Task ID: 425.013

Task Title: Non-PFOS Photoacid Generators: Environmentally Friendly Candidates for Next Generation Lithography

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Deliverable: Report on the completion of testing to determine the removal of PFOS-free photoacid generators by biological and physico-chemical treatment methods.

Summary Abstract:
Perfluorooctyl sulfonate (PFOS) and related long-chain perfluorinated compounds (PFAS) are under increased scrutiny as priority environmental contaminants due to recent reports of their detection in environmental and biological matrices as well as concerns regarding their persistence and toxicity. Nevertheless, PFOS and other long chain perfluorinated materials are vital to many industrial processes, including semiconductor manufacturing where they are utilized in photoacid generators (PAGs), anti-reflective coating (ARCs) and certain surfactants.

This project aims to develop new PFOS-free (and PFAS-free) PAGs and investigate the environmental behavior of these PFOS-free alternatives. Our strategy is to create PAGs that have acidity equivalent to that of PFOS based materials by incorporating short (1, 2 or 3) CF_2 units next to the sulfonic acid. Our hypothesis is that these materials are environmentally friendly because the additional functions on the PAG lack fluorination.

The objective of this task is to investigate the treatability of new PFOS-free PGAs developed by the Ober Lab using conventional physico-chemical and biological methods. Treatment of PAGs is not only a prerequisite for discharge but will also be required for the reuse of water. The physico-chemical treatment methods considered in this study included activated carbon adsorption, chemical reduction with zero-valent iron, and advanced oxidation (Fenton reaction). The biological treatment methods investigated included: aerobic degradation by activated sludge, anaerobic degradation by anaerobically digested sludge, and cooxidation potential under aerobic heterotrophic conditions. Biodegradation of the PAGs by cometabolism and their utilization as sole carbon source was evaluated in laboratory assays simulating the conditions prevailing in biological wastewater treatment plants.

The results obtained indicate that functional groups such as lactones improve the environmental compatibility, particularly the biodegradation potential, of the non-PFOS PAGs. The rapid degradation observed for the lactone PAG under aerobic and anaerobic conditions suggests that the compound would be readily removed during municipal wastewater treatment.

Method of Approach

Activated carbon adsorption. Adsorption isotherms for the various PAGs have been determined on granular activated carbon (GAC, Filtrasorb 400, Calgon Corp.). The isotherms were measured at 30°C in 160 ml flasks supplied with GAC (0.1 g) and 100 ml

of pH-7.2 phosphate buffer (3 mM) spiked with the PAG compound (0.052 to 0.78 mM of SF1; 0.037 to 0.56 mM of SF2; 0.037 to 0.55 mM of PF1; 0.025 to 0.38 mM of lactone PAG). The samples were equilibrated for 24 h in an orbital shaker and solution concentrations of the different PAGs were determined by high performance liquid chromatography (HPLC) with ultraviolet absorption detection or suppressed conductivity detection. Both, the Freundlich and Langmuir isotherm models were used to fit the experimental data. The Freundlich model describes the adsorbed concentration (C_s, mg PAG/mg sorbent) as a function of the aqueous concentration (C_E, mg/L), the Freundlich capacity coefficient (K_F), and the exponent (n), is given by:

$$C_s = K_F C_E^{1/n}$$

The expression for the Langmuir model is given by:

$$C_S = \frac{abC_E}{1 + bC_E}$$

Where *a, b* are the Langmuir parameters.

Reduction with zero-valent iron. The susceptibility of the different PAGs to reductive degradation by zero-valent iron (ZVI, -325 mesh, 97% purity. Sigma Aldrich) was determined in 160-ml serum flasks containing 40 ml of a pH-6.5 phosphate buffer (100 mM) spiked with the PAG compound (1 mM). Flasks was amended with 1 g ZVI, flushed with H_2/CO_2 gas (80/20), and then incubated in an orbital shaker for 2 d at 30°C. Controls lacking ZVI were run in parallel. Liquid samples were withdrawn periodically and the degradation of the PAG compounds was monitored by HPLC. Fluoride release was determined using an ion selective electrode.

Oxidation using the Fenton's reaction. Oxidative degradation of PAGs by the Fenton's reagent was evaluated in 160-ml serum flasks supplied with 50 ml of a solution containing ferrous sulfate (10 mM, pH 3-4) and spiked with the PAG compound (1 mM). Flasks were sealed with rubber butyl septa and aluminum caps, subsequently, 0.5 ml of H_2O_2 (30% wt) were added at 1 h intervals for 4 h. Controls lacking ferrous sulfate or peroxide were run in parallel. Flasks were incubated at 30°C and sampled periodically for PAG and fluoride concentrations. The reaction was stopped immediately after sampling by addition of 50 ml of a phosphate buffer (100 mM, pH 7.5).

Microbial degradation: Experiments were set up to evaluate the susceptibility of the various PAG compounds to microbial degradation. Biodegradation was investigated under different redox conditions, namely, aerobic degradation as sole carbon source, aerobic cometabolism, and anaerobic reductive dehalogenation. Test solutions containing the various PAG compounds were supplied at a concentration of 1 mM. Control assays (e.g. abiotic treatments; killed-cell controls) were run in parallel to account for the loss of the compounds by mechanisms other than degradation. Methane was utilized as cosubstrate in assays evaluating aerobic cometabolic degradation. To promote reductive dehalogenation, hydrogen gas (H_2) was supplied as the electron donor. Fluoride

concentration using an ion selective electrode and analysis of fluorinated compounds by HPLC were performed periodically to determine if the PAGs were susceptible to microbial attack.

Figure 1 shows the chemical structure of the ionic PAG compounds evaluated in this study.

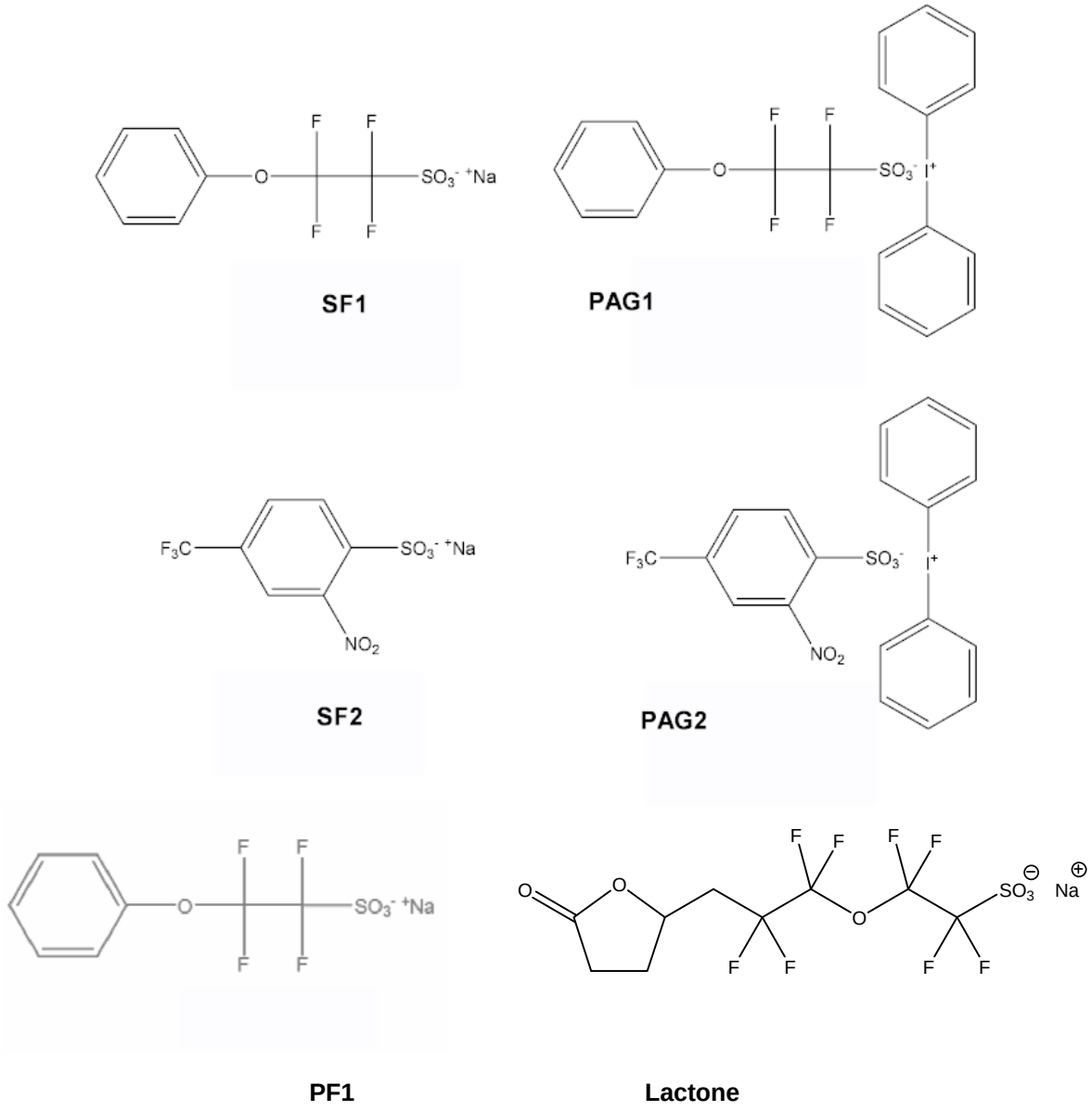

Figure 1*. Chemical structures of the ionic non-PFOS PAGs and their corresponding sodium sulfonates evaluated in this study.*

Technical Results and Data:

Activated carbon adsorption: The adsorption of the various PAGs from aqueous solutions onto granular activated carbon was demonstrated. The results obtained were adjusted to Langmuir and Freundlich models (Table 1). The fitting parameters are compared with those obtained for PFOS and PFBS using the same activated carbon. The Langmuir model usually gave the best fit for all the isotherms. In general, activated carbon provided a moderate to low adsorptive capacity for these compounds. Among the various non-PFOS PAGs, SF2 showed the highest affinity for activated carbon as shown in Figure 2.

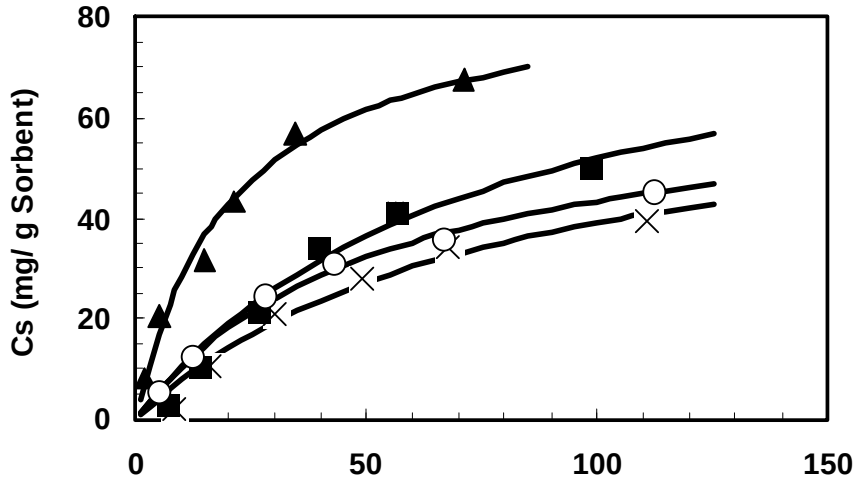

Figure 2. *Comparison of non-PFOS PAG adsorption on activated carbon at 30°C in pH 7.2 phosphate buffer (3 mM). PAGs: (▲) SF2; (○) lactone; (■) PF1; (X) SF1. Continuous lines show the fitting of the isotherm data to the Langmuir model.*

Table 1. Freundlich and Langmuir isotherm parameters for the adsorption of the novel PAG compounds by granular activated carbon.

	Freundlich			Langmuir		
	K_F	n	r^2	a	b	r^2
SF1	1.82	1.47	0.945	68.9	0.013	0.946
SF2	6.32	1.68	0.958	87.1	0.048	0.983
PF1	1.45	1.24	0.945	90.7	0.013	0.917
Lactone	2.03	1.44	0.965	66.8	0.019	0.993
PFOS	60.9	3.46	0.969	236.4	0.124	0.959
PFBS	9.3	2.16	0.959	98.7	0.034	0.985

Reduction by zero-valent iron: Treatment of the non-PFOS PAGs compounds SF1, SF2 and PF1 with ZVI at ambient conditions of temperature and pressure revealed that only the compound SF2 was susceptible to reductive attack. None of the other tested compounds were degraded by ZVI even after 2 d. Similarly, PFOS and PFBS were also resistant to reductive degradation by ZVI. HPLC data showed that SF2 was complete degraded to an initially unidentified product (Fig. 3). Mass spectrometry analysis confirmed that degradation of SF2 involved reduction of the nitro-aromatic compound to the respective amino compound, which did not undergo further transformation. In agreement with these results, low fluoride release was detected (ca. 2.1%).

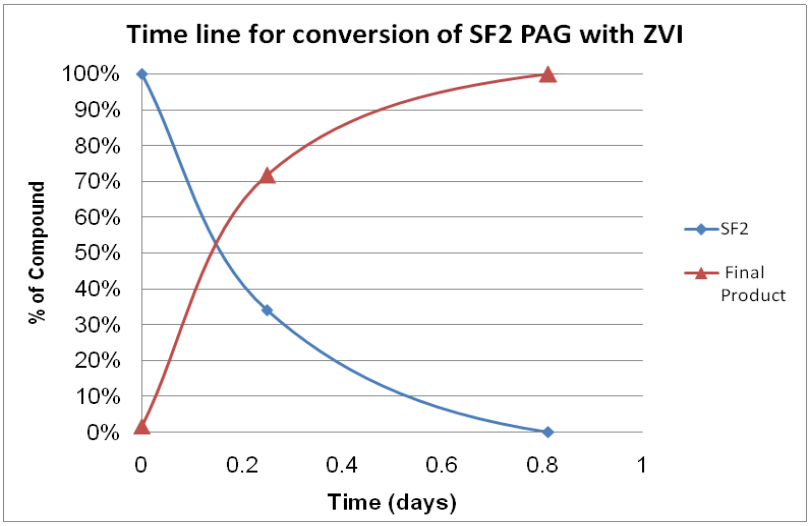

Figure 3. *Dissapearence of SF2 (blue line) and formation of a degradation product (red line) following treatment of the PAG compound with ZVI as a function of time.*

Oxidation by the Fenton's reagent

Experiments to test the susceptibility of the PAGs to oxidative degradation by the Fenton's reagent (H_2O_2/Fe(II)) are currently in progress.

Removal by biological treatment methods

Two of the PAGs studied underwent microbial transformation. The lactone PAG was the compound most susceptible to biodegradation, and complete removal of this chemical was observed after only 5-15 d of incubation under different redox conditions, namely, aerobic degradation as sole carbon source, aerobic cometabolism, and anaerobic reductive dehalogenation (Table 2). Fluoride release was also observed in the aerobic assays (approx 5% after 15 d).

Figure 4 illustrates the rapid disappearance of the lactone PAG in the anaerobic bioassay. The PAG was not removed in the abiotic controls indicating that the disappearance of the compound is biologically mediated. The rapid degradation observed for the lactone PAG under aerobic and anaerobic conditions suggests that the compound would be readily removed during municipal wastewater treatment. Mass spectroscopy studies are currently in progress to identify the biotransformation products formed.

SF2 was also completed degraded under anaerobic conditions after less than 2 wks of incubation (Table 2). Conversion of SF2 coincided with the formation of an

unidentified compound, most likely the corresponding amino compound. Aromatic nitro groups have been reported earlier to undergo microbial reduction in anaerobic environments with formation of the amino compound. In contrast with the lactone PAG, SF2 was not degraded in the aerobic assays. SF1 and PF1 were not degraded under any of the conditions investigated even after extended periods of incubation (> 365 d, Table 2).

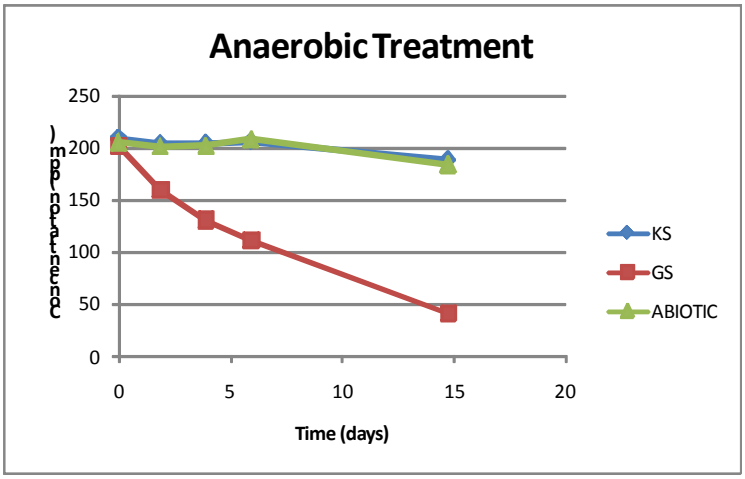

Figure 4. *Time course of degradation for the lactone PAG in anaerobic batch bioassays. (KS) Abiotic control with killed-sludge; (GS) complete treatment with active sludge; (ABIOTIC) sterile, non-inoculated control.*

Table 2. Percent PAG removed (based on initial concentration) by biological treatment.

PAG	Initial conc (mg/l)	Aerobic Treatment		Anaerobic Treatment
		Solely Carbon / Energy Source	Methane Cooxidation	Hydrogen as Electron Donor
SF1	100	1.9 ± 0.7%	-2.3 ± 1.3%	3.5 ± 2.7%
SF2	100	5.2 ± 0.1%	2.5 ± 2.6%	100.0 ± 0.0%[#]
PF1	100	4.4 ± 0.1%	2.7 ± 1.6%	1.3 ± 6.6%
Lactone	200	100± 0 %[$]	100 ± 0%[$]	80 ± 1.2%*

[#] Determined after 2 wks; [$] after 5 d; [*] after 15 d.

Future Work:

Investigation of the biotransformation of the lactone PAG will be continued in order to identify the main degradation intermediates and determine if the compound is completely mineralized under aerobic or anaerobic conditions. The susceptibility of the various compounds to chemical oxidative degradation by the Fenton reaction will also be assessed. In addition, the treatability of additional PAGs sent by Dr Ober's group in the course of this year will be evaluated using the approach described.