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# An alternative treatment method for fluorosurfactant-containing wastewater by aerosol-mediated separation

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## ABSTRACT

The treatment of fluorosurfactant-containing wastewater is still challenging nowadays. Here, a method is presented to remove fluorosurfactants from water, amongst others from electroplating wastewater. This elimination technique is based on the generation of gas bubbles in solution, enrichment and scavenging of fluorosurfactants by transport of the gas bubbles to the water surface. Finally the bubbles collapse and release an aerosol which is enriched with fluorosurfactants. By sampling of the released aerosols a mass balance was established for 6:2 fluorotelomer sulfonic acid (6:2 FTSA). Thereby 99.8% of the initial amount was revocered in the collected aerosols. Fluorosurfactant concentration in solution decreased exponentially with half-lives ranging from 2 to 6 min for 6:2 FTSA as well as perfluorooctane carboxylate (PFOA) and perfluorooctane sulfonate (PFOS). Elimination rate in defined matrix (0.2 M $H_2SO_4$) within 60 min was 99.6, 99.9 and 99.8% for 6:2 FTSA, PFOA and PFOS, respectively. The removal rate of 6:2 FTSA increased in solutions with higher ionic strength. Different wastewater from an electroplating industry containing 6:2 FTSA was treated with the described method without any sample pre-treatment and elimination of 6:2 FTSA took place with the same effectiveness as in synthetic matrices.

## 1. Introduction

Poly- and perfluoroalkyl substances (PFAS) are widely distributed in the environment, as has been published extensively (Giesy and Kannan, 2001; Key et al., 1997; Moody and Field, 1999; Yamashita et al., 2005). Perfluorinated surfactants possess a high thermal and chemical stability (Kissa 2001) and are not biodegradable (Frömel and Knepper, 2010). Perfluorooctane sulfonate (PFOS) fulfils the criteria of a PBT-substance (persistent, bioaccumulative and toxic) and has been listed under Annex B of the Stockholm Convention on persistent organic pollutants (POP) in 2010 (OECD, 2002, Commission Regulation (EU) 2010).

In electroplating industries, surfactants are needed in Cr(VI)-containing electrolytes to reduce the discharge of toxic aerosols in the interest of health safety and to achieve wetting of the workpieces with electrolyte to ensure uniform chromium deposits. PFOS meets all the criteria of this application as it is stable under the acidic and oxygenic conditions in chromium electrolytes (Dams and Szameitat, 2009). Due to the harmful behaviour of PFOS in the environment, PFOS was substituted in Germany in the majority of electroplating factories by the polyfluorinated surfactant 6:2 fluorotelomer sulfonate (6:2 FTSA) (Wang et al., 2013). This development is enforced by public authorities.

In contrast to PFOS and PFOA, there is limited information regarding toxicology, distribution and fate of 6:2 FTSA in the environment so far. Biotransformation studied under aerobic conditions was found to be relatively slow with 63.7% of the initial amount remaining after 90 days (Wang et al., 2011). Perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA) were identified as stable degradation products, but amounted to only 7% of the initial 6:2 FTSA concentration. However, in closed-bottle-tests with municipal sewage sludge no biotransformation of 6:2 FTSA was observed (Saez et al., 2008). Concerning the enrichment of 6:2 FTSA in the environment, bioaccumulation of 6:2 FTSA in earthworms had been demonstrated (Norwegian Pollution Control Authority, 2008). As a consequence of firefighting 6:2 FTSA was also found in groundwater in the mg/l range (Schultz et al., 2006). So far there are no guideline values concerning 6:2 FTSA in industrial wastewater yet.

There are various treatment options for PFAS-containing wastewater. Because of their high chemical stability, perfluorinated surfactants resist even advanced oxidation processes

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(Schröder and Meesters, 2005). The polyfluorinated 6:2 FTSA was degraded by means of UV/$H_2O_2$ and $O_3$ at pH = 11, whereas no or only minor degradation was observed using UV, $H_2O_2$, $H_2O_2/Fe^{2+}$ or $O_3/H_2O_2$ (Yang et al., 2014). Nonetheless, experiments were performed under laboratory conditions without any matrix present.

To remove fluorinated surfactants from wastewater, sorption processes either with activated carbon or ion exchange materials are common (Rahman et al., 2014). Especially ion exchange methods are often used for treating fluorosurfactant-containing industrial wastewater. But the negative chromium species and sulphate present in high amounts compete for exchange sites and thereby lower the sorption capacity (Deng et al., 2010). However, the presence of chromium has a higher adverse impact on the sorption efficiency of 6:2 FTSA than of PFOS (Albers, 2011). Quantitative desorption of PFOS from the ion exchange materials cannot be accomplished by NaCl or NaOH solutions, so that the regeneration and recycling of the surfactants is hindered (Deng et al., 2010). Another drawback of sorption treatments is the disposal of PFAS-containing sorption-materials. High temperature incineration (>1200 °C) is needed to ensure that cleavage of all C–F bonds takes place and no volatile fluor-organic degradation products are formed. For reasons mentioned above, there is the need for alternative treatment options in electroplating industries, at best with the possibility to recycle the surfactants used.

In this paper, the removal of fluorosurfactants from water is based on the release of an aerosol which is enriched with surfactants. The enrichment of surfactants during aerosol formation has been published before for marine aerosols (Giovannelli et al., 1988). Further, Ahrens et al. assumed that fluorosurfactant emissions from sewage treatment plants might occur due to an aerosol mediated transport (Ahrens et al., 2011).

There are many parameters which influence the efficiency of surfactant transport with rising gas bubbles in solution as well as ejection of enriched aqueous phase during aerozolisation. Vecitis determined air-water interface partitioning constants for PFOS, PFHxS, PFBS and PFBA by concentration dependent surface tension measurements (Vecitis, 2009). Lemlich observed that increasing the water column and decreasing the inner diameter results in a higher separation value (Lemlich, 1968). By addition of $Na_2SO_4$ to the solution a higher separation could be achieved. In the work of Skop et al. a depletion of surfactants in the solution is described due to the release of aerosols. Further, surfactant transport was found to be higher when gas flow rate was increased (Skop et al., 1994). The concentration decrease followed an exponential function and can be described by the following equation, in which $C_t$ is the concentration after a duration of bubbling t, $C_0$ the initial concentration and γ the depletion rate constant, which is specific for the surfactant, gas flow rate as well as bubble size distribution (Skop et al., 1994).

$$C_t = C_0 \cdot e^{-\gamma \cdot t}$$

The depletion rate constant γ can be described by the following equation assuming a well-mixed solution as well as constant conditions (number of gas bubbles are constant) (Skop et al., 1994).

$$\gamma = Nw\frac{\pi d^2}{4}\beta(f)\eta K_\alpha$$

where:N: Number of bubbles per unit volume of water ($cm^{-3}$).w: bubble rise velocity (cm $s^{-1}$).d: diameter of a single bubble (cm).β(f): factor for correction of the differences of a single bubble from bubbles in a bubble plume.η: contact efficiency (the quantity of surfactant striking a bubble)/(quantity of surfactant passing the bubble).$K_\alpha$: adsorption coefficient.

## 2. Experimental

### 2.1. Materials, chemicals and solvents

All chemicals used were reagent grade or higher unless specified otherwise. 6:2 FTSA was purchased from ABCR GmbH & Co KG (Karlsruhe, Germany). K-PFOS, K-PFBS, $NH_4$-PFOA, perfluoroheptanoic acid (PFHpA) and perfluoropentanoic acid (PFPeA) were from Sigma–Aldrich GmbH (Steinheim, Germany). Perfluorobutanoic acid (PFBA) and perfluorohexanoic acid (PFHxA) were from Fluorochem Ltd. (Hadfield, Great Britain). HPLC grade methanol and ethyl acetate were purchased from VWR International (West Chester, PA, USA). Ammonium acetate was from Sigma Aldrich (St. Louis, MO, USA) and LC-MS ultragrade. Sulphuric acid was purchased from Carl Roth GmbH & Co KG (Karlsruhe, Germany) and nitric acid was from Merck KGaA (Darmstadt, Germany). Tetrabutylammonium bromide was from Ridel-de Haën AG (Seelze, Germany). Pure water (18.2 MΩ $cm^{-1}$ at 25 °C) was provided by a TKA GenPure module (Thermo Fisher Scientific, Niederelbert, Germany). Sodium chloride was purchased from Carl Roth GmbH & Co., (Karlsruhe, Germany) and sodium sulphate was from Merck KGaA (Darmstadt, Germany). Metal sheets (lead, brass) were from Phywe (Göttingen, Germany).

### 2.2. Analytical methods

Fluorosurfactants were analyzed by HPLC-ESI-MS/MS with a Waters 2695 Separation Module, Waters GmbH (Eschborn, Germany) and a Varian 320 MS triple quadrupole (Varian Inc., Darmstadt, Germany). Chromatographic separation was accomplished with a C18 monolithic column (100 × 3 mm, Phenomenex Inc., Torrance, USA) and 10 mM ammonium acetate in water (A) and methanol (B) as eluents. Samples were analyzed under isocratic conditions with 45% A and 55% B with a flow rate of 0.2 ml/min and injection volume of 20 μl.

Quantification was carried out in negative ESI-mode. Mass transitions for PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFOS and 6:2 FTSA were 213 → 169, 263 → 219, 313 → 269, 363 → 319 413 → 369, 299 → 80, 499 → 80 and 427 → 407. External calibration with 8 standards was arranged between 1 and 250 μg/l (coefficient of correlation $R^2 > 0.99$) and was based on integration of the mass transitions named above.

As sample pretreatment a liquid-liquid-extraction (LLE) was carried out to remove inorganic ions. LLE was accomplished with ethyl acetate containing 0.1 mM tetrabutylammonium bromide as ion pair reagent and 1% (v/v) water. Ethyl acetate was evaporated under nitrogen at 40 °C and the residue was resolved in water. Recovery of fluorosurfactants was determined by synthetic standards consisting of the corresponding matrix and was between 85 ± 9% (PFOS) and 117 ± 18% (6:2 FTSA).

Hexavalent chromium and total chromium in wastewater samples was determined by an accredited laboratory according to DIN 38405-24:1987-05 and DIN EN ISO 11885.

### 2.3. Electrolytic aerosol formation

Electrolysis experiments were performed in a beaker and under constant voltage of 6 V with a Laboratory Power Supply EA-PS 3032-10 B (EA Elektroautomatik, Viersen, Germany). Lead-anode and brass-cathode (metal sheets with dimensions of 75 × 7 × 1 mm) were arranged with a fixed distance of 1.5 cm. Sulphuric acid (0.2 M) was used as an electrolyte and the solution was continuously stirred with a glass-coated magnetic stirrer to prevent contamination and adsorption effects.