours for maximum yield of non-fluorinated ester).

Example 2:

[0089] The inventors next explored whether the hydrophobic properties of PFOA could be exploited to carry out esterification without the addition of a surfactant (DBSA).

[0090] Manabe et al. argue that aqueous dehydration reactions function because of the formation of hydrophobic emulsion droplets which exclude water. In their studies, Manabe et al. added surfactant DBSA to the reaction to aid in the formation of emulsion droplets. However, perfluorinated compounds such as PFOA behave differently from their non-fluorinated analogues, since long fluorinated chains repel water due to their extreme electronegativity and bulkiness. The inventors were curious to see if the hydrophobic fluorinated chains of PFOA alone would be enough to form hydrophobic emulsions which allowed for successful esterification. Based thereon, the esterification experiments were repeated without the addition of DBSA by simply adding decanol (100 mM) to PFOA in water (50 mM).

[0091] The results are shown in Fig. 12 which depicts ^{19}F NMR spectra of PFOA in H_2O alone (a) and after the addition of decanol (b) and decanol and DBSA (c). All spectra were obtained by adding PFOA to H_2O at 40° C, stirring for 15 minutes to allow full dissolution, and then sampling 400 uL (a) or adding decanol (b) or decanol and DBSA (c), letting the reaction stir for 30 seconds, and then taking a 400 uL sample. 400 uL samples were transferred to clean NMR tubes, into which 50 uL of D_2O (for NMR lock) and internal standard (trifluoroacetic acid) were

also added. ^{19}F NMR spectra demonstrate that when PFOA is alone in H_2O (a), it is sparingly soluble and the peak at -117.76 ppm fails to integrate to match the concentration of internal standard TFA. As soon as decanol is added to solution (b), the PFOA ^{19}F NMR shift moves from -117.76 ppm to -119.96 ppm. When DBSA and decanol are both added to solution and a sample is taken after 30 seconds, a small amount of ester is generated due to DBSA quickening the esterification reaction, corresponding to the ester peak at -119.79 ppm. Unreacted PFOA can be observed via the peak at -119.96 ppm. Given the proximity of the PFOA and ester peaks, quantitative ^{19}F NMR was verified with ^{1}H NMR data: Relative integration of the ester peak at 4.08 ppm compared to the decanol peak at 3.38 was used to confirm that ^{19}F NMR peaks were properly assigned.

[0092] Based thereon, it was determined that esterification proceeded with just PFOA and decanol alone, without the addition of a surfactant, albeit slower (72 hours for 90% maximum yield without DBSA versus 24 hours for 90% maximum yield with DBSA).

[0093] Thus it can be seen that omitting DBSA greatly reduces the toxicity of the process, and the difference in clarity of treated water is visible to the human eye.

[0094] The inventors of the present invention hypothesized that the esterification reaction succeeded without DBSA due to the water-repellant properties of the fluorinated tail on PFOA.

[0095] To test this hypothesis, esterification of octanoic acid, the non-fluorinated analogue of PFOA, was carried out with DBSA (as a control) and without DBSA. It was found that while ester formed when DBSA was employed, ester did not form in the absence of DBSA. It was therefore concluded that PFOA could be converted into an ester without the addition of a surfactant due to the remarkably hydrophobic fluorinated tails of PFOA, which lead to the formation of hydrophobic emulsions without the addition of other chemicals.

[0096] Figure 8 depicts ^{1}H NMR spectra for monitoring the behavior of octanoic acid (nonfluorinated) in the reaction system. Spectra are displayed of esterification starting materials (octanoic acid and decanol) and esterification products (when DBSA is included and omitted from the reaction). Ester formation is demonstrated by a novel triplet peak at 3.86 ppm. When DBSA is omitted from the reaction, ester formation is not observed, as there is no novel peak at 3.86 ppm. These results indicate that nonfluorinated octanoic acid does not have the surfactant properties of PFOA which enable the reaction to proceed without additional surfactant DBSA.

[0097] Finally, the inventors of the present invention sought to determine the scalability of the aqueous fisher esterification reaction. At the 50 mM PFOA concentration employed for initial experiments, PFOA is present in solution well above reported aqueous solubility values, thus enabling formation of hydrophobic emulsions which facilitate reaction progress. It was believed that the reaction would only be feasible above the aqueous solubility values of PFOA. Due to the unpredictable and inconsistent behavior of PFAS in water, reported aqueous solubility values of PFOA vary dramatically, typically between 5.5 and 11 mM.

[0098] Based thereon, this reaction was tested at 5 mM to ensure that it was below the reported aqueous solubility value, and other chemical concentrations were adjusted stoichiometrically. Surprisingly, by tracking reaction progress by presence or lack of ester peaks in ^{19}F NMR, it was found that the reaction proceeded at 5 mM (below aqueous solubility value of PFOA) but failed at 2.5 mM.

[0099] It was first hypothesized that the reaction proceeded below the PFOA aqueous solubility value because of the presence of DBSA. However, the reaction still proceeded at a concentration of 5 mM even without the use of DBSA (PFOA and decanol alone) as shown in Fig. 9. This suggests that interactions between PFOA and decanol alone are strong enough to form emulsions even at a concentration lower than reported PFOA solubility values.

[0100] Fig. 9 depicts in-situ ^{19}F NMR spectra of the esterification reaction in H_2O scaled-down to 5 and 2.5 mM PFOA concentrations. Presence of ester peak at -119.79 ppm for the 5 mM reaction indicates that the esterification reaction proceeds at a concentration of 5 mM, while lack of ester peak at -119.79 ppm (and retention of a large PFOA peak at -117.76 ppm) for the 2.5 mM reaction indicates that the esterification reaction fails at a concentration of 2.5 mM.

[0101] Fig. 10 depicts In-situ ^{19}F NMR spectra of the esterification reaction in H_2O at an initial PFOA concentration of 5 mM, with and without DBSA. Retention of an ester peak at -119.79 ppm for both reactions with and without DBSA indicates that DBSA is not vital to reaction progress, even at a lower starting PFOA concentration of 5 mM. Integration of PFOA and ester peaks demonstrates that inclusion of DBSA in the reaction does improve ester yield, as ester is produced at a 43% yield when DBSA is included in the reaction, but ester is produced at a 34% yield when DBSA is omitted from the reaction.

[0102] The success of the reaction below PFOA aqueous solubility values supports the findings that the presence of alcohol (i.e., decanol) in aqueous PFOA solution is sufficient to form the

hydrophobic emulsions wherein esterification proceeds. It was therefore concluded that the reaction could be scaled down from 50 mM to 5 mM, a concentration that is more relevant for environmental applications.

[0103] **Additional Embodiments:**

[0104] **Clause 1:** A method of treating a source of water contaminated with poly and perfluoroalkyl substances (PFAS) to transform the PFAS into a fluorinated ester precipitate, the method comprising the steps of:

a) providing a volume of the source of water contaminated with the PFAS;
b) optionally, adjusting a concentration of PFAS in the volume of source of water;
c) adding at least one alcohol to the volume of the source of water for a period of time and under process conditions to esterify the PFAS in the volume of the source of water into a fluorinated ester; and
d) separating the fluorinated ester from the volume of the source of water.

[0105] **Clause 2:** The method according to Clause 1, wherein the source of water is selected from the group consisting of a source of drinking water, municipal wastewater, industrial wastewater, ground water, other industrial waste streams, and any other source of water containing a measurable concentration of PFAS.

[0106] **Clause 3:** The method according to Clause 1 or Clause 2, wherein the PFAS in the source of water comprises perfluoroalkyl carboxylic acids (PFCAs), preferably wherein the PFCAs comprise perfluorooctanoic acid (PFOA).

[0107] **Clause 4:** The method according to any of Clauses 1 to 3, wherein the PFAS in the source of water is at least a C4 chain PFAS, more preferably at least a C6 chain PFAS, even more preferably at least an C8 chain or higher PFAS or wherein the PFAS contains a mixture of C4+ carbon chains.

[0108] **Clause 5:** The method according to any of Clauses 1 to 4, wherein the fluorinated ester precipitates out of solution.

[0109] **Clause 6:** The method according to any of Clauses 1 to 5, wherein the concentration of PFAS in the volume of the source of water is adjusted to a range of about 2 mmol to about 75 mmol, preferably about 5 mmol to about 50 mmol, optionally wherein the concentration of PFAS

in the volume of the source of water is adjusted by passing the volume of water through a reverse osmosis (RO) membrane or with a sorbent such as activated carbon.

[0110] **Clause 7:** The method according to any of Clauses 1 to 6, wherein the at least one alcohol added to the volume of contaminated water in step c) comprises an alcohol that is capable of generating a hydrophobic emulsion.

[0111] **Clause 8:** The method according to any of Clauses 1 to 7, wherein the at least one alcohol added to the volume of contaminated water in step c) comprises one or more fatty alcohols having a chain length of C6 to C20, optionally, wherein the at least one alcohol comprises decanol.

[0112] **Clause 9:** The method according to any of Clauses 1 to 8, wherein the concentration of the at least one alcohol is added to the volume of contaminated water is within a range of about 1 to 3 times the concentration of PFAS in the contaminated waste stream, more preferably within the range of about 1.5 to about 2.5 times the concentration of PFAS in the contaminated waste stream, most preferably within the range of about 1.8 to about 2.2 times the concentration of PFAS in the contaminated waste stream, most preferably about 1.9 to about 2.1 times the concentration of PFAS in the contaminated waste stream.

[0113] **Clause 10:** The method according to any of Clauses 1 to 9, wherein step c) operates at a pH which may be within the range of less than 7 or less than 6 or less than 5 or less than 4 or less than 3 or less than 2 or within a range of 1 to 2.

[0114] **Clause 11:** The method according to any of Clauses 1 to 10, wherein step c) operates a temperature within the range of room temperature to about 100°C, more preferably between about 30 and about 60°C, more preferably within the range of 35 to 45°C.

[0115] **Clause 12:** The method according to any of Clauses 1 to 11, wherein the period of time is at least 1 hour or at least 2 hours or at least 4 hours or at least 8 hours or at least 12 hours or at least 24 hours or at least 48 hours or at least 72 hours.

[0116] **Clause 13:** The method according to any of Clauses 1 to 12, wherein the solution is stirred to make the solution more homogeneous.

[0117] **Clause 14:** The method according to any of Clauses 1 to 13, wherein step c) is performed without the addition of a surfactant.

[0118] **Clause 15:** The method according to any of Clauses 1 to 13, further comprising the step of adding a surfactant to the volume of the source of water along with the at least one alcohol.

[0119] **Clause 16:** The method according to Clause 15, wherein the surfactant is selected from the group consisting of dodecylbenzene sulfonic acid (DBSA), octyl benzene sulfonic acid, sodium lauryl sulfoacetate, ammonium lauryl ether sulfate, sodium lauryl ether sulfate, ammonium lauryl sulfate, potassium octanoate, sodium allylsulfonate, sodium stearate, sodium lauroylsarcosinate, sodium myreth sulfate, and sodium pareth sulfate, tridecylbenzene sulfonic acid, sorbitan monooleate, polyethylene glycol sorbitan monolaurate, polyethylene glycol tert-octylphenyl ether, itaconic acid 1-dodecyl ester, sodium dodecyl sulfate, ethylene glycol, rhamnolipid biosurfactants, cocamidopropyl betaine, saponin, lecithin, and combinations of one or more of the foregoing, more preferably, wherein the surfactant comprises DBSA.

[0120] **Clause 17:** The method according to Clause 15 to Clause 16, wherein the concentration of surfactant added to the volume of the source of water is in the range of about 1 to about 20%, more preferably within a range of about 8 to about 15% of the concentration of the PFAS in the contaminated water.

[0121] **Clause 18:** The method according to any of Clauses 1 to 17, further comprising the step of removing the separated fluorinated ester for subsequent disposal.

[0122] **Clause 19:** Use of an alcohol capable of generating a hydrophobic emulsion for treating a water source contaminated with PFAS according to the process of any of Clauses 1-18.

WHAT IS CLAIMED IS:

1. A method of treating a source of water contaminated with poly and perfluoroalkyl substances (PFAS) to transform the PFAS into a fluorinated ester precipitate, the method comprising the steps of:

   a) providing a volume of the source of water contaminated with the PFAS;
   b) optionally, adjusting a concentration of PFAS in the volume of source of water;
   c) adding at least one alcohol to the volume of the source of water for a period of time and under process conditions to esterify the PFAS in the volume of the source of water into a fluorinated ester; and
   d) separating the fluorinated ester from the volume of the source of water.

2. The method according to claim 1, wherein the source of water is selected from the group consisting of a source of drinking water, municipal wastewater, industrial wastewater, ground water, other industrial waste streams, and any other source of water containing a measurable concentration of PFAS.

3. The method according to claim 1, wherein the PFAS in the source of water comprises perfluoroalkyl carboxylic acids (PFCAs), preferably wherein the PFCAs comprise perfluorooctanoic acid (PFOA).

4. The method according to claim 1, wherein the PFAS in the source of water is at least a C4 chain PFAS, more preferably at least a C6 chain PFAS, even more preferably at least an C8 chain or higher PFAS or wherein the PFAS contains a mixture of C4+ carbon chains.

5. The method according to claim 1, wherein the fluorinated ester precipitates out of solution.

6. The method according to claim 1, wherein the concentration of PFAS in the volume of the source of water is adjusted to a range of about 2 mmol to about 75 mmol, preferably about 5 mmol to about 50 mmol.

7. The method according to claim 6, wherein the concentration of PFAS in the volume of the source of water is adjusted by passing the volume of water through a reverse osmosis (RO) membrane or with a sorbent such as activated carbon.

8. The method according to claim 1, wherein the at least one alcohol added to the volume of contaminated water in step c) comprises an alcohol that is capable of generating a hydrophobic emulsion.

9. The method according to claim 1, wherein the at least one alcohol added to the volume of contaminated water in step c) comprises one or more fatty alcohols having a chain length of C6 to C20.

10. The method according to claim 9, wherein the at least one alcohol comprises decanol.

11. The method according to claim 1, wherein the concentration of the at least one alcohol is added to the volume of contaminated water is within a range of about 1 to 3 times the concentration of PFAS in the contaminated waste stream, more preferably within the range of about 1.5 to about 2.5 times the concentration of PFAS in the contaminated waste stream, most preferably within the range of about 1.8 to about 2.2 times the concentration of PFAS in the contaminated waste stream, most preferably about 1.9 to about 2.1 times the concentration of PFAS in the contaminated waste stream.

12. The method according to claim 1, wherein step c) operates at a pH which may be within the range of less than 7 or less than 6 or less than 5 or less than 4 or less than 3 or less than 2 or within a range of 1 to 2.

13. The method according to claim 1, wherein step c) operates a temperature within the range of room temperature to about 100°C, more preferably between about 30 and about 60°C, more preferably within the range of 35 to 45°C.

14. The method according to claim 1, wherein the period of time is at least 1 hour or at least 2 hours or at least 4 hours or at least 8 hours or at least 12 hours or at least 24 hours or at least 48 hours or at least 72 hours.

15. The method according to claim 1, wherein the solution is stirred to make the solution more homogeneous.

16. The method according to claim 1, wherein step c) is performed without the addition of a surfactant.

17. The method according to claim 1, further comprising the step of adding a surfactant to the volume of the source of water along with the at least one alcohol.

18. The method according to claim 17, wherein the surfactant is selected from the group consisting of dodecylbenzene sulfonic acid (DBSA), octyl benzene sulfonic acid, sodium lauryl sulfoacetate, ammonium lauryl ether sulfate, sodium lauryl ether sulfate, ammonium lauryl sulfate, potassium octanoate, sodium allylsulfonate, sodium stearate, sodium lauroylsarcosinate, sodium myreth sulfate, and sodium pareth sulfate, tridecylbenzene sulfonic acid, sorbitan monooleate, polyethylene glycol sorbitan monolaurate, polyethylene glycol tert-octylphenyl ether, itaconic acid 1-dodecyl ester, sodium dodecyl sulfate, ethylene glycol, rhamnolipid biosurfactants, cocamidopropyl betaine, saponin, lecithin, and combinations of one or more of the foregoing, more preferably, wherein the surfactant comprises DBSA.

19. The method according to claim 17, wherein the concentration of surfactant added to the volume of the source of water is in the range of about 1 to about 20%, more preferably within a range of about 8 to about 15% of the concentration of the PFAS in the contaminated water.

20. The method according to claim 1, further comprising the step of removing the separated fluorinated ester for subsequent disposal.

21. Use of an alcohol capable of generating a hydrophobic emulsion for treating a water source contaminated with PFAS according to the process of any of claims 1-20.

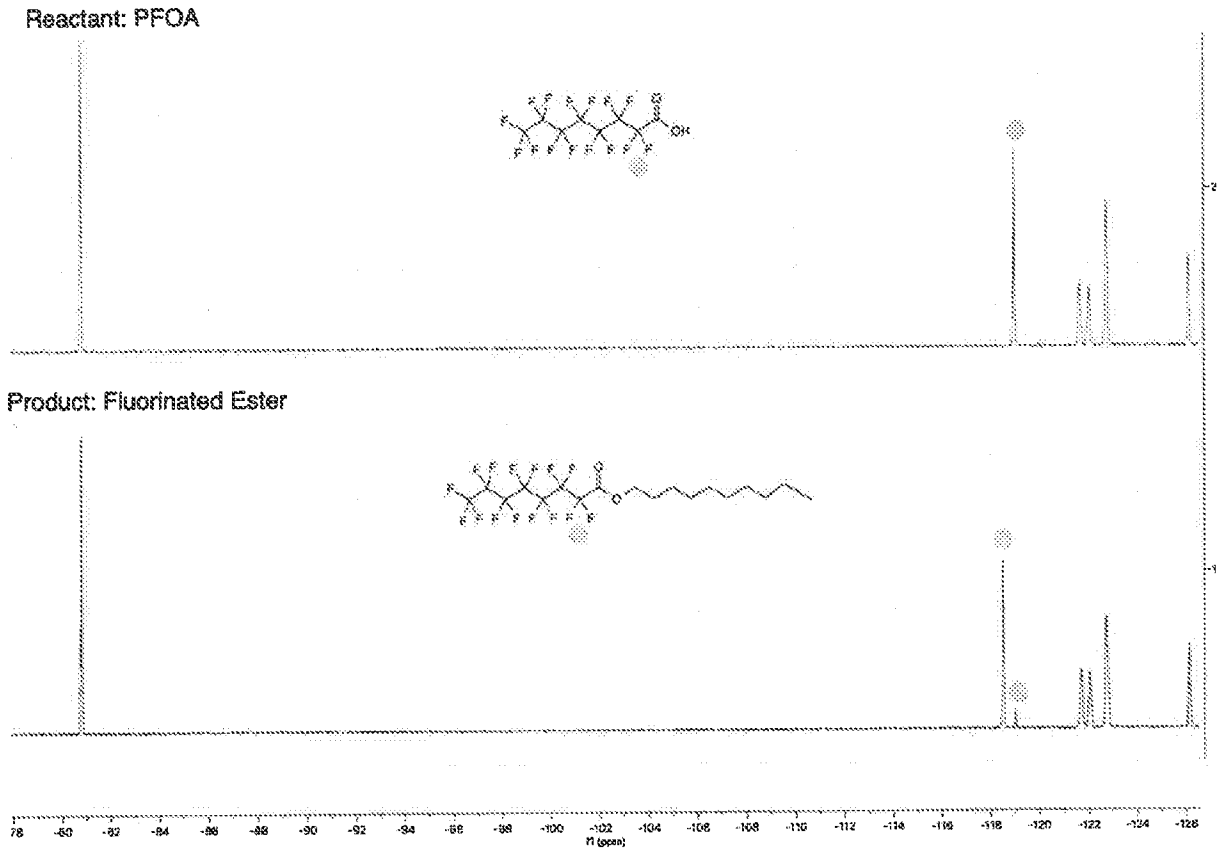


Fig. 1

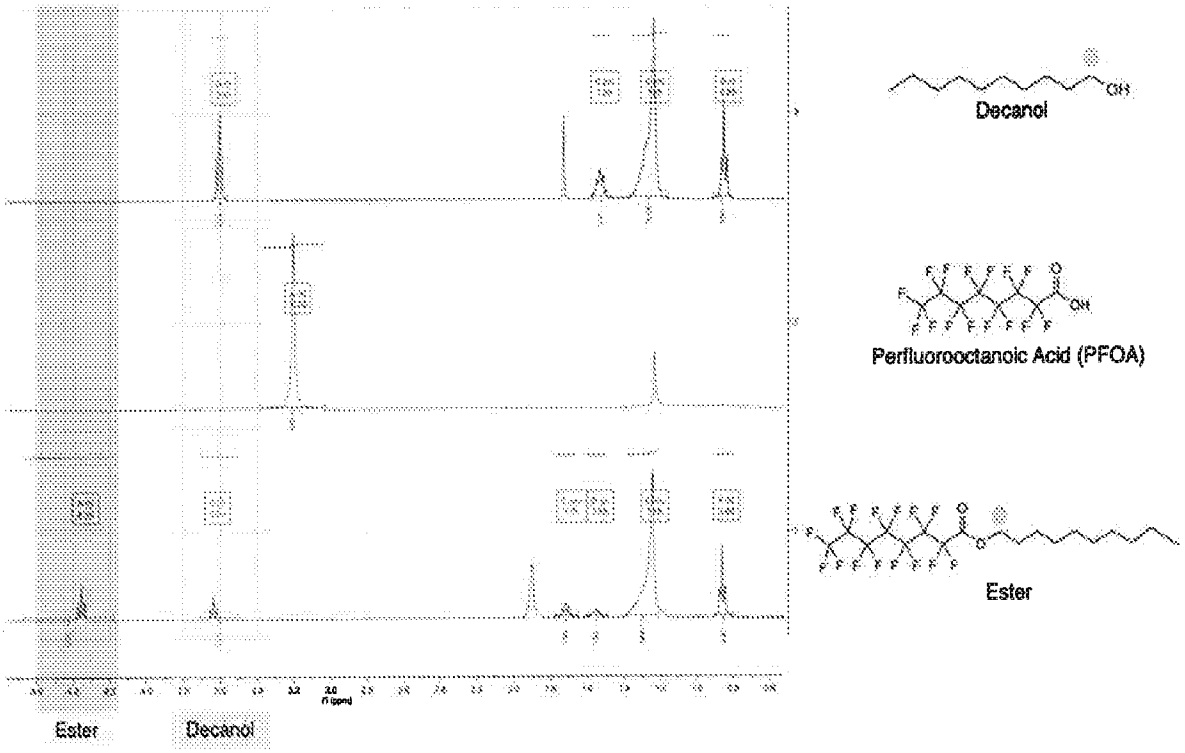


Fig. 2

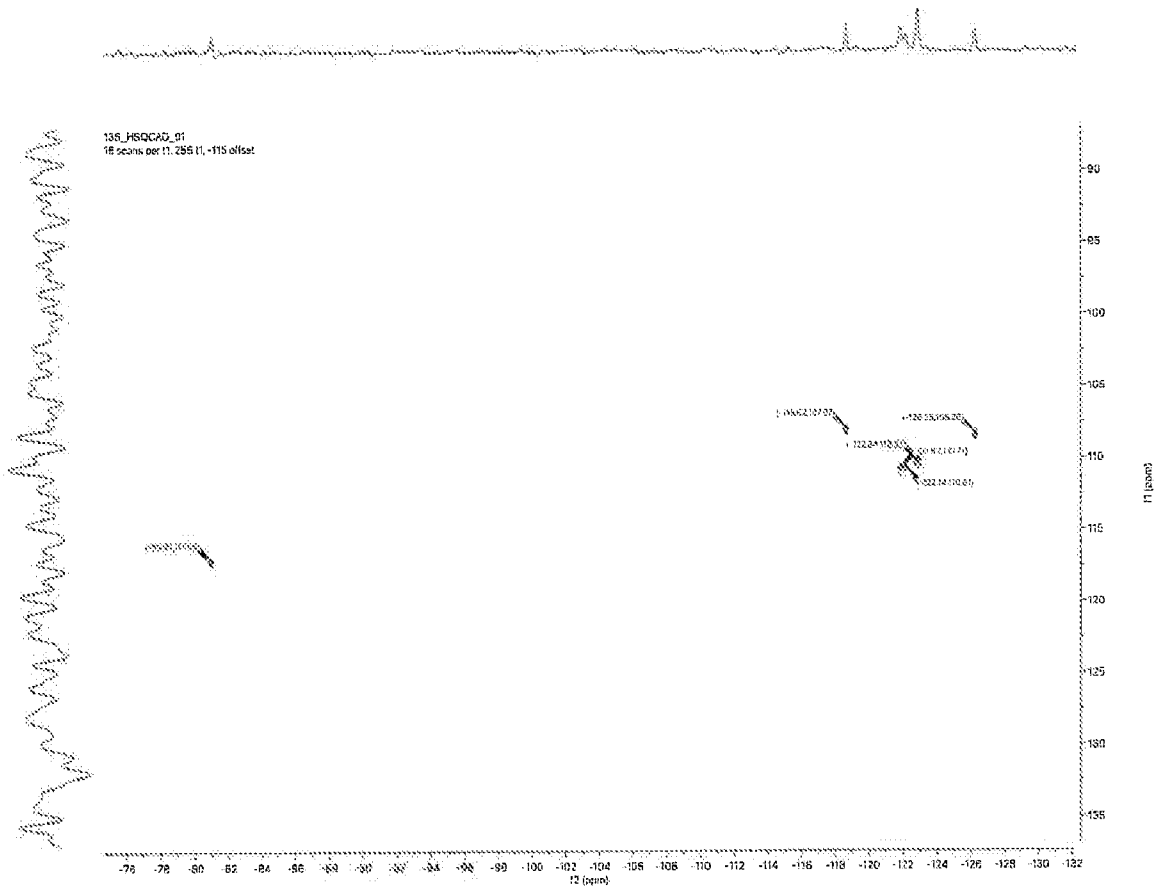
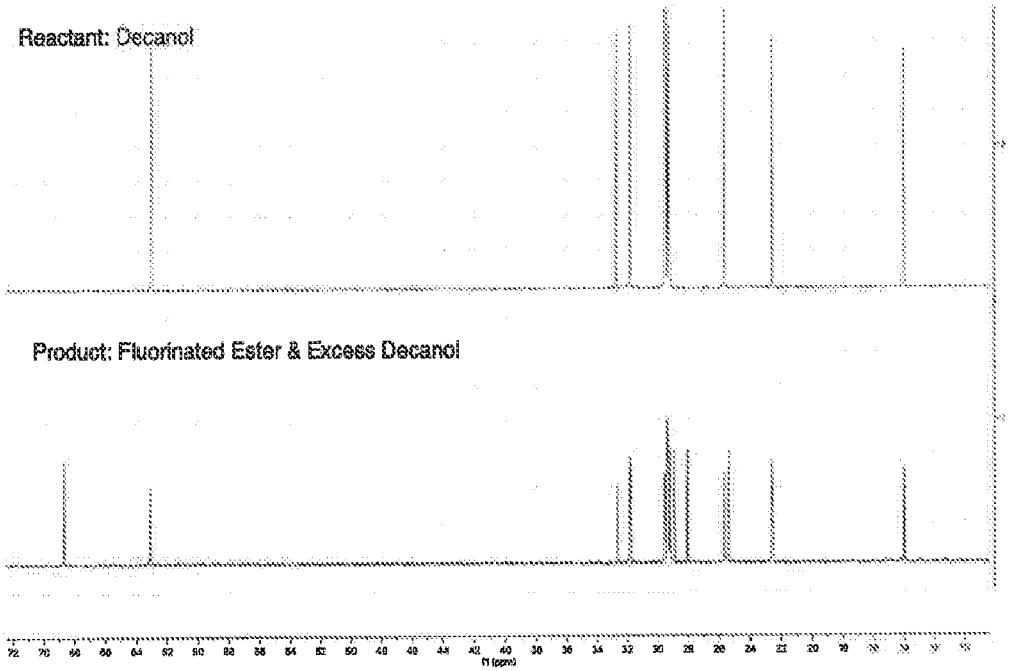


Fig. 3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Product: Fluorinated Ester & Excess Decanol

Fig. 4

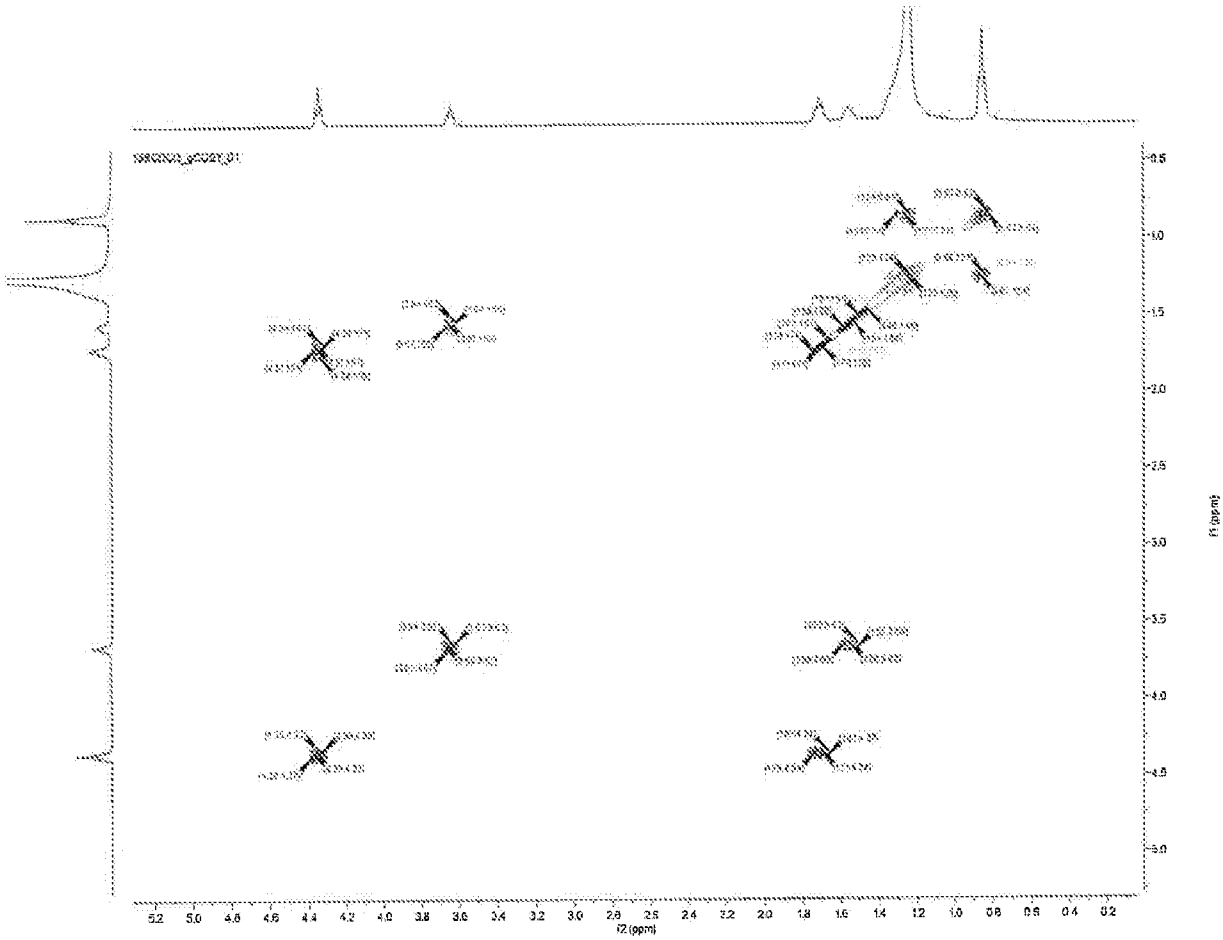
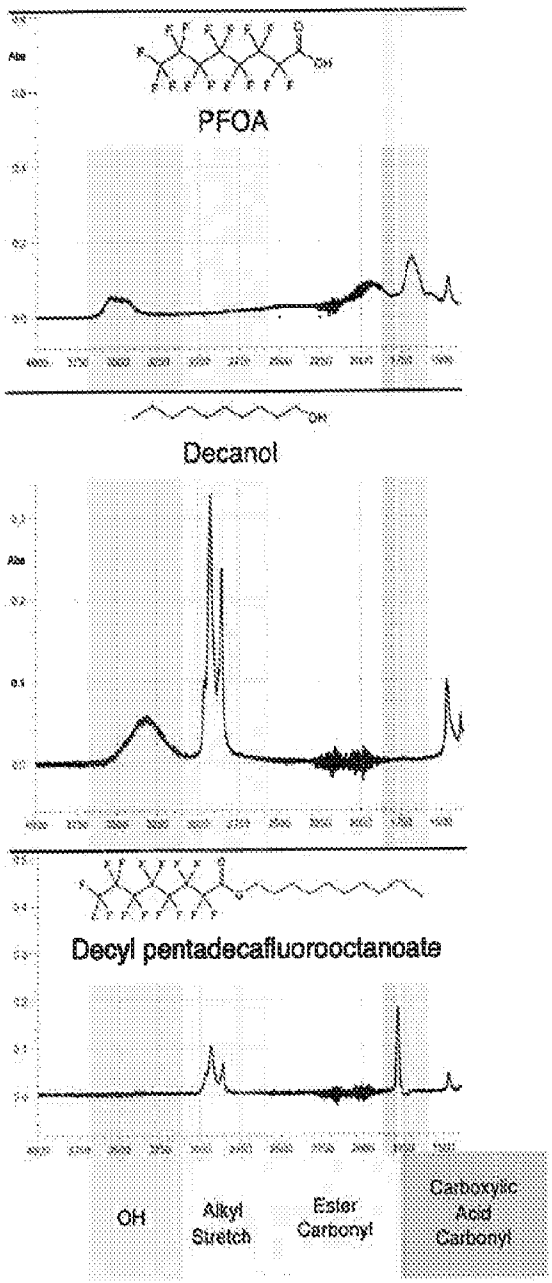


Fig. 5


PFOA
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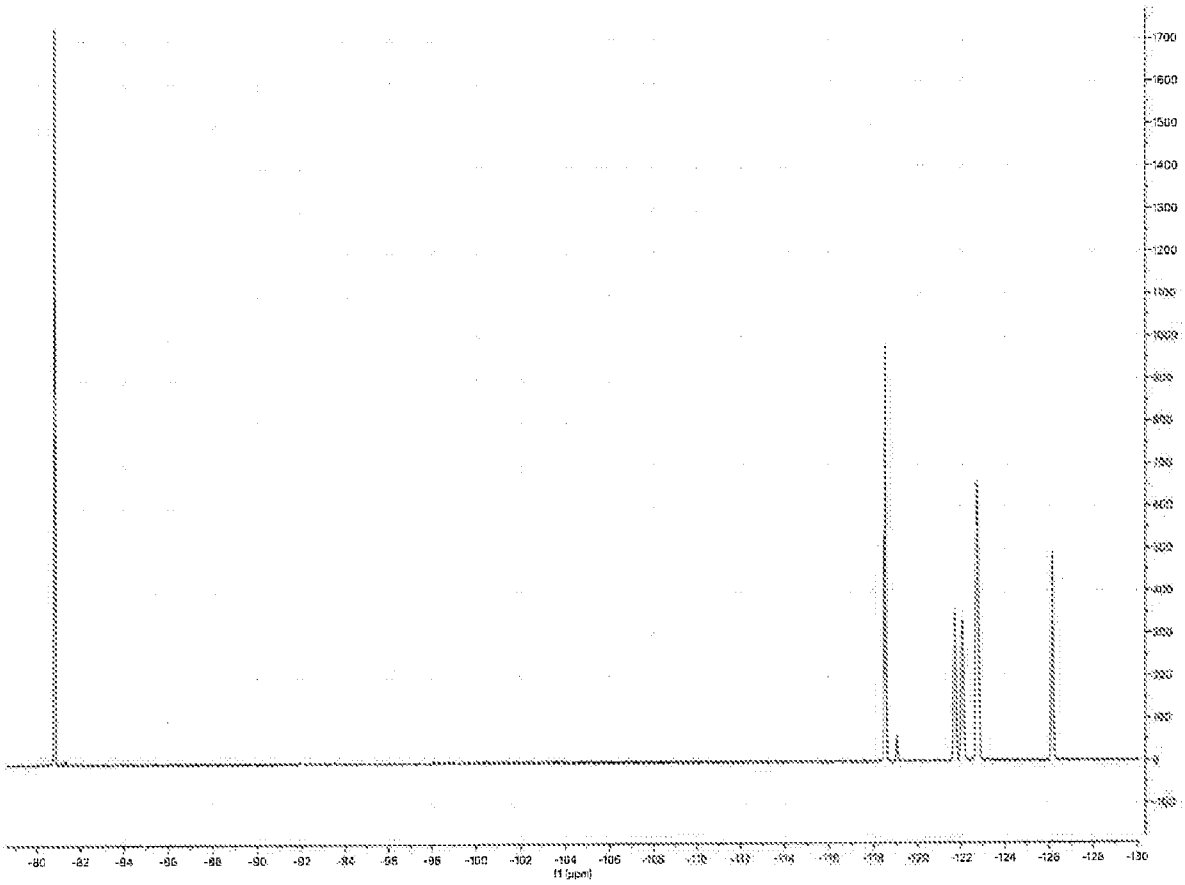
Decyl pentadecafluorooctanoate
OH
Alkyl Stretch
Ester Carbonyl
Carboxylic Acid Carbonyl

Fig. 6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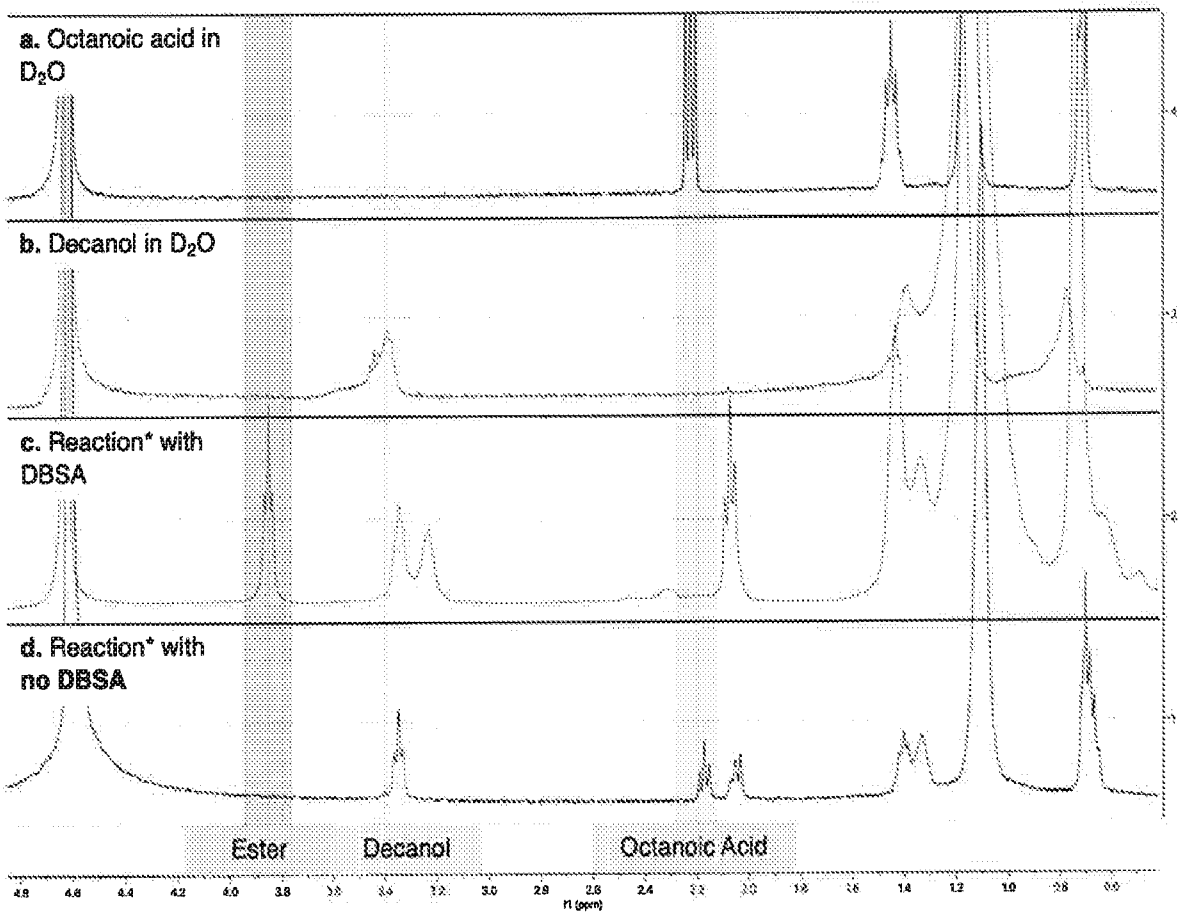
-122
-124
-126
-128
-130
f1 (ppm)

Fig. 7



*Reaction of octanoic acid and decanol in D_2O, stirred for 24 hrs.

Fig. 8

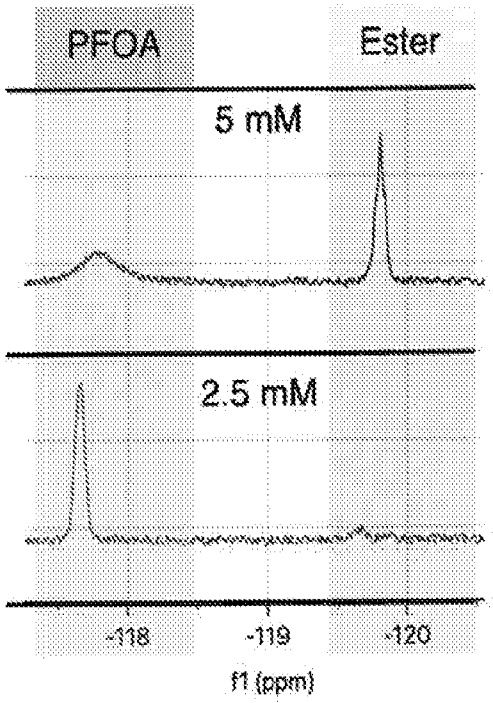


Fig. 9

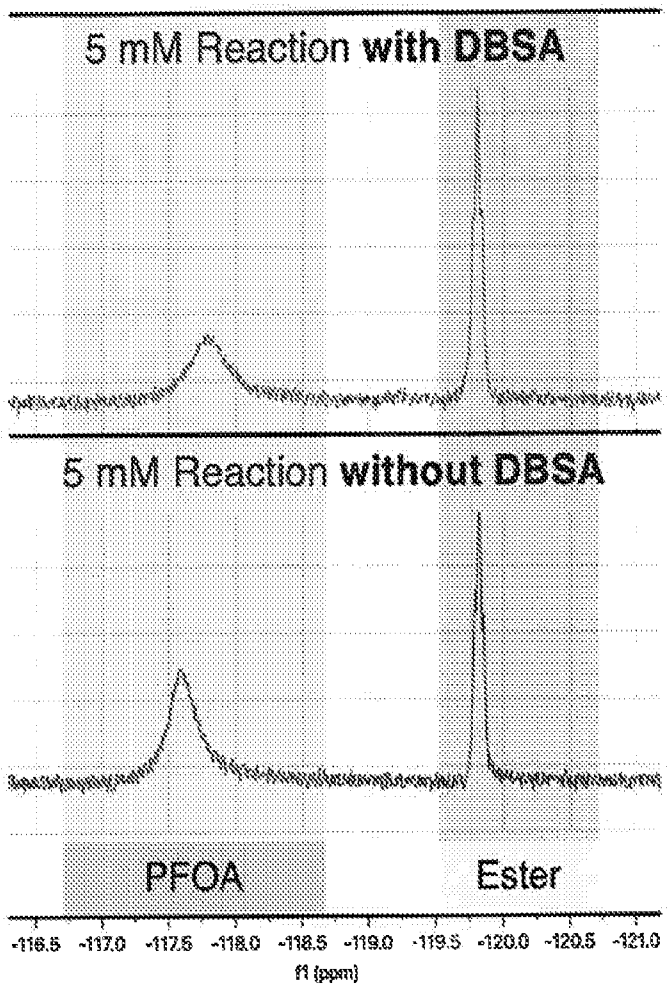

5 mM Reaction with DBSA
5 mM Reaction without DBSA
PFOA
Ester
-116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5 -120.0 -120.5 -121.0
f1 (ppm)

Fig. 10

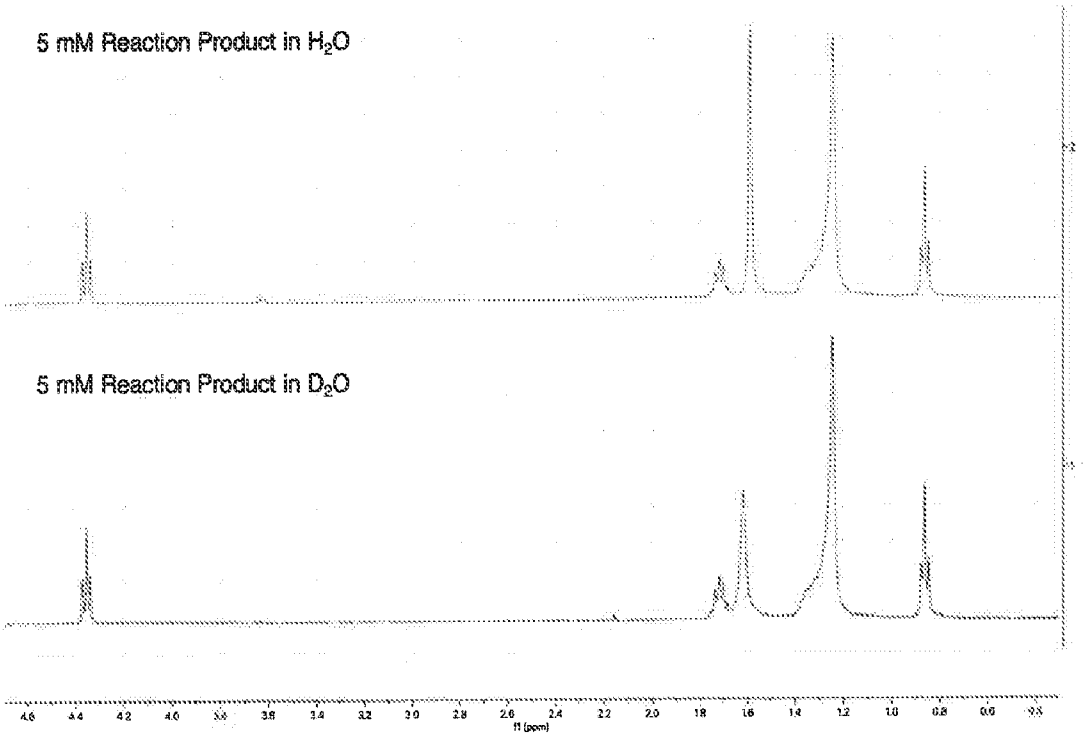

5 mM Reaction Product in H_2O
5 mM Reaction Product in D_2O
f1 (ppm)

Fig. 11A

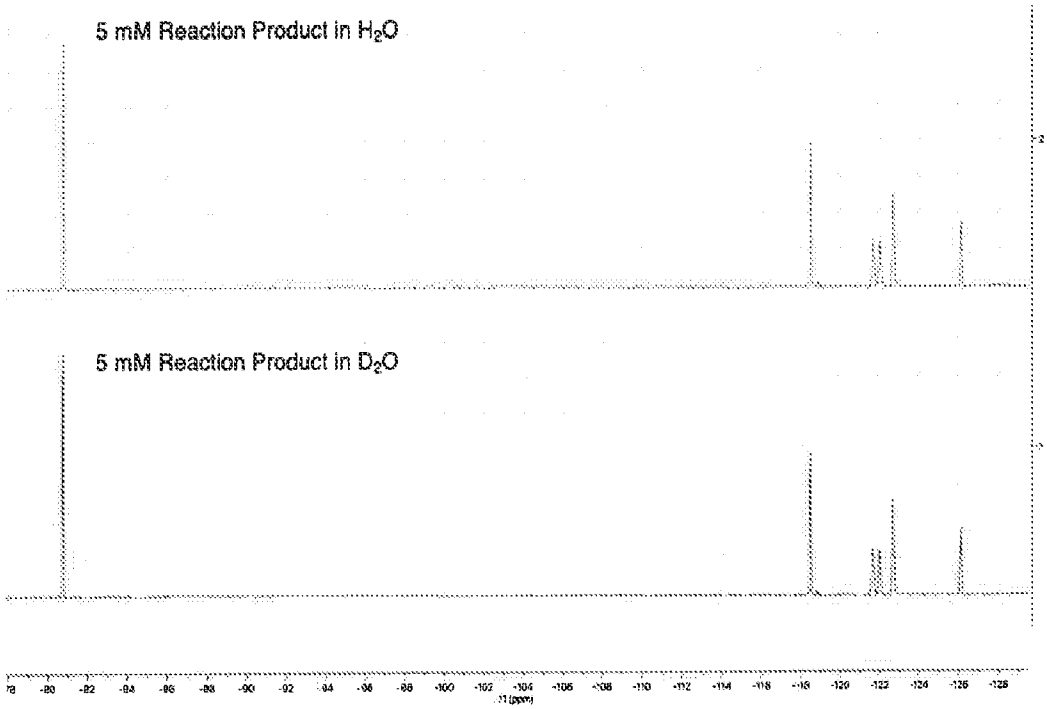


Fig. 11B

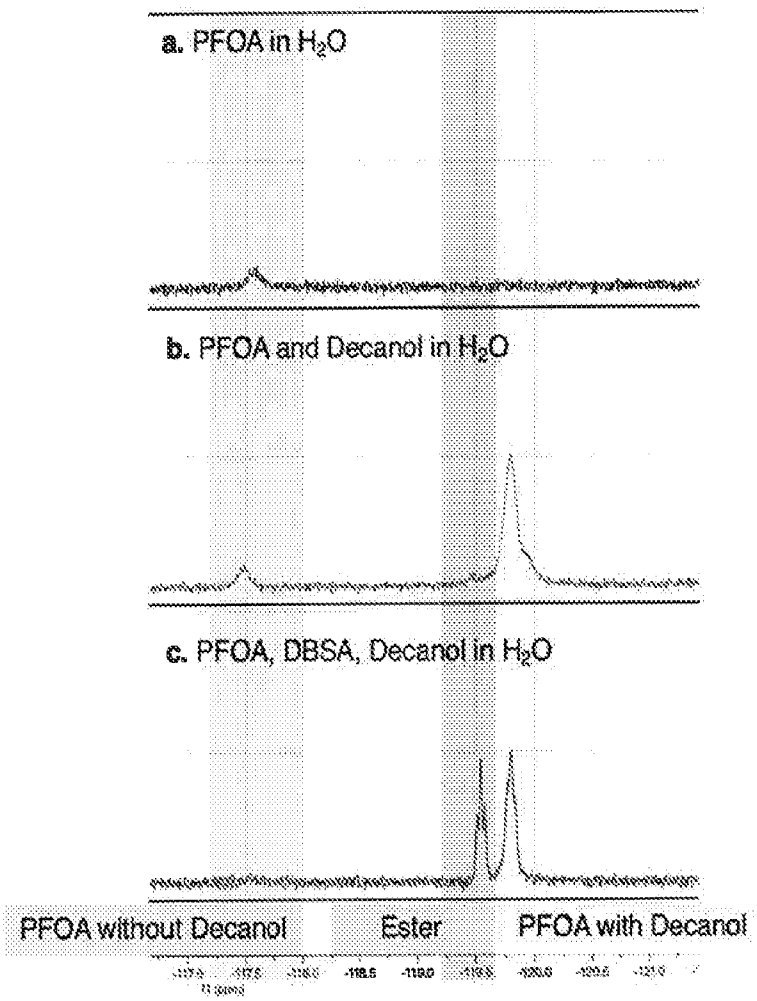

a. PFOA in H_2O
b. PFOA and Decanol in H_2O
c. PFOA, DBSA, Decanol in H_2O
PFOA without Decanol
Ester
PFOA with Decanol

Fig. 12