
Optimization of experimental conditions of PFOA defluorination using DMSO/NaOH mixture

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ABSTRACT

Per- and polyfluoroalkyl substances, PFAS, are a large group of around 5,000 synthetic chemical compounds widely used in industrial and consumer applications since the 1950s, most usually where extremely low surface energy or surface tension and/or durable water- and oil-repellency is needed. Their persistent nature results in diffuse pollution issues in the environment and adverse health effects.

Trang et al.¹ investigated low-temperature thermal treatment (80-120°C) of perfluorooctanoic acid, PFOA (36 g/L), using a mixture of dimethyl sulfoxide, DMSO (145/1 DMSO/PFOA molar ratio), sodium hydroxide, NaOH (30/1 NaOH/PFOA molar ratio) and milliQ water (8/1 DMSO/water volume ratio). Based on density functional theory calculations and by-products analyses, the authors proposed PFOA degradation mechanism during which the joint action of temperature, aprotic, polar and nucleophile solvent results in fluoride ions, F⁻ (90% vs total F provided by PFOA in 24 hours), carbonate, formate, oxalate, glycolate, tartronate and trifluoroacetic acid CF₃COOH (TFA). We pursued the optimization of the degradation process with the ultimate goal of proposing a practical solution for addressing PFOA environmental contamination and its supposed main degradation by-product, TFA.

PFOA doping concentration (C₀ = 893 mg/L) was selected to decrease the dilution factor to analyse PFOA and its by-products at the µg/L level, while keeping optimum conditions for measuring fluoride by potentiometric titration, at the mg/L level, in the range from 20 mg/L to 20 µg/L. The degradation kinetics of PFOA was investigated over a period of six days at 90, 120, and 140°C. The influence of the DMSO/water volume ratio as well as the NaOH/PFOA molar ratio on the treatment efficiency was studied to minimize DMSO volume while optimizing PFOA and by-products degradation.

PFOA defluorination process was verified by Ultra-high-Pressure Liquid Chromatograph coupled with Mass Spectrometer (UPLC-MS), potentiometric titration and SEM-EDS. UPLC-MS analysis was used to quantify PFOA, perfluoroheptanoic acid (PFHPa), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA) and qualify 325 m/z, 275 m/z, 229 m/z, 225 m/z and 114 m/z (TFA) by-products. Fluoride selective electrode was used for F⁻ analysis. SEM-EDS allowed us to characterize NaF on dried surface of a PFOA/DMSO/NaOH mixture (20 µL) after interaction.

The removal reaction follows a first order kinetics that reached 95% at 90°C, after six days. The complete abatement was observed only after six hours at 120°C and one hour at 140°C. Experiments conducted at 120°C highlighted the necessity of maintaining at least twice larger the DMSO/H₂O volume and twenty to one higher the NaOH/PFOA mole ratio to ensure effective PFOA defluorination while minimizing by-products. PFHPa, PFHxA, PFPeA fell below the limit of quantification after 30 minutes; PFBA after 12 hours, while peaks surfaces of 325 m/z, 275 m/z, 229 m/z, 225 m/z and 114 m/z (TFA) by-products were declining versus time without reaching zero after six days. In the same time, the F⁻ content reached its maximum (≤ 80% vs total F provided by PFOA) after 18 hours. This 80 % maximum is not exceeded even at 140°C. These results tend to demonstrate that TFA is not the only persistent degradation by-product that accumulates. The identification and quantification of unusual by-products are under investigation.

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References:

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