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Environmental Solutions

Destruction of Perflourooctane Sulfonate (PFOS) and Perflourooctanoic Acid (PFOS) Using Activated Persulfate

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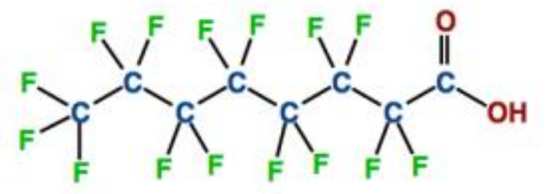
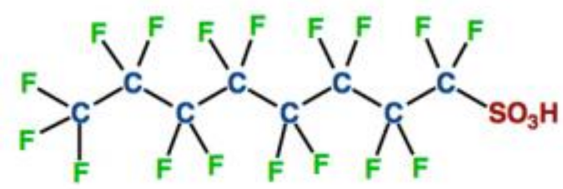
Outline

- Activated Persulfate
  - Overview
  - Activation Methods
- Perflourooctanoic Acid (PFOA)
- Perflourooctaine Sulfonate (PFOS)
- Conclusions



PFOA - perfluorooctanoic acid



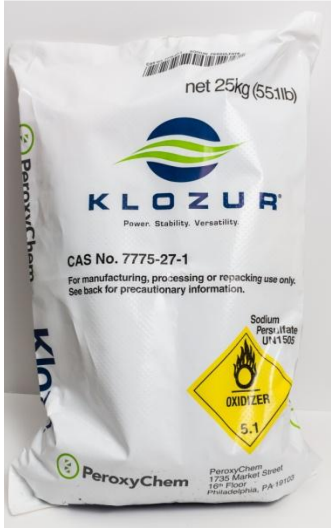
PFOS - perfluorooctanesulfonic acid

Activated Persulfate

Introduction to Activated Persulfate

Klozur® Persulfate is:

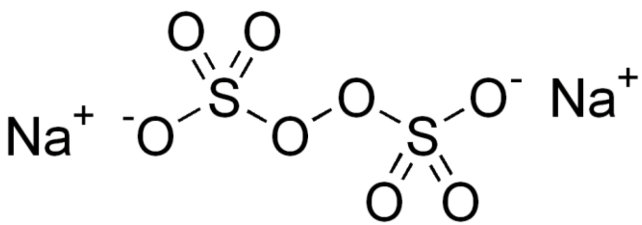
- Based on the sodium persulfate molecule
- A strong oxidant used for the destruction of contaminants in soil and groundwater
- Aggressive and fast acting chemistry with extended subsurface lifetime (weeks to months) and little to no heat or gas evolution
- Applicable across a broad range of organic contaminants
- Highly soluble in water (significant oxidant mass in smaller volumes)



Field solubility of more than 500 g/L possible

Fundamental Chemistry

- Klozur® Activated Persulfate is based upon the persulfate anion:



- Persulfate is a peroxygen, and similar to hydrogen peroxide, can be split at the O-O bond thus forming the sulfate radical:

$$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \rightarrow {}^{-}O_3S\text{-}O\bullet \quad \bullet O\text{-}SO_3^{-}$$

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Fundamental Chemistry

Common activation methods include:

- Alkaline activation
  - (OH•, SO4•-, O2•-)
- Iron or iron chelate activation
  - (SO4•-)
- Heat activation
  - (Temperature dependent: OH•, SO4•-, O2•-)
- Hydrogen peroxide activation
  - (OH•, SO4•-, O2•-)

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical (OH•)	2.59	Siegrist et al.
Sulfate radical ($SO_4•^-$)	2.43	Siegrist et al.
Ozone	2.07	Siegrist et al.
Persulfate anion	2.01	Siegrist et al.
Hydrogen Peroxide	1.78	Siegrist et al.
Permanganate	1.68	Siegrist et al.
Chlorine (HOCl)	1.48	CRC (76th Ed)
Oxygen	1.23	CRC (76th Ed)
Oxygen	0.82	Eweis (1998)
Fe (III) reduction	0.77	CRC (76th Ed)
Nitrate reduction	0.36	Eweis (1998)
Sulfate reduction	-0.22	Eweis (1998)
Superoxide ($O_2•^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

PFOA

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PFOA: Key Characteristics

- Strong acid (pKa -0.5)
  - Other reports of pKa of 2.8 and 3.8
- Solubility
  - Anion-highly soluble (500-9,500 mg/L)
  - Neutral form- low solubility (0.025 mg/L)
- Unlikely to volatilize
- Moderate K_{oc}
- Half Life
  - Likely to persist in groundwater if left untreated

Key Characteristics of PFOA	
CAS Number	335-67-1
Physical Description (Typical Room Conditions)	White powder/waxy white solid
Molecular Weight (g/mol)	414
Water Solubility (mg/L @ 25°C)	9,500
pKa [Goss (2008) ES&T]	-0.5
Boiling Point (°C)	188
Vapor Pressure (mm Hg at 20 °C)	0.017
Koc	115
Half Life	
Atmospheric (years)	0.25
Water (years @ 25°C)	>92
Source: EPA May 2012	

Treatment of PFOA

Showed that PFOA can be degraded by the sulfate radical (SO4•-)

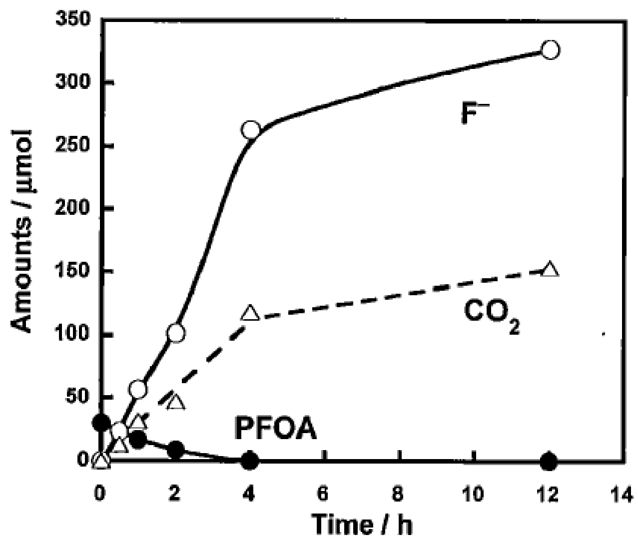
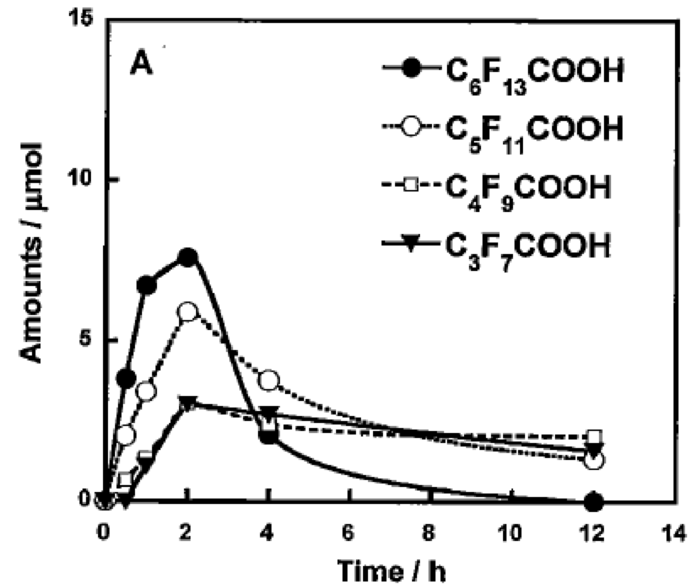


FIGURE 2. Irradiation-time dependence of PFOA decomposition with $S_2O_8^{2-}$: detected molar amounts of PFOA, CO_2, and F^-. An aqueous solution (22 mL) containing $S_2O_8^{2-}$ (1.10 mmol; 50.0 mM) and PFOA (29.6 μmol; 1.35 mM) was irradiated with a xenon–mercury lamp under oxygen (0.48 MPa).



Horiet al (2005) *Environ Sci & Tech*

Heat Activated Persulfate

Yee et al (2012) Chemical Engineering Journal

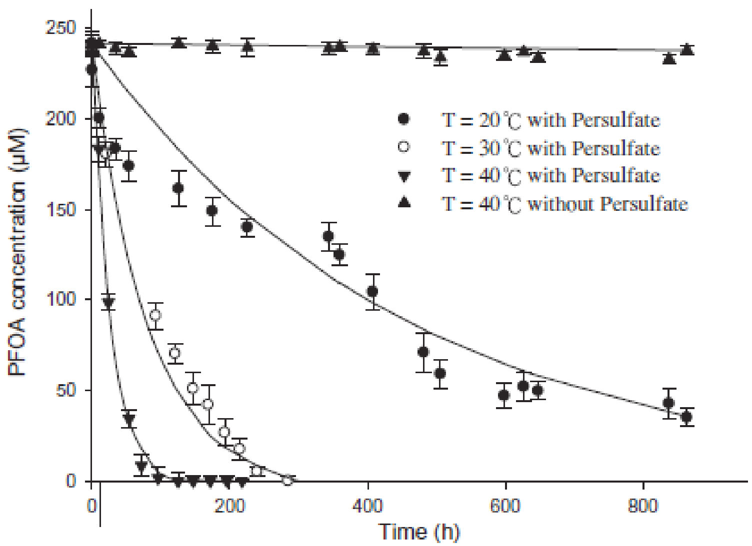


Fig. 1. Effects of temperature on PFOA degradation ($[PFOA]_0 = 241.5$ µM; $[persulfate]_0 = 200$ mM; initial pH = 2.5). The control experiment of PFOA degradation without persulfate at initial pH 2.5 and 40 °C.

Other Articles:

- Hori et al (2008) Environ. Sci. & Technol.
- Medina (2014) EPA 542-N-14-002 No 66

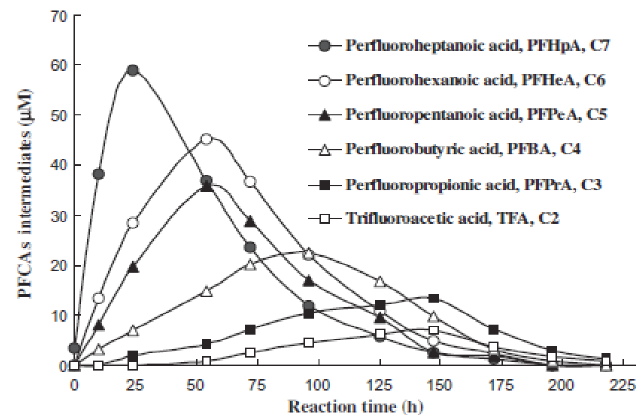


Fig. 3. Concentrations of PFCAs intermediates formed at various reaction times by degradation of PFOA (241.5 µM) with 200 mM persulfate (initial pH = 2.5, $T = 40$ °C).

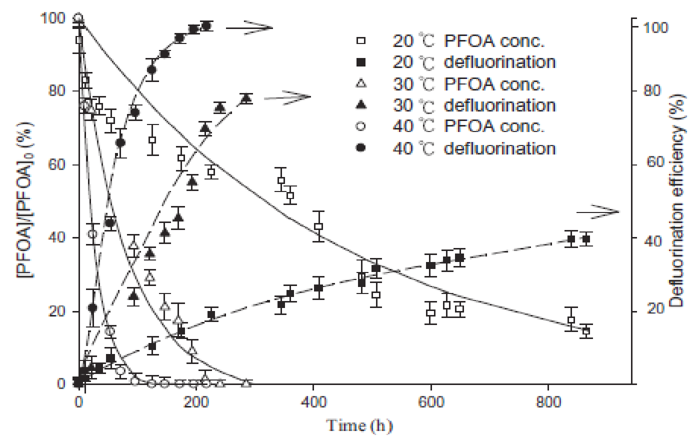


Fig. 2. Decomposition and defluorination efficiencies of PFOA ($[PFOA]_0 = 241.5$ µM; $[persulfate]_0 = 200$ mM; initial pH = 2.5; $T = 20$, 30 and 40 °C). Solid lines are for the ratios of [PFOA]/[PFOA]0 and dash lines are for the defluorination efficiencies of PFOA.

Nucleophilic Pathway

- Destruction of PFOA in catalyzed hydrogen peroxide system
- Authors concluded that this was accomplished by nucleophiles hydroperoxide (HO_2^-) and superoxide ($O_2^{-}\bullet$)
- Superoxide and hydroperoxide can also be formed in activated persulfate systems

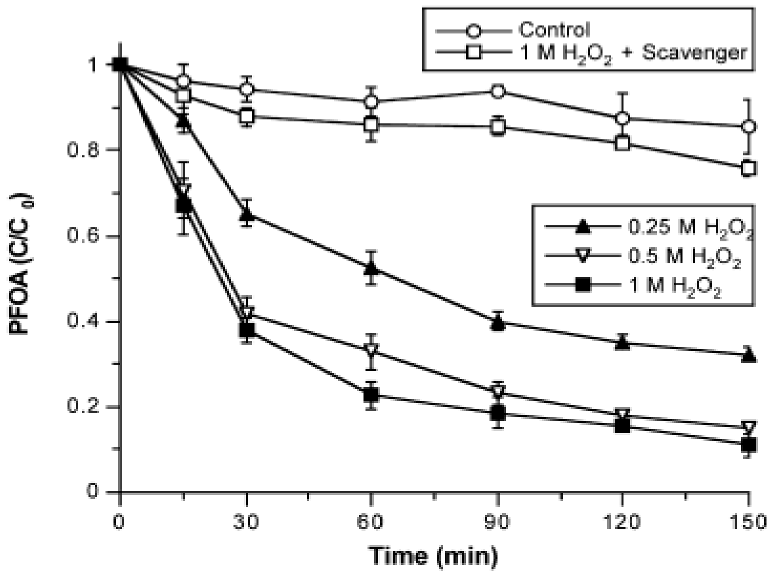


Figure 1. Degradation of PFOA in CHP systems [100 μg/L PFOA, 0.5 mM iron(III), 0 M (control), 0.25 M, 0.5 M, or 1 M hydrogen peroxide at pH 3.5, 0 or 1 M 2-propanol, total volume of 40 mL, 20 ± 2 °C].

Mitchell et al (2014) *Environ. Sci. & Tech. Lett.*

PFOS

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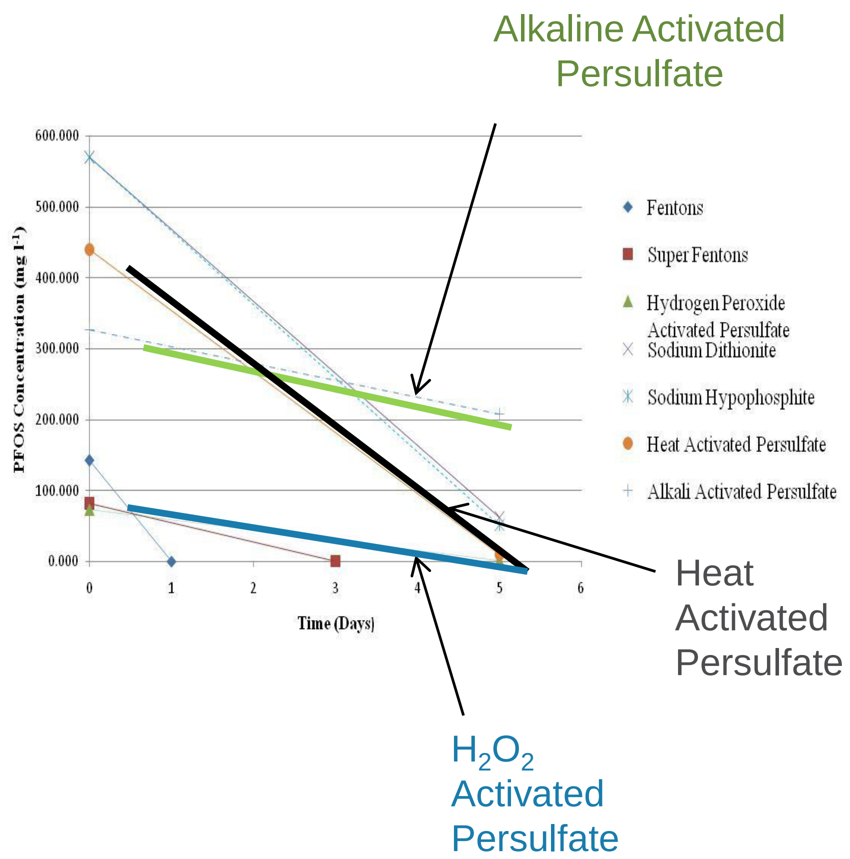
Key Characteristics of PFOS

- Moderate solubility
  - Decreases depending upon solute
- Unlikely to volatilize
- Moderate K_{oc}
- Half Life
  - Likely to persist in groundwater if left untreated

Key Characteristics of PFOS	
CAS Number	2795-39-3
Physical Description (Typical Room Conditions)	White powder
Molecular Weight (g/mol)	538 (potassium salt)
Water Solubility (mg/L @ 25°C)	
Purified Water	570
Freshwater	370
Filtered Seawater	25
Vapor Pressure (mm Hg at 20 °C)	0.00000248
Koc	372
Half Life	
Atmospheric (years)	0.31
Water (years @ 25°C)	>41
Source: EPA May 2012	

Treatment of PFOS

Data shows treatment of PFOS by alkaline, heat and hydrogen peroxide activation of persulfate



Kingshott (2008) Imperial College London

Treatment of PFOS

- Persulfate activated with UV, Heat, Fe (II), and Ultrasonic
- Lower pH more effective

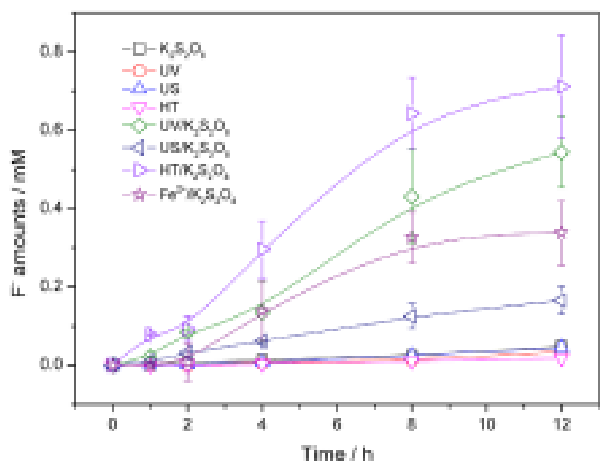


Figure 3. Time course of PFOS defluorination in activated $K_2S_2O_8$ oxidation systems.

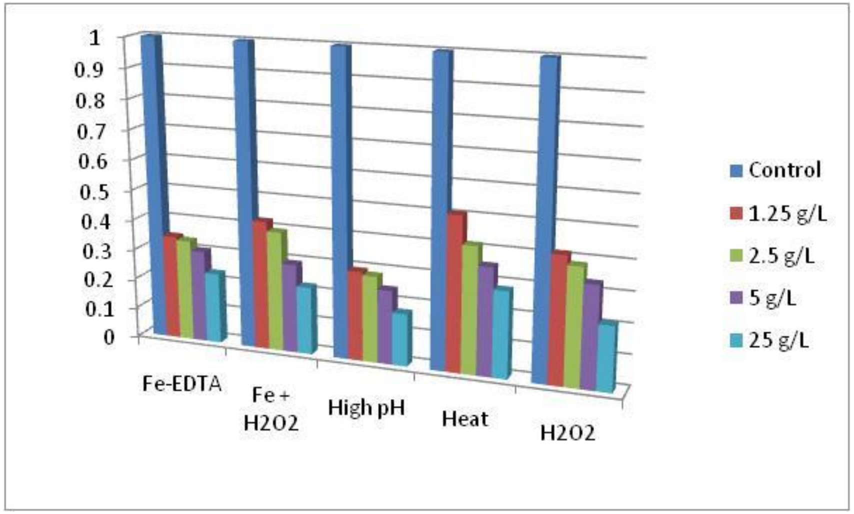
Table 2. The calculated pseudo-first-order constants and defluorination efficiency (%) of PFOS with 18.5 mM persulfate in activated $K_2S_2O_8$ oxidation systems at different initial pH values.

system	Initial pH	Rate constant (per hour)	Reaction time (h)			
			1	4	8	12
$UV/K_2S_2O_8$	3.13	0.018	0.94	5.57	15.91	19.32
	6.91	0.016	0.70	4.27	13.63	17.21
	11.11	0.009	-	3.23	6.89	10.56
$US/K_2S_2O_8$	3.11	0.005	-	2.47	4.90	5.82
	7.04	0.004	0.25	1.93	3.95	5.22
	10.92	0.003	-	0.98	3.10	3.51
$HT/K_2S_2O_8$	3.11	0.025	2.18	10.56	19.96	25.71
	6.94	0.023	2.47	9.35	20.33	22.52
	10.95	0.013	0.16	4.87	10.15	15.24
$Fe^{2+}/K_2S_2O_8$	3.11	0.013	0.44	4.93	12.57	13.88
	7.12	0.010	-	4.36	10.31	10.68
	11.24	0.005	-	1.77	4.02	6.07

Yang et al (2013) PLoS ONE

21 Day Study

- Bench scale jar test:
  - Data showed 49 to 83 percent reduction in PFOS concentration
  - Treatment increased with increasing persulfate concentration
  - Each activator effective
  - Minimal evolution of fluoride



Conclusions

- PFOA and PFOS have complex aqueous chemistry

- PFOA can be degraded by sulfate radical, hydroperoxide and superoxide radical formed by activated persulfate

- Treatment of PFOS by activated persulfate has been observed
    - Reactive species not yet identified

- Typical pathway with persulfate, academic studies with heat activation followed by field implementation including other activation methods

Questions

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