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Degradation Studies of New Substitutes for Perfluorinated Surfactants

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Abstract Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are manmade, stable perfluorosurfactants. The properties of perfluoroalkylated compounds that cause them to persist in the environment are also the properties that made them attractive compounds for industrial usage for over 50 years. Due to the unique properties of the carbon–fluorine bond and the polarity of perfluoroalkyl groups, potential substitutes to replace perfluorinated surfactants in most cases continue to be perfluoroalkyl based. Thus, issues of persistence in the environment remain. There is a need to test emerging new substitute surfactants for biodegradability. This study involved degradability measurements of emerging perfluorinated surfactant substitutes. The stability of the substitutes of perfluorinated surfactants was tested by employing advanced oxidation processes, which were based on degradation by ultraviolet lamp, hydrogen peroxide, or both, followed by conventional tests, among them an automated method based on the manometric respirometry test (OECD 301 F; OxiTop), closed-bottle test (OECD 301 D), and standardized fixed-bed bioreactor on perfluorobutane sulfonate, fluorosurfactant Zonyl, two fluoraliphatic esters (NOVEC FC-4430 and NOVEC FC-4432), and 10-(trifluoromethoxy) decane 1 sulfonate. Most of these new surfactants are well established in the marketplace and have been used in several applications as alternatives to PFOS- and PFOA-based surfactants. Ready biodegradation tests for fluoroaliphatic esters, the fluorosurfactant Zonyl, perfluorobutane sulfonate, and 10-(trifluoromethoxy) decane-1-sulfonate using the manometric respirometry test (OxiTop) did not meet the ready biodegradability test criteria. However, 10-(trifluoromethoxy) decane-1-sulfonate was observed to be degradable when a standardized fixed-bed bioreactor test was applied.

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Perfluorinated compounds (PFCs), which include perfluorooctane sulfonate (PFOS; $C_8HF_{17}O_3S$) and perfluorooctanoic acid [PFOA; $CF_3(CF_2)_6COOH$], constitute a diverse class of chemicals that occurs in a wide range of industrial and household products (Kannan et al. 2005; Kissa 2001). The widespread presence of perfluoroalkyl sulfonates (PFASs) in wildlife (Giesy and Kannan 2001; Hansen et al. 2001; Orata et al. 2009; Tao et al. 2006)—and their bioaccumulation, potential toxicity, and adverse health effects (Barker 2006; Fuentes et al. 2006; Lau et al. 2007)—makes the study of their environmental fate a major concern. The extreme strength of the C–F bond that makes PFCs suitable for certain uses also makes them potentially significant environmental contaminants, due to their persistence property (Sáez et al. 2008).

Since the phase-out of manufacturing perfluorooctanesulfonyl fluoride (POSF; $C_8F_{17}SO_2F$)-based materials, alternative compounds in use as surfactants are

typically fluorinated compounds with a shorter chain length, such as fluorotelomer alcohols (mainly C_6 chain length), perfluorobutane sulfonate (PFBS), and perfluorinated polyethers based on a CF_3 or a C_2F_5 structure. Polyfluorinated compounds with an alkyl chain length of C_5 or less do not seem to be significant bioaccumulative and toxic (Lieder et al. 2009; Newsted et al. 2008; Olsen et al. 2009). Materials derived from perfluorobutanesulfonyl fluoride (PBSF; $C_4F_9SO_2F$) have been introduced as replacements for eight-carbon homologue products (manufactured from POSF) and, since then, have been used in industrial and commercial processes (Lieder et al. 2009; Olsen et al. 2009). PFBS ($C_4F_9SO_3^-$) is a surfactant and potential degradation product of PBSF-derived materials. Olsen et al. (2009) evaluated the elimination half-life of PFBS in rats, monkeys, and humans, which showed much lower potential for accumulation in human serum after repeated occupational, nonoccupational (e.g., consumer), or environmental exposures, being more efficiently eliminated compared to the six- and eight-carbon perfluorinated homologues. However, due to the limited numbers of subjects analyzed and studies, the implications of these short-chain perfluorinated compounds for human health and the environment are still unclear (Lieder et al. 2009; Newsted et al. 2008; Olsen et al. 2009).

Testing for persistence of emerging surfactants begins with tests for ready biodegradability, which provide information about the biodegradability of a substance under most common environmental conditions, to avoid time and more extensive and costly research. An advanced oxidation process (AOP) was used as an indicator of the degradation potential of the materials. It was considered the initial step for the evaluation of the substance persistence in the environment. Though fluorinated surfactants can resist conventional oxidative chemical reagents, AOPs, with their high oxidation potential, seemed to be a promising alternative for use before classical physicochemical and biological processes (Schröder and Meesters 2005). It is expected that some portion of the molecules suffers decomposition, however, when applied to perfluorinated surfactants, lipophilic linear perfluorinated parts of the molecules remained unaltered (Schröder and Meesters 2005).

Readily biodegradability tests are commonly used to obtain a first characterization of organic compounds in terms of their accessibility to microbial degradation (Alexy et al. 2004; Guhl and Steber 2006) and play an important role in the EU environmental classification of chemicals (EC 1993), as well as in environmental risk assessments (EC 2003). Among the OECD tests for ready biodegradability, the manometric respirometry test (OECD 301F) has been widely used, providing a good reproducibility, precision, and accuracy (Guhl and Steber 2006; Lapertot and Pulgarin 2006), and has many advantages including reduced sample preparation time, use of nondiluted samples, easy and continuous reading of the measuring data, and a faster measuring time (Roppola et al. 2006). In this test, a biological oxygen demand (BOD) value $\geq$60% of the theoretical oxygen demand (ThOD), within the 10-day window of time before the final plateau (lag period) in a 28-day period, is regarded as evidence of ready biodegradability (Stasinakis et al. 2008; OECD 1993). The manometric respirometry test (OxiTop) is based on automatic pressure measurement in a closed bottle under constant temperature. Micro-organisms consume oxygen when degrading organic matter and the CO_2 gas formed is chemically bound by the sodium hydroxide pellets. This results in a pressure decrease in the bottle. The BOD values (mg L^{-1}) are read continuously during the test and are calculated according to the ideal gas law modified equation for conditions in a closed space (Reuschenbach et al. 2003; Vähäoja et al. 2005).

The biological fixed-bed reactor (FBBR) is considered to be a good model system, due to the fact that it is able to simulate biological degradation in different waters. It has been satisfactorily used for investigating both the primary degradation of various organic chemicals and their further breakdown pathway (Knepper et al. 2003). The FBBR system was completely described by Knepper et al. (2003). The experimental setup was based on a mixed microbial community from a natural setting other than isolated cultures, as this guaranteed greater environmental relevance of the outcomes (Peschka et al. 2008a).

Despite the rising number of published studies looking at the detection of perfluorinated acids in the environment, comparably few have examined their potential sources (Hagen et al. 1981; Key et al. 1998; Ellis et al. 2001; Lange 2002; Dinglasan et al. 2004; Wang et al. 2005a, b; Hori et al. 2006; Sinclair et al. 2007). PFOS and PFOA, besides being produced for many years as commercial products, which may be directly released into the environment (Prevedouros et al. 2006), are also the final degradation products of a host of precursor perfluorinated chemicals. Available evidence suggests that the transformation or biodegradation of precursor molecules occurs by both abiotic and biotic biodegradation pathways (Xu et al. 2004; Dinglasan et al. 2004; Ellis et al. 2001; Lange 2002; Wang et al. 2005a, b).

The toxicity and kinetics of PFOA and PFOS have been studied in animals (Abbott et al. 2007; Lau et al. 2006) and have been shown to elicit toxic effects in exposed laboratory animals (Austin et al. 2003; Kennedy et al. 2004). Human toxicology for PFOA and PFOS has recently been reviewed (Kennedy et al. 2004; Kudo and Kawashima 2003; Lau et al. 2007). The mechanisms and pathways leading to the presence of PFOS in human blood likely

involved environmental exposure to PFOS, or to precursor molecules and residual levels of PFOS or PFOS precursors in industrial and commercial products (Olsen et al. 2007).

Potential sources of human exposure to PFCs included manufacturing operations and waste streams of POSF-based fluorochemical products, and the use or degradation of some final commercial and consumer products, including indirect food-contact applications (3M Company 2003). Possible exposure pathways that are being examined include drinking water, dust in homes, and food or migration from food packaging and cookware (Begley et al. 2005; Emmett et al. 2006; Falandysz et al. 2006; Kubwabo et al. 2005; Powley et al. 2005; Sinclair et al. 2007; Tittlemier et al. 2007).

The aim of the present work was to perform AOPs, based on the degradation of emerging surfactants by ultraviolet (UV) lamp and H_2O_2, followed by conventional tests, among them an automated method based on the manometric respirometry test (OECD 301 F; OxiTop), a closed-bottle test (CBT; OECD 301 D), and a standardized FBBR on PFBS, fluorosurfactant Zonyl, two fluoroaliphatic esters (NOVEC FC-4430 and FC-4432), and 10-(trifluoromethoxy)decane-1 sulfonate.

Materials and Methods

The stability of the substitutes of perfluorinated surfactants was tested employing AOPs, followed by conventional tests, among them an automated method based on the manometric respirometry test (OECD 301 F; OxiTop), a CBT (OECD 301 D), and a standardized FBBR on perfluorobutane sulfonate standard, two fluoroaliphatic esters (NOVEC FC-4430 and NOVEC FC-4432), a 50% fluorosurfactant (Zonyl), and 10-(trifluoromethoxy)decane-1 sulfonate. Some of these surfactants are well established in the marketplace and have been used in several applications as alternatives to PFOS and PFOA compounds. The molecular structure of the studied compounds is shown in Fig. 1, while Table 1 reports a general summary of the test method applied, substance concentrations, inocula used, and test duration in degradation experiments.

Chemicals and Analytical Standards

PFBS standard (98%) was obtained from Sigma–Aldrich (Germany). The fluoroaliphatic ester NOVEC FC-4430 (90% polymeric fluorochemical actives, 8% non-fluorochemical actives, and 2% co-solvents), fluoroaliphatic ester NOVEC FC-4432 (87% polymeric fluorochemical actives, 7% non-fluorochemical actives, 5% 1-methyl-2-pyrudidinone, and <1% toluene), and fluorosurfactant Zonyl (50% fluorosurfactant, 25% water, and 25% dipropyleneglycol

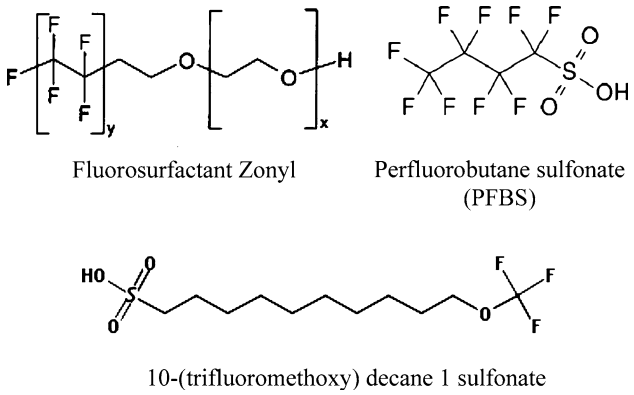

Fig. 1 Molecular structures of studied compounds

methyl ether) were obtained from 3 M and DuPont, respectively. 10-(Trifluoromethoxy)decane-1 sulfonate (concentration: 91 mg L^{-1}), a prototype substance, was obtained from Merck (Germany). The internal standard perfluoro-*n*-[1,2,3,4,-$^{13}C_4$] octanoic acid (MPFOA) (Wellington Laboratories, Canada) was dissolved in methanol at a concentration of 50 µg/mL. Other reagents used were obtained from Merck Darmstadt (Germany).

Degradation Using Advanced Oxidation Processes

In AOP reagents UV/H_2O_2 or only UV radiation was applied to test substances dissolved in ultrapure water at a concentration of 100 mg L^{-1} (standard solution). Samples were taken for analysis every 20 min during the treatment period of 120 min to monitor degradation. The effect of dilution on concentration of surfactants was tested by preparing samples of 50 and 25 mg L^{-1} diluted solutions. One hundred microliters of 30% H_2O_2 was added to each vial sample. Samples were analyzed using the software Tiamo (with sample changer; Metrohm) and an ion selective electrode for fluoride.

Measurement of Biological Oxygen Demand Using the Manometric Respirometry Test

The manometric respirometry test was done by adopting the method of Roppola et al. (2006) and the OECD (1993), with slight modifications. Inoculum was preconditioned to the experimental conditions but not preadapted to the test substance. The inoculum was sewage effluent which was collected from a sewage treatment plant in Darmstadt, Germany, fresh from the aeration tank of a sewage treatment plant. Preconditioning consisted of aerating activated sludge in a secondary effluent for 7 days at the test temperature, with the aim of improving the precision of the test method (OECD 1993). Coarse particles were removed by filtration and the sludge was kept aerobic thereafter. Flasks

Table 1 Summary of methods used in degradation tests for each compound and concentration in each experiment

Test substance	Replicate	Method	Inoculum	Concentration (mg L^{-1})	Test duration
PFBS	2	CBT	Rhine River water	73	28 days
	2	OxiTop	Activated sludge	100	40 days
	3	AOP		100	120 min
	2	FBBR	Surface water	100	28 days
NOVEC FC-4430	2	CBT	Rhine River water	3	28 days
	2	OxiTop	Activated sludge	100	40 days
	3	AOP		100	120 min
NOVEC FC-4432	2	CBT	Rhine River water	5	28 days
	2	OxiTop	Activated sludge	100	40 days
	3	AOP		100	120 min
Fluorosurfactant Zonyl	2	CBT	Rhine River water	0.03	28 days
	2	OxiTop	Activated sludge	100	40 days
	3	AOP		100	120 min
10-(Trifluoromethoxy)decane sulfonate	2	CBT	Rhine River water	0.03	28 days
	2	OxiTop	Activated sludge	91	40 days
	3	AOP		91	120 min
	2	FBBR	Surface water	100	28 days

Note: Sodium acetate was used as a reference compound

containing the following were used: test substance and inoculum (test suspension); only inoculum (inoculum blank); and reference compound and inoculum (procedure control). Each glass bottle contained appropriate volumes of mineral medium (8.5 mg L^{-1} KH_2PO_4, 21.75 mg L^{-1} K_2HPO_4, 33.40 mg L^{-1} $Na_2HPO_4 \times 2H_2O$, 0.5 mg L^{-1} NH_4Cl, 27.50 mg L^{-1} $CaCl_2$, 22.50 mg L^{-1} $MgSO_4 \times 7H_2O$, and 0.25 mg L^{-1} $FeCl_3 \times 6H_2O$) as described by the OECD (1993) and 1.6 mL of inoculum (1.6 mL of sludge supernatant). The weight of 16.4 mg of samples and control standards was chosen for all chemicals tested and put in round glass-bottle flasks, which were filled to the brim (164 mL) using the mineral medium. Each bottle was sealed with a rubber sleeve containing three tablets of NaOH as CO_2 absorber. Magnetic stirring rods were put in the bottle. Samples were analyzed in duplicate. Measuring heads were screwed onto the bottles and the samples were stabilized in an incubation cabinet (20.0 ± 0.2°C) for 6 h before measurement began. The experiment was carried out for 40 days and sodium acetate (NaAc) was used as reference compound.

The Closed-Bottle Test

The CBT is recommended as the first, simple test for assessment of the biodegradability of organic compounds. The CBT was performed according to test guidelines OECD 301 D (OECD 1993) in the dark at room temperature (20 ± 1°C), as described in detail elsewhere (Kümmerer et al. 1996). The standard test period for the CBT was 28 days. Each test vessel contained a mineral salt solution (mineral medium) prepared the same way as for the manometric respirometry test. The inoculum used in this method was water from the Rhine River taken at Rhine km 463.6 (Biebesheim, Germany) in spring 2008, instead of the domestic or industrial sludge that is commonly used. Experimental bottles were run in duplicate for all tested compounds and parallel blanks. The progress of aerobic biodegradation was monitored by measuring the dissolved oxygen concentration using Winkler's method, described elsewhere (Carpenter 1965; Winkler 1888), at weekly intervals during the 28-day incubation. The amount of oxygen taken up by the microbial population during biodegradation of the test substance was corrected for uptake by a blank run, and is expressed as a percentage of ThOD or chemical oxygen demand (COD). Total organic carbon (TOC) and COD for each compound were measured following EPA Methods 415.1 and 410.4, respectively.

Biodegradation Simulation Using a Fixed-Bed Bioreactor

An FBBR was developed to determine the biodegradability of single compounds under aerobic conditions. A glass column filled with glass beads (18-cm filling level) forms the main part of an FBBR, enabling micro-organisms to accumulate on the surface. The micro-organisms derived from Rhine water (used as inoculum) circulated at a flow

rate of 16 mL min^{-1} in a closed loop. A membrane pump aerates the water in the storage bottle. Three FBBRs were run with 5 L surface water each, taken from a pristine creek (Biebesheim, Germany). PFBS and 10-(trifluoromethoxy)decane-1 sulfonate biodegradability were tested using this method. The duration of the degradation experiment was 28 days at room temperature with a neutral pH. To avoid photodegradation, the experiment was set up in the dark.

For the analytical procedure for extraction, slight modifications were incorporated in the procedure described elsewhere (Hansen et al. 2002), with some modifications (Taniyasu et al. 2003), including the use of water Oasis HLB SPE cartridges (60 mg), previously conditioned, at a flow rate of 3–6 mL min^{-1}. Cartridges were washed with 40% methanol (6 mL) and then completely dried. Target analytes were then eluted with 6 mL of methanol. The eluent was evaporated with a gentle stream of nitrogen gas to a final volume of 1000 µL for analysis by HPLC–MS/MS.

For PFBS analysis a 1-mL sample was taken weekly and diluted to 1 L with Milli-Q water to which an internal standard was added for SPE analysis using Oasis HLB cartridges (60 mg; Waters), previously conditioned with hexane, 40% methanol, methanol and then Milli-Q water, at a flow rate of 1 drop s^{-1} (3–6 mL min^{-1}). Target analytes were then eluted with 6 mL of methanol. The eluate was evaporated with a gentle stream of nitrogen gas to a final volume of 1000 µL. This final extract was then taken for HPLC–MS/MS analysis.

LC/MS/MS Analysis

LC/MS analysis was carried out with HPLC (HP 1090) interfaced with an Ion Trap MS (Thermo LCQ-Duo). Separation was done with a Betasil C_{18} column (2.1-mm i.d. × 100-mm length; 5-µm particle size; Thermo Fischer Scientific) at a flow rate of 0.3 mL min^{-1}. An isocratic elution was used for analysis using a mobile phase of 2 mmol L^{-1} ammonium acetate in methanol. Samples were injected at a volume of 10 µL. Acquisition of mass spectra was performed using a quadrupole mass spectrometer operated in negative electrospray ionization mode. The capillary voltage was 2.5 kV, while the cone voltage was set at 25 V. The source block and desolvation temperatures were 120 and 450°C, respectively. Nebulizer and desolvation gas flow rates were 60 and 740 L h^{-1}, respectively. The following ion transitions were monitored for PFBS (SRM ms/ms, 80 and 299; collision energy, 35 V) and 10-(trifluoromethoxy)decane-sulfonic acid (SRM ms/ms, 85 and 219; collision energy, 25 V). The details of the operation parameters for LC–MS/MS have been reported elsewhere (Taniyasu et al. 2005).

Results and Discussion

Results for ThOD, TOC, and COD were as follows: PFBS, ThOD = 0.45 mg oxygen/mg test substance, TOC = 0.15 mg C/mg test substance; fluoroaliphatic ester NOVEC FC-4430, COD = 1.56 mg oxygen/mg test substance, TOC = 0.45 mg C/mg test substance; fluoroaliphatic ester NOVEC FC-4432, COD = 1.42 mg oxygen/mg test substance, TOC = 0.44 mg C/mg test substance; fluorosurfactant Zonyl, COD = 0.99 mg oxygen/mg test substance, TOC = 0.28 mg C mg test substance; and 10-(trifluoromethoxy)decane-1-sulfonate, COD = 0.84 mg oxygen/mg test substance, TOC = 0.21 mg C/mg test substance.

For AOPs, it was observed that only a small fraction, representing 1.5% of the original PFBS, was degraded using UV or the UV/H_2O_2 system for all tested concentrations (Fig. 2). This demonstrates that, even in a more oxidative environment, PFBS is not readily degradable. From the original concentration of 100 mg L^{-1} PFBS, a slightly lower concentration (96.5 ± 2.0 mg L^{-1}) was obtained after the experiment. This represented about 3.35×10^{-6} mol of fluoride removed from a concentration of 3.35×10^{-4} mol of fluoride. Insignificantly higher fluoride concentrations were obtained when the original PFBS concentration was diluted to 50 and 25 mg L^{-1} as shown in Fig. 2. For the fluoroaliphatic esters NOVEC FC-4430 and NOVEC FC-4432, significant degradation was observed with time of exposure to UV radiation and even more accelerated degradation when in association with H_2O_2 (Fig. 3). The fluoride concentrations in the final solution were 6 and 10 orders of magnitude for NOVEC FC-4430 and NOVEC FC-4432, respectively, which are higher than that observed for PFBS.

The final step in the AOP was accompanied by a lag phase (the plateau) of fluoride concentration in solution at 120 min in all experiments. The fluoroaliphatic esters NOVEC FC-4430 and NOVEC FC-4432 demonstrated a degradation plateau at 6 and 10 mg L^{-1} of fluoride concentration,

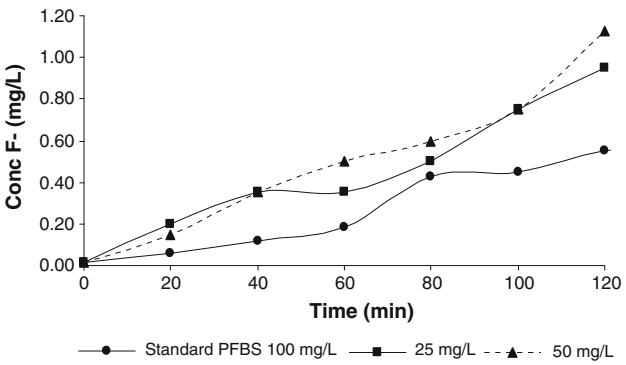

Fig. 2 Degradation of PFBS using UV/H_2O_2 at different concentrations

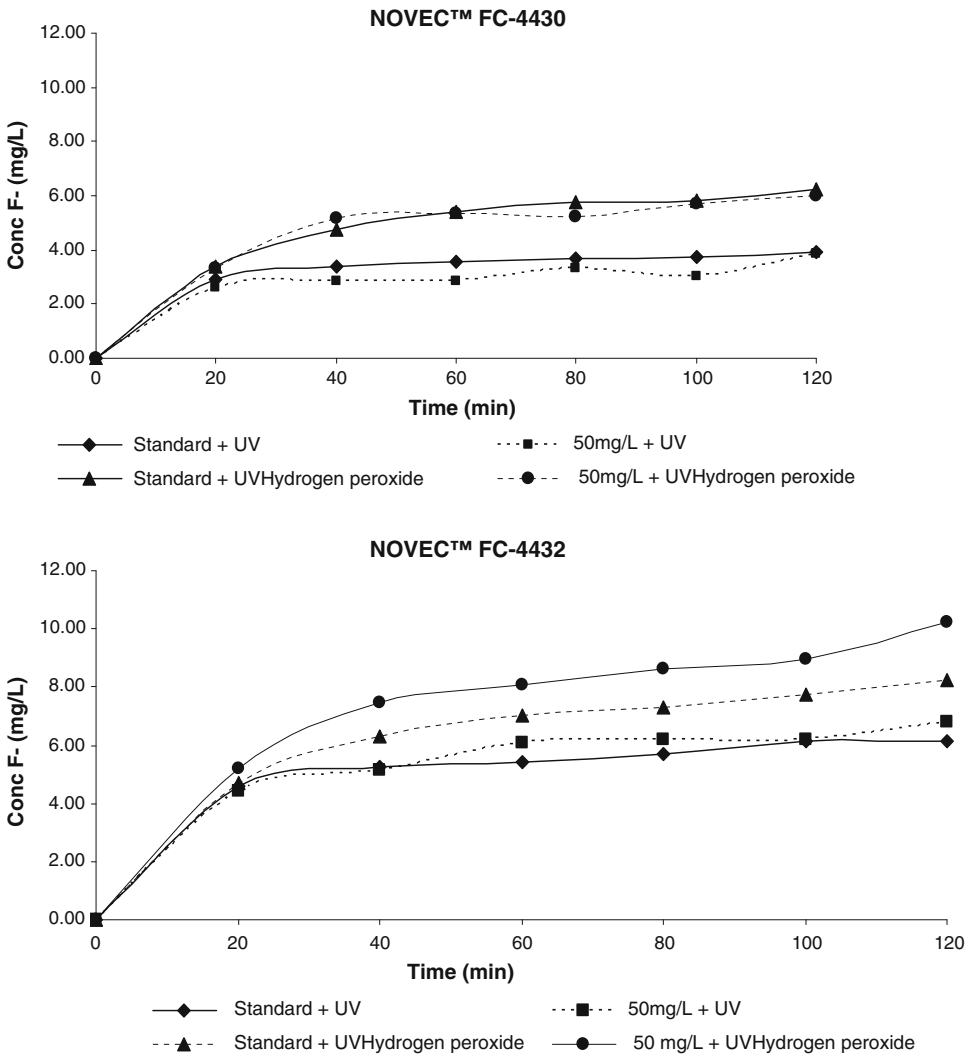

Fig. 3 Degradation of fluoroaliphatic esters NOVEC FC-4430 and NOVEC FC-4432 at two concentrations when submitted to UV radiation and the UV/H_2O_2 system

respectively, when using UV radiation alongside H_2O_2. It can be concluded that the fluoroaliphatic ester NOVEC FC-4432 degrades more than NOVEC FC-4430 as shown in Fig. 3. However, the addition of H_2O_2 showed a more distinct effect for NOVEC FC-4430 than for NOVEC FC-4432, which resulted in a higher degradation increment of NOVEC FC-4430 when submitted to a more oxidative environment.

Upon reduction of the concentration of both ester substances, a slight increase in fluoride concentration in resultant solution was noted, though this was insignificant for NOVEC FC-4432. Figure 4 shows a more elevated concentration of fluoride in the resultant concentration after degradation using standard + UV for 10-(trifluoromethoxy)decane-1 sulfonate (plateau at 18 mg L^{-1}), which represents 3.16×10^{-4} mol of the theoretical 3.28×10^{-4} mol of fluoride in the initial solution. Furthermore, complete degradation was observed when oxidation was applied (112% calculated value) as well as for diluted solution (50 mg L^{-1}), which gave a 21 mg L^{-1} fluoride concentration. The plateau for the fluorosurfactant Zonyl was at 18 mg L^{-1} (Fig. 4). A decrease in TOC measurements was also observed, confirming the proportional degradation of the carbon chain. This could be an indication of biodegradation potential by micro-organisms for 10-(trifluoromethoxy)decane-1 sulfonate and the fluorosurfactant Zonyl. Results in the AOP experiment also showed that there was no significant influence of the compound concentrations on degradation. Relative standard deviations calculated from the mean of concentration differences resulting from AOP experiments were $\leq$20%.

OxiTop ready biodegradation results are shown in Fig. 5. To calculate the percentage biodegradation at the end of each test, the amount of oxygen taken up by the microbial population in the test suspension (corrected for uptake by blank control, run in parallel) is expressed as a percentage of the ThOD. A flask containing sodium acetate was used as a positive control in each experiment to check the activity of the inoculum (OECD 1993). In all experiments, sodium acetate was rapidly biodegraded, and

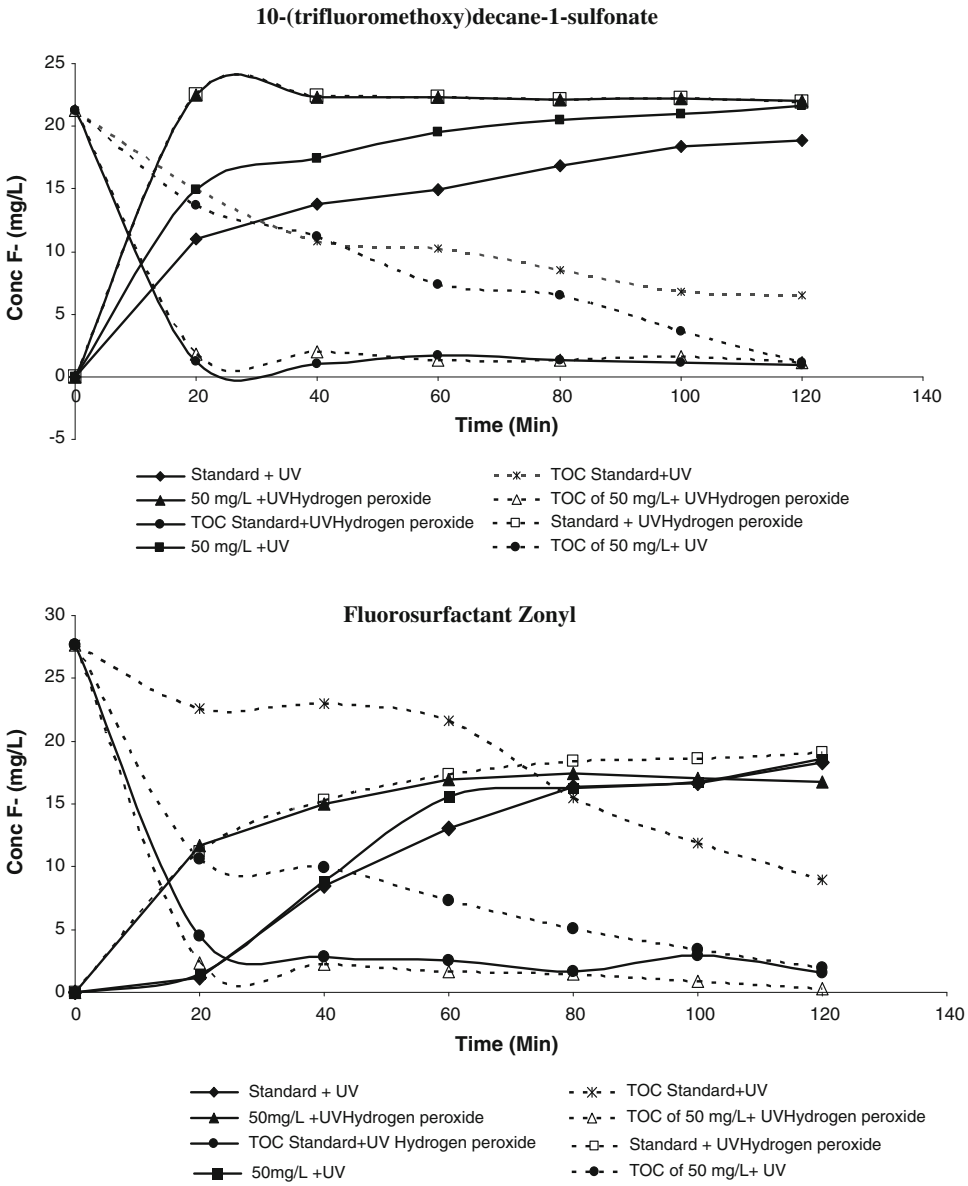

Fig. 4 Degradation of 10-(trifluoromethoxy)decane-1-sulfonate and the fluorosurfactant Zonyl at different concentrations when submitted to UV radiation and simultaneous UV/H_2O_2, by TOC analysis

within 28 days, the calculated BOD reached 70.4% of the ThOD as shown in Fig. 5. These results indicate that the microbial biomass used in OxiTop tests was viable and all tests were valid according to the OECD (1993) protocol. Ready biodegradation test of the fluoroaliphatic esters NOVEC FC-4430 and NOVEC FC-4432, the fluorosurfactant Zonyl, and 10-(trifluoromethoxy)decane-1 sulfonate using the OxiTop test showed incomplete biodegradability during the 10-day criterion. Results of OxiTop measurements show biodegradation of 25%, 28%, 13%, and 40%, respectively, for fluoroaliphatic ester NOVEC FC-4430, fluoroaliphatic ester NOVEC FC-4432, fluorosurfactant Zonyl, and 10-(trifluoromethoxy)decane-1 sulfonate within the experimental duration. Meanwhile, PFBS was observed to biodegrade <1% of the total biodegradation within the experimental duration of 40 days. Results obtained in the OxiTop test compared well to those obtained in the CBT.

For the CBT, biodegradation curves were plotted as a percentage of biodegradation and are expressed as a percentage of the ThOD versus time for each vessel. The mean value of replicates was calculated and average biodegradation curves were plotted (Fig. 6). No significant biodegradation of PFBS—less than 3% biodegradation—was observed. Figure 6 shows that the compounds fluorosurfactant Zonyl, fluoroaliphatic ester NOVEC FC-4430, and NOVEC FC-4432 present 47%, 22%, and 19% biodegradation, respectively, in the CBT. Hence, biodegradation was not completed in the 28-day test duration time. However, 10-(trifluoromethoxy)decane-1 sulfonate showed >80% biodegradation in the test period of 28 days, proving to be readily biodegradable when Rhine River water

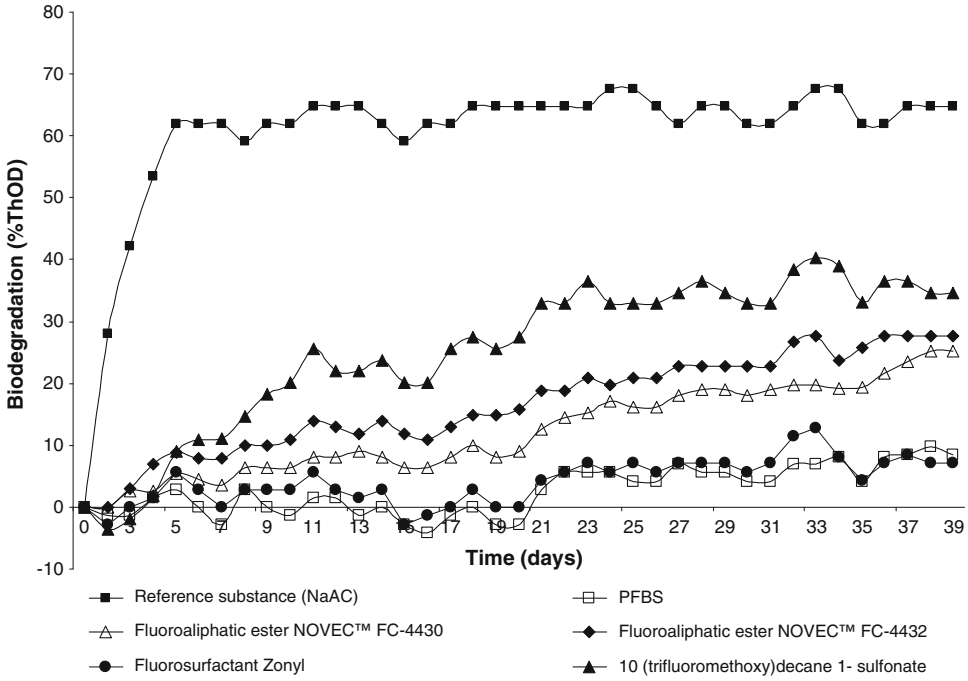

Fig. 5 OxiTop BOD values resulting from biodegradation test of studied surfactant compounds, using preconditioned activated sludge as inoculum

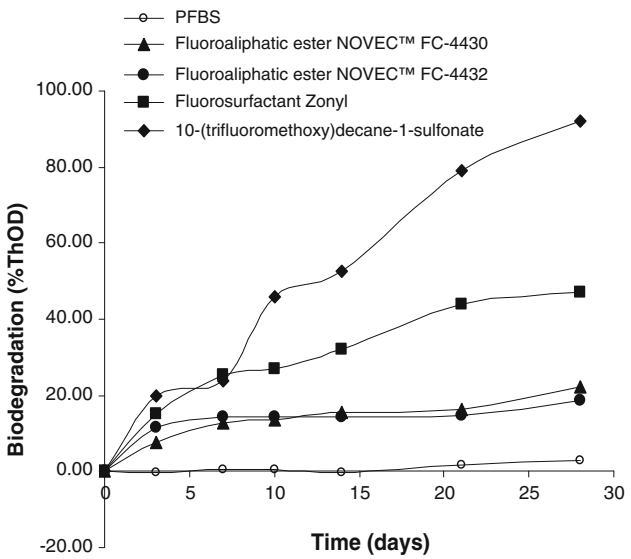

Fig. 6 Biodegradation values expressed as a percentage of the theoretical oxygen demand (ThOD) of studied surfactants compounds in the closed-bottle test, using Rhine River water as the inoculum

was used as the inoculum for bacterial culture. Biodegradation values for fluoroaliphatic esters NOVEC FC-4430 and NOVEC FC-4432 (22% and 19%, respectively) and PFBS (<3%) compared well to those obtained in the OxiTop test (25%, 28%, and <10,% respectively).

The FBBR test was performed for PFBS and 10-(trifluoromethoxy)decane-1 sulfonate. During the degradation test carried out with 10-(trifluoromethoxy)decane-1-sulfonate in an FBBR, primary degradation was already accomplished after 6 days. Primary degradation accompanied desulfonation and oxidation of the alkyl chain at different positions (Peschka et al. 2008a). In previous studies by Peschka et al. (2008a, b) on the prototype substance 10-(trifluoromethoxy)decane-1 sulfonate itself had shown biomineralization to fluoride by ubiquitous micro-organisms in which LC/MS/MS analysis gave an intense signal at RT = 27.7 min and exhibited two characteristic fragment ions (m/z = 85 and m/z = 219) next to its molecular ion $[M\text{-}H]^-$ with $m/z = 305$, where fragments were formed by the cleavage of the fluorinated methoxy group. 10-(Trifluoromethoxy)decane-1 sulfonate was found to meet the ≥60% biodegradability criteria in 28 days and can, therefore, be considered ultimately biodegradable. In the current study, an FBBR experiment was also conducted for PFBS in duplicate at a concentration of 100 mg L^{-1}. Samples were extracted by SPE using Oasis HLB cartridges and prepared for LC/MS/MS analysis. A blank experiment (same conditions without the test substance) was run in parallel. Throughout the experimental period of 28 days, weekly analyses were performed, but no significant difference (relative standard deviation ≤7%) in the areas of the PFBS peak was observed, indicating that the compound did not biodegrade under the experiment conditions.

Complete mineralization of fluorinated surfactants requires cleavage of the carbon–fluorine bond, which is very stable against physical and chemical attack. Based on the present results, only 10-(trifluoromethoxy)decane-1-sulfonate presented a biodegradability >80% in the CBT. Studies have also shown that fluorinated compounds with a fluoride content of the order of more than 50% will not

biodegrade over a period of 60 days (Remde and Debus 1996), which explains the fact that the fluorosurfactant Zonyl showed only 47% and 13% biodegradation in the CBT and OxiTop test, respectively. It is also reasonable to assume that the slow degradation of the tested compounds observed in these experiments is probably caused by the stability of the C–F bond, although there are examples of microbially catalyzed defluorination reactions (Parsons et al. 2008) and biochemical cleavage and release of fluoride (Alexy et al. 2004).

A substance attaining the 60% mineralization threshold level would be expected to undergo fast and virtually complete ultimate biodegradation in the aquatic environment (Commission of the European Communities 1994). Hence, surfactants failing to reach the 60% threshold pass level within the 28-day period would require additional evidence to prove their environmental safety. Further biodegradation studies should, therefore, be performed using FBBR for the fluoroaliphatic esters NOVEC FC-4430 and FC-4432 and the fluorosurfactant Zonyl in order to identify potential metabolites which could be generated from biodegradation of the compounds while elucidating the possible degradation pathway of the surfactants.

Conclusion

PFBS is not biodegradable. Micro-organisms are capable of degrading 10-(trifluoromethoxy)decane-1 sulfonate using the CBT. Moreover, biodegradation of most of the tested surfactants proved to be <60% within the 28-day period of the experiment using the CBT when Rhine River water was used as the inoculum for bacteria culture. The fluoroaliphatic esters NOVEC FC-4430 and NOVEC FC-4432 and fluorosurfactant Zonyl in both methods did not meet the criterion to satisfy ready biodegradation, however, they showed slow degradation throughout the test's duration. The low biodegradation of NOVEC products is probably due to the fact that they are based on PFBS; otherwise the presence of other fluorinated chemicals among the ingredients (unknown formula) could be the reason for the degree of degradation shown in our results. For PFBS, degradation due to UV and oxidation exposure method was not significant within 120 min. Other compounds showed increased degradation with time of exposure to UV radiation and even more accentuated degradation when it was applied alongside H_2O_2. Ready biodegradability tests of all substances using the OxiTop test showed incomplete biodegradability within the 10-day criterion for ready biodegradation, even when biodegradation continued to the 40-day mark, showing a very low biodegradation percentage. The biodegradability test carried out with 10-trifluoromethoxy)decane-1 sulfonate in an FBBR, primary degradation was already accomplished after 6 days, showing biomineralization to fluoride, while no biodegradation was observed for PFBS, under these test conditions.

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