# Desulfonation of Perfluoroalkyl Sulfonate Enabled by Iron Photocatalysis

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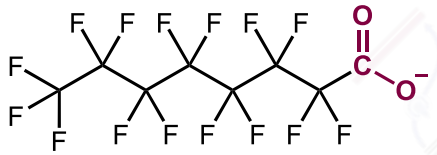
20230506 || Zuo Group

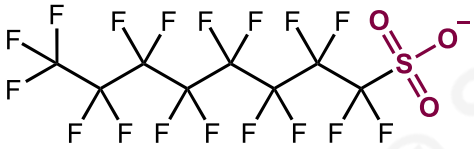
# Per- and Polyfluoroalkyl Substances (PFASs)

## Per- and polyfluoroalkyl substances in industry



PFOA

- Oilophilic tail
- Hydrophilic head



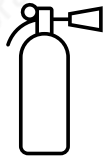
PFOS

- Chemical and thermal stability
- Both hydrophilic and oilophilic

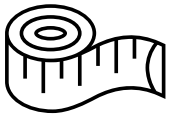
- >200 use areas

Food

Mining



Fire-fighting



Textile

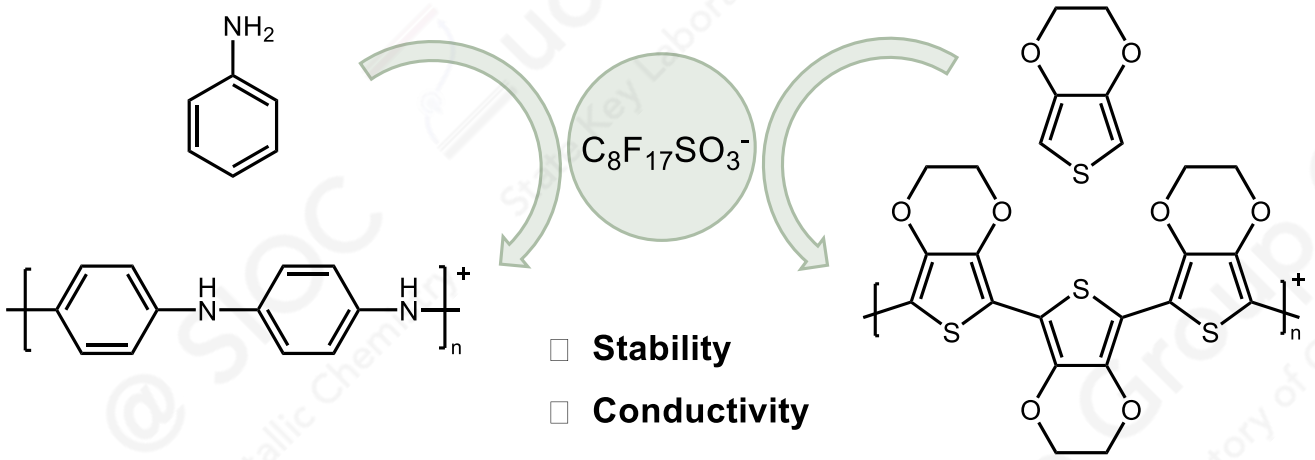
PFOA ⇒

PFOS ⇒

# Polyfluorooctane Sulfonate (PFOS)

## Polyfluorooctane sulfonate in organic chemistry

### Improve polymer properties

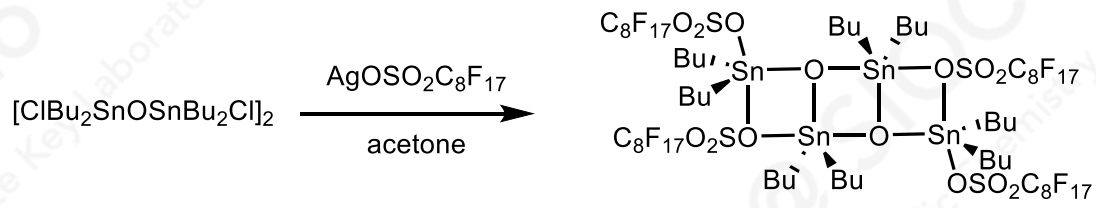



- Stability
- Conductivity

Fujii, S. et al. *Polymer.* **2018**, *148*, 217-227.

Fujii, S. et al. *Polymer Journal* **2019**, *51*, 761-770.

### Improve Lewis acid stability



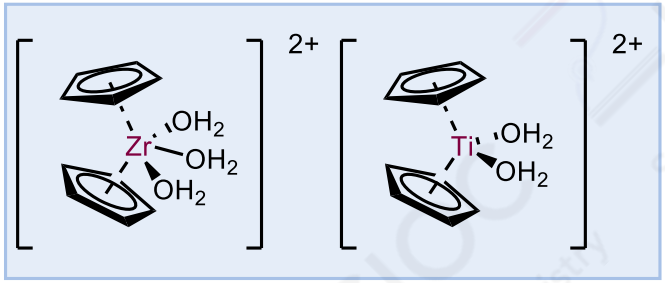

- Strong Lewis acid
- $C_8F_{17}SO_3^-$ *vs* $CF_3SO_3^-$
- Tolerance toward hydrolysis

Otera, J. et al. *Organometallics* **2005**, *24* , 2567-2569.

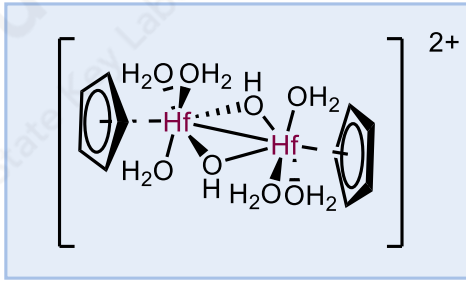
# Polyfluorooctane Sulfonate (PFOS)

## Polyfluorooctane sulfonate in organic chemistry

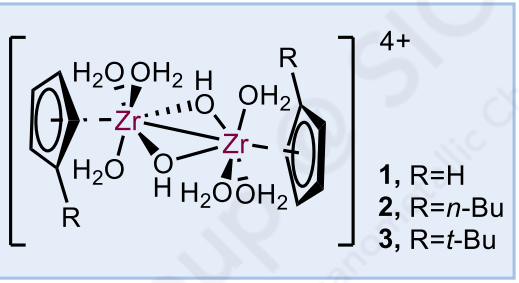
**Stable complex with $C_8F_{17}SO_3^-$ and THF**



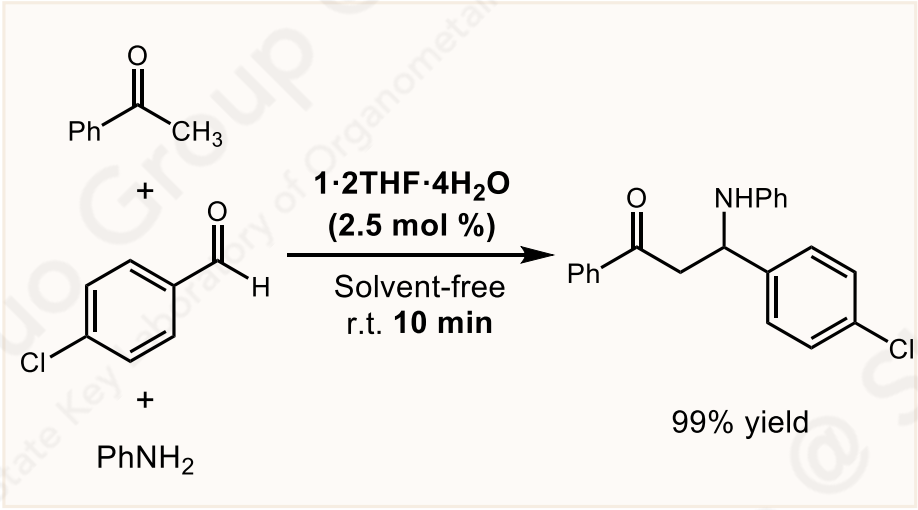

Junzo Otera **(2009)**

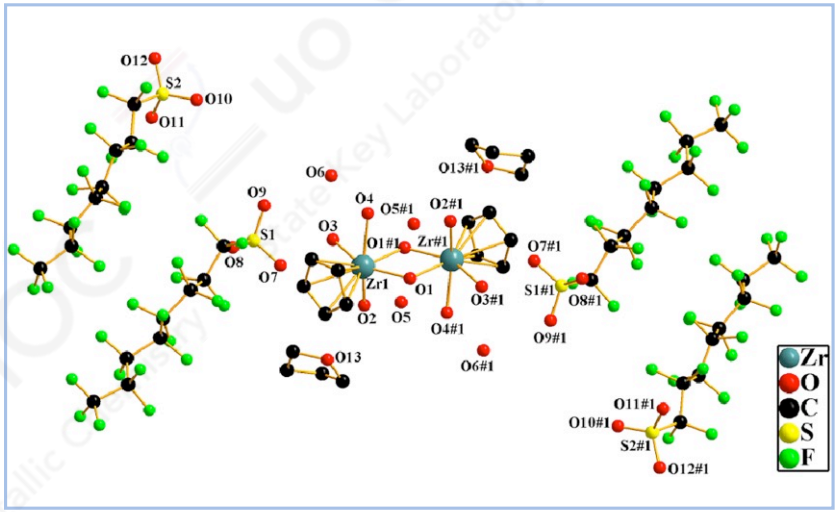



Shuangfeng Yin (**2009**)




Zilong Tang (**2018**)




Crystal structure of **1·2THF·4H2O**

- **Strong Lewis acid & highly catalytic activity**
- **Water tolerance**
- **Air & thermal stability**
- **Good recyclability**

Tang, Z. et al. *Tetrahedron* **2018**, *74*, 1926-1932.

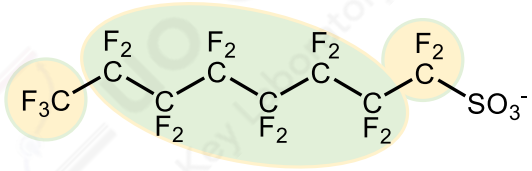
# Polyfluorooctane Sulfonate (PFOS)

## Environmental problems caused by polyfluorooctane sulfonate

United Nations

Stockholm Convention

~~PFOS~~ (2018)



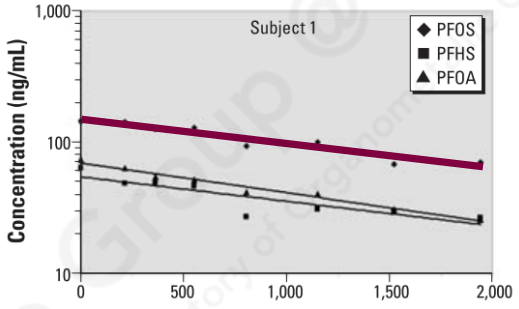

C — F BDE:105 — 110 kcal/mol

C — F BDE:110 — 120 kcal/mol

70 ng/L (EPA, 2016)

4 ng/L (EPA, 2023)

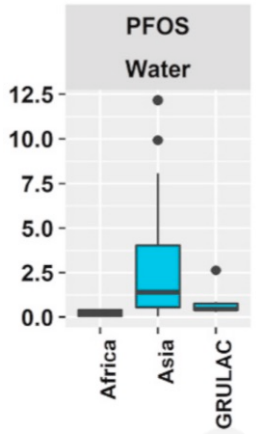
### Persistent




$T_{1/2}$: 4.8 years
in fluorochemical workers

$T_{1/2}$: 41 years
in water

### Globally distributed




water[a]:
1.93 ng/L

sediment[a]:
110 ng/L

*a*: mean of enough samples

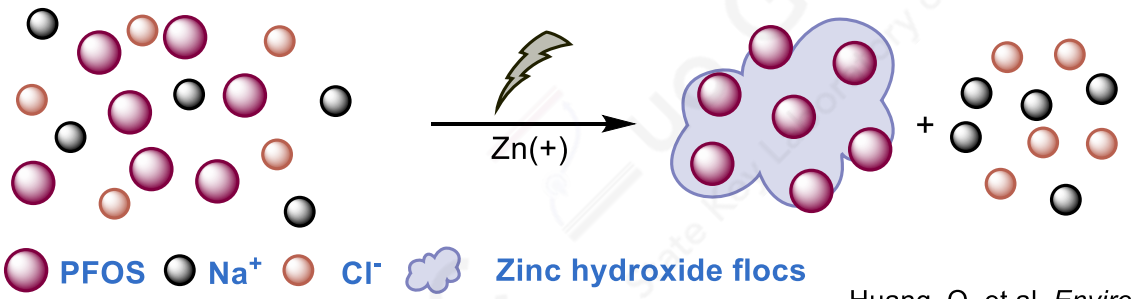
### Toxicity

- Hepatotoxicity
- Developmental Toxicity
- Immunotoxicity
- Hormonal Effects
- Underlying Biochemical Effects

Fiedler, H. et al. *Chemosphere* **2022**, *307*, 136038.

# Sorption and Removal of Polyfluorooctane Sulfonate

## Electrocoagulation

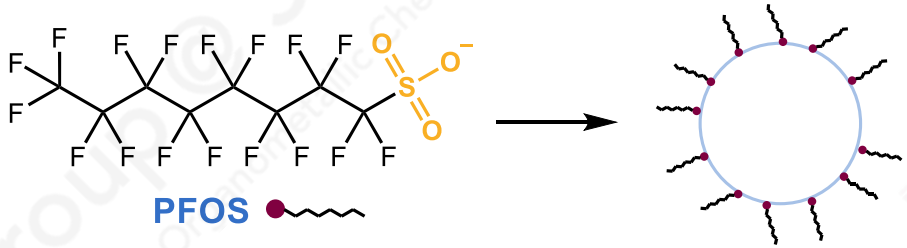



- *via* Hydrophobic interaction
- 96.7% removal within 10 min
- sorption rate:

$v_0 = 1.81 \times 10^3$ mmol $g^{-1}$ $h^{-1}$

Huang, Q. et al. *Environ. Sci. Technol.* **2015**, *49*, 10562-10569.

## Foam fractionation

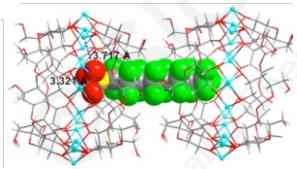



- highly enriched
- 99.9% removal after 2 h

Yu, G. et al. *Chemosphere* **2018**, *203*, 263-270.

## Adsorbent

PFOS $\xrightarrow[\text{β-CD = β-cyclodextrin}]{[Pb_{14}(\beta\text{-CD})_2]\cdot 3C_6H_{12}O\cdot 35H_2O)}$

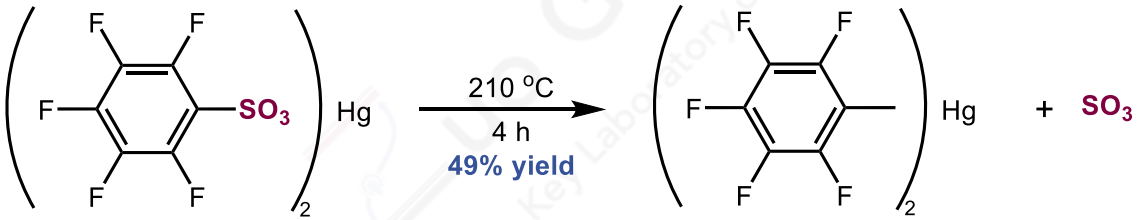


- Bifunctional Molecular Material
- 97% removal within 20 min
- only 9% reduction after 5 cycles

Shi, W. et al. *J. Am. Chem. Soc.* **2023**, *145*, 260-267.

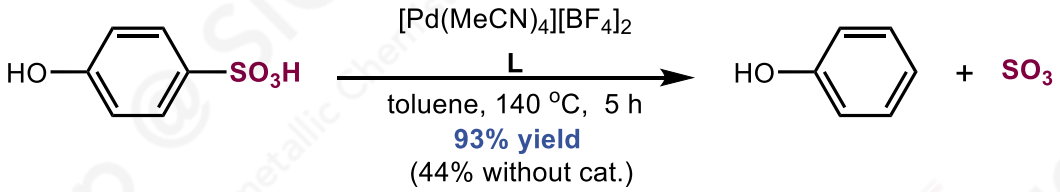
# Desulfonation Reaction

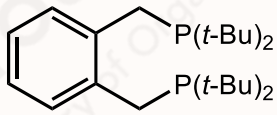
## The first desulfonation reaction




Deacon, G. B. et al. *J. Organomet. Chem.* **1971**, *27*, C9.

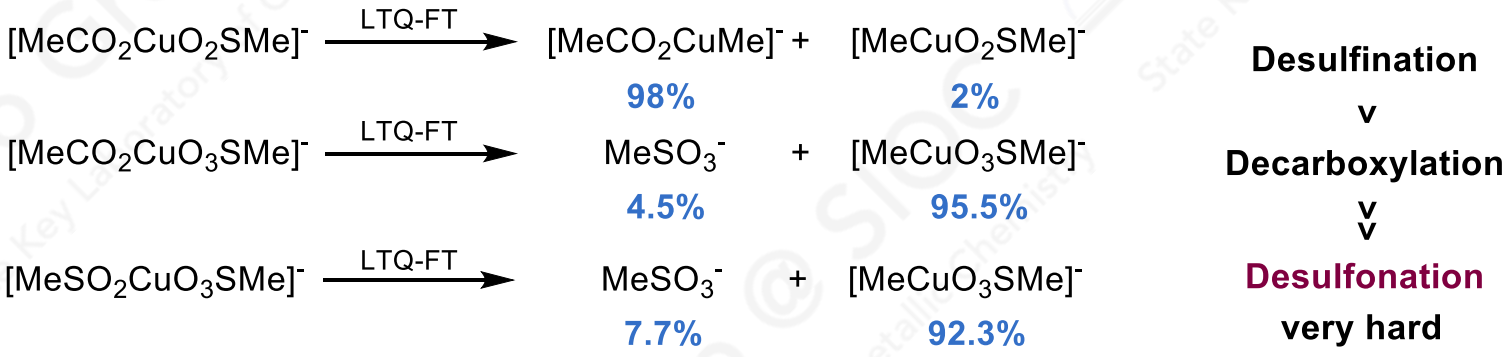
## Desulfonation enabled by palladium-catalysis




**L** BDTBPMB

Cole-Hamilton, D. J. et al. *Dalton Trans*. **2009**, 4683-4688.




**Desulfination**

**v**

**Decarboxylation**

**v**

**v**

**Desulfonation**

**very hard**

O, Hair, R. A. J. et al. *Organometallics* **2012**, *31*, 1801-1807.

# Biodegradation of Polyfluorooctane Sulfonate

**2014**

***P. aeruginosa*** Strain HJ4

pH range of 7–9

temperature range of 30–37 °C

0.1% glucose

degraded by **68%** at **48 h**

**2017**

***Pseudomonas plecoglossicida*** Strain 2.4-D

pH range of 6.8–7.2

temperature range of 26–30 °C

5% NaCl

degraded by **100%** at **6 day in water**

degraded by **75%** at **3 month in soil**

**2019**

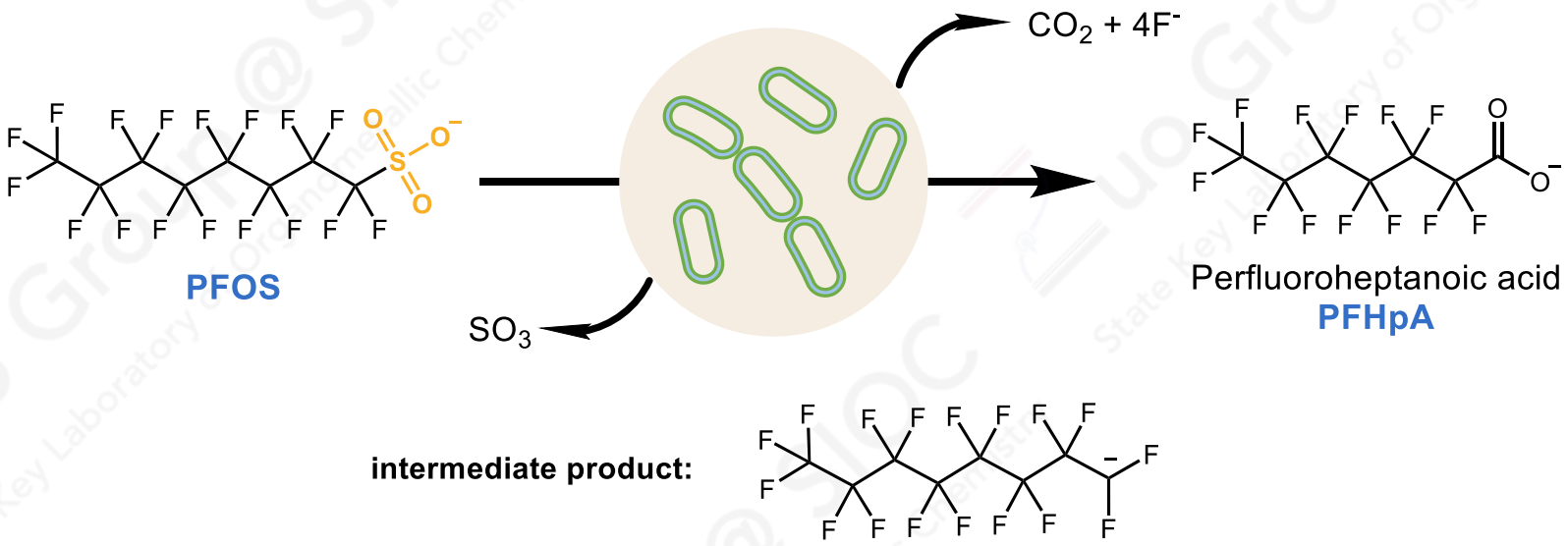
***Ensifer adhaerens*** Strain M1

pH range of 6–8

temperature range of 26–28 °C

2% NaCl

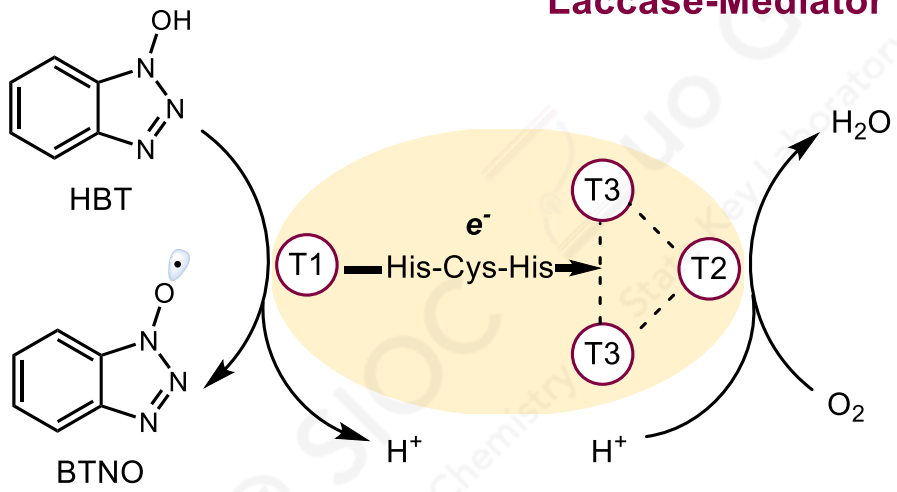
degraded by **100%** at **6 day**




Loginov, O. N. et al. *Applied Biochemistry and Microbiology* **2017**, *53*, 533-538.

# Degradation of Polyfluorooctane Sulfonate in Laccase-Mediator System

## Laccase-Mediator System




1.0 μM PFOS

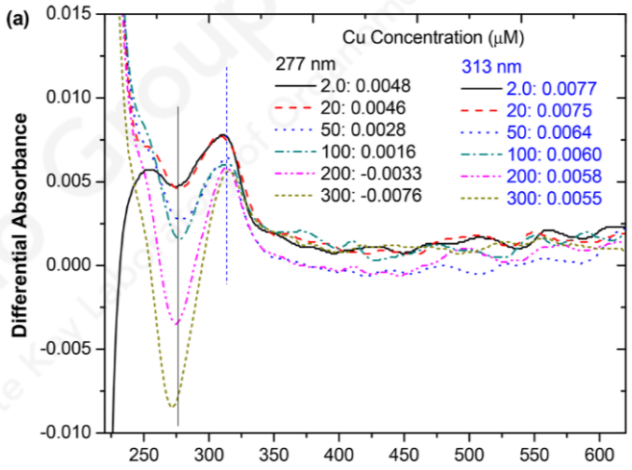
10 mM $Cu^{2+}$($CuSO_4$)

1 U/mL Laccase every 6 days

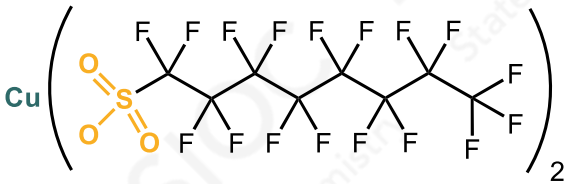
20 μM HBT every 6 days

degraded by **59%** at **162 day**

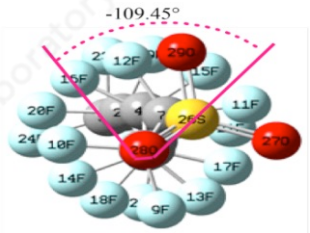
- UV−vis absorbance spectra of **Cu-PFOS**

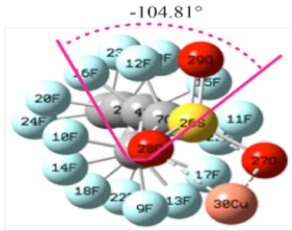



- Formation of **Cu-PFOS** complex unlocks the helical structure




**Cu-PFOS**




Huang, Q. et al. *Environ. Sci. Technol.* **2018**, *52*, 10617-10626.

# Degradation of Polyfluorooctane Sulfonate *via* Sulfate Radical

## Low degradation rate

0.186 mM PFOS

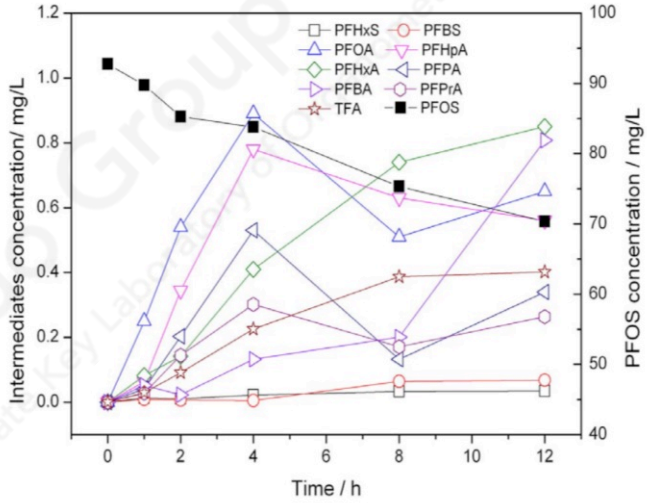
18.5 mM $K_2S_2O_8$

Initial pH = 6.94

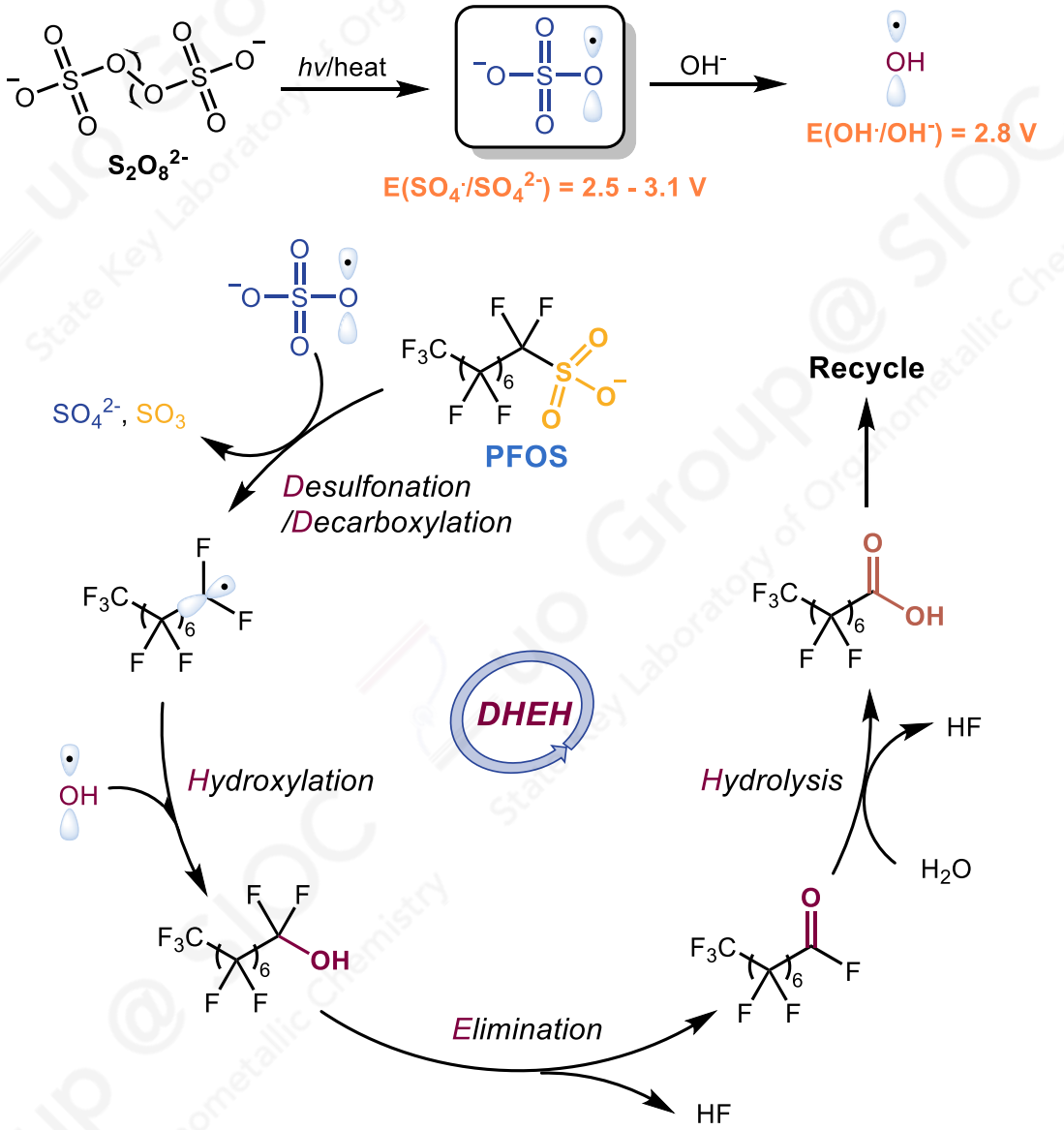
degraded by **22.52%** at **12 h**

$k(F^-) = 0.23\ h^{-1}$

## Multiple by-products




Liang, X. et al. *PLoS One* **2013**, 8, e74877.



# Degradation of PFOS *via* Mg-Aminoclay Coated Nanoscale Zero Valent Iron

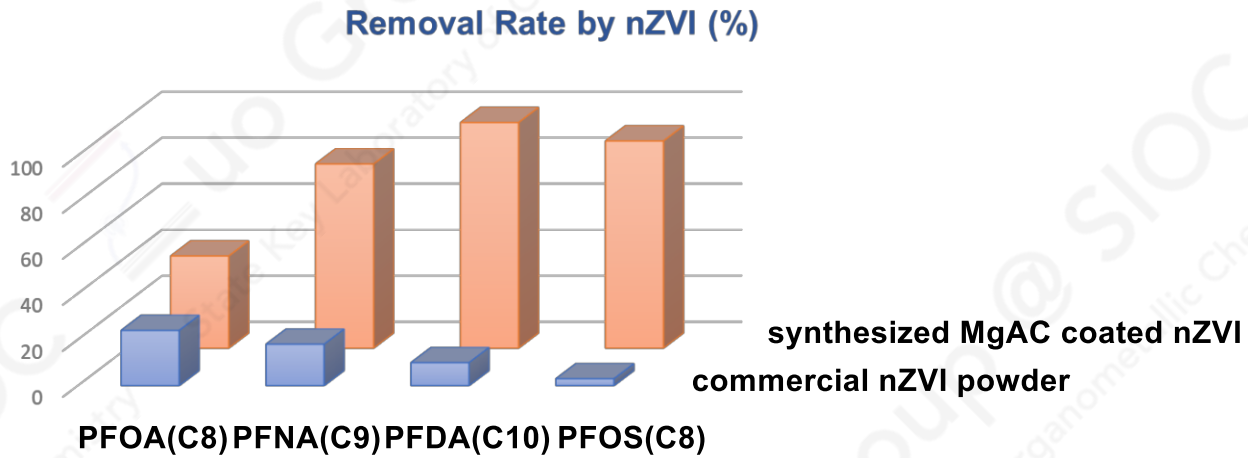
200 μg/L PFOS

100 mg/L nZVI

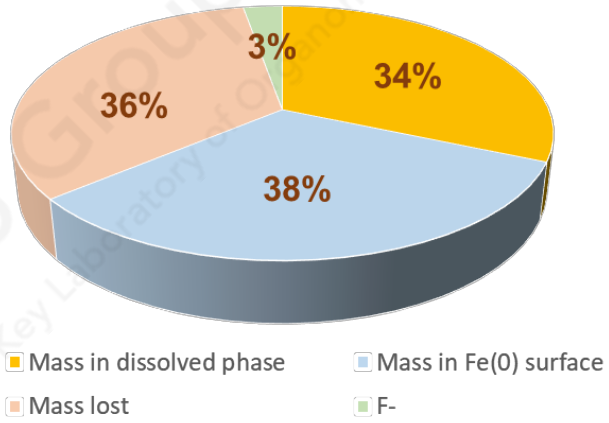
Initial pH = 3

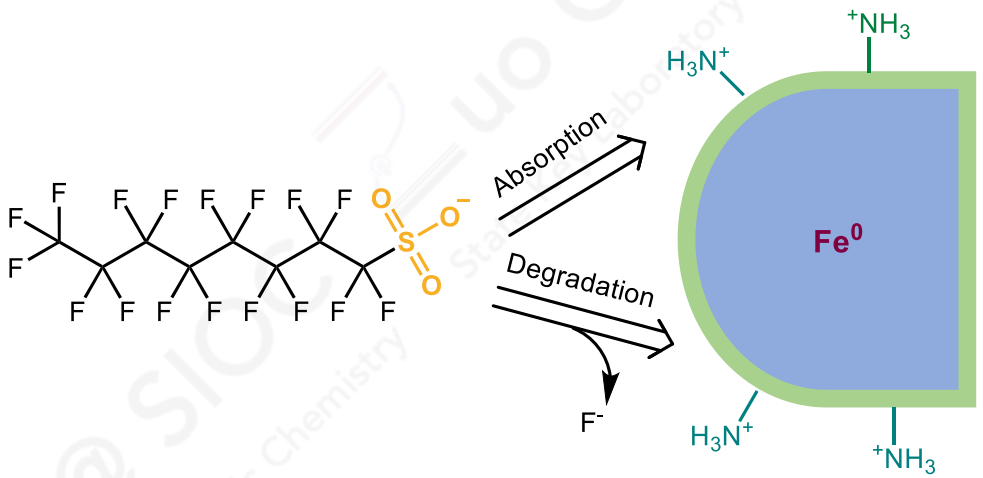
T = 20 °C

Removal rate >90% at **1 h**




- **Both absorption and degradation**




Aloupi, M. et al. *Chemical Engineering Journal* **2015**, *262*, 133-139.

# Destruction of Polyfluorooctane Sulfonate *via* Ball Milling

**2013**

0.05 g PFOS:4.75 g KOH (1:95)

275 rpm (turn every 30 min)

**99.88%** destruction at **6 h**

sulfate recovery **97.7%**

fluoride recovery **92.3%**

Yu, G. et al. *Environ. Sci. Technol.* **2013**, *47*, 6471-6477.

**2019**

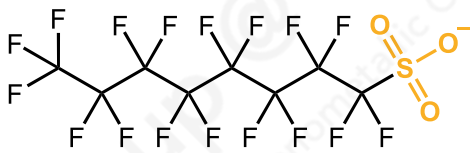
0.2 g PFOS : 2.6 g $Al_2O_3$ : 1.4 g $K_2S_2O_8$ (1:13:7)

350 rpm (turn every 15 min)

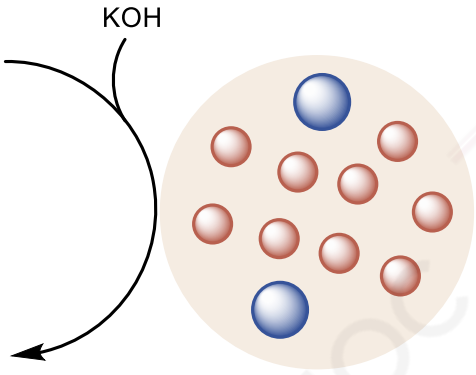
**56%** destruction at **2 h**

fluoride recovery **9.7%**

Tang, H. et al. *Environ. Sci. Technol.* **2019**, *53*, 8302-8313.



**PFOS**



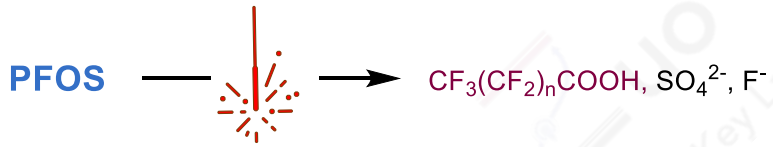

Big ball(d = 9.6 mm)

Small ball(d = 5.5 mm)

Planetary ball mill (QM-3SP2)

# Degradation of Polyfluorooctane Sulfonate *via* High Energy Pathway

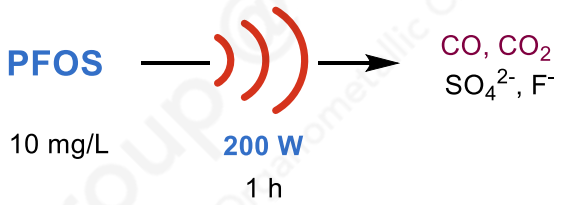
## Electron Beam




| PFOS concentration | 900 kGy(9 min) | 200 kGy(20 min) |
|---|---|---|
| 0.1 mg/L | 85.1% | 92.1% |
| 1 mg/L | 65.9% | 76.6% |
| 10 mg/L | 61.9% | 65.6% |

Kim, S. D. et al. *Chemical Engineering Journal* **2019**, *361*, 1363-1370.

## Sonochemical Decomposition

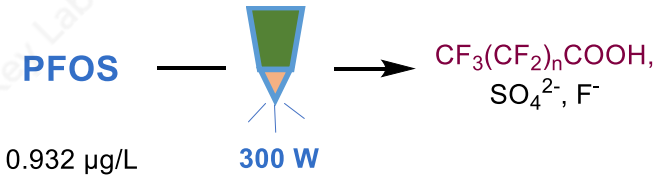



- **Mostly pyrolyzed (1000 K - 4000 K)**

| Air | Argon | Argon(with *tert*-butyl alcohol) |
|---|---|---|
| 28% | 60% | 48% |

Maeda, Y. et al. *Environmental Science & Technology* **2005**, *39*, 3388-3392.

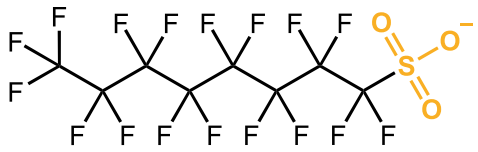
## Plasma




| | R1-N1 (3 min) | R1-N2 (5 min) | R2-N1 (3 min) | R2-N2 (5 min) |
|---|---|---|---|---|
| Final Concentration | 0.391μg/L | 0.669 μg/L | 0.336 μg/L | 0.346 μg/L |
| Degradation rate | 58.0% | 28.2% | 63.9% | 63.0% |

Delgado, A. et al. *Energies* **2018**, *11, 1290-1303.*

# Degradation of Polyfluorooctane Sulfonate *via* Electrochemical Treatment



**PFOS** 0.4 mM

100 mL/min
20 mA/cm$^2$
BDD(+), Pt(-)
**BDD**: **B**oron-**D**oped **D**iamond

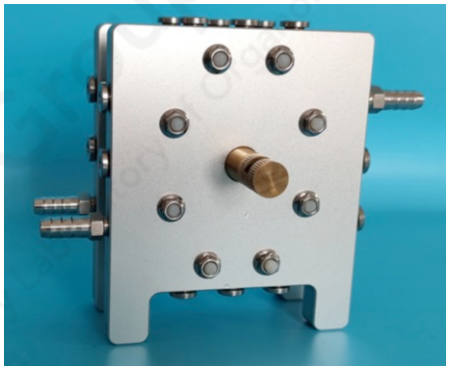
$SO_4^{2-}$, $F^-$, $CO_2$

- **Complete removal at 8 min**
- **k = 0.13 min$^{-1}$**
- **by-products: $ClO_4^-$**

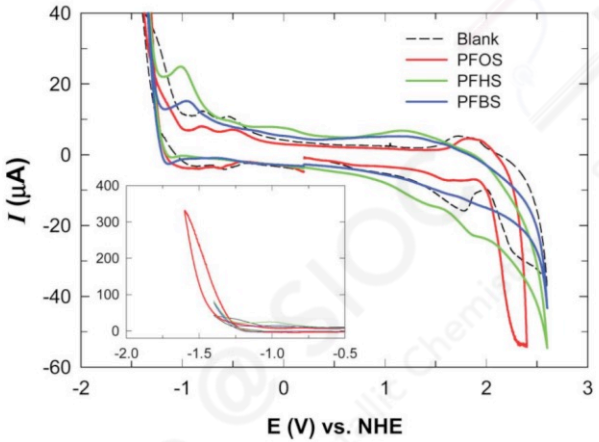
Farrell, J. et al. *Environmental Science & Technology* **2008**, *42*, 6111-6115.

| | Ochiai(2011) | zhuo(2011) | Lin(2012) | Schaefer(2015) | Chaplin(2019) |
|---|---|---|---|---|---|
| Anode | BDD | Ti/$SnO_2$-Sb-Bi | Ti/$SnO_2$-Sb | Ti/$RuO_2$ | $Ti_4O_7$ |
| Normalized Rate Constant [(min$^{-1}$) (mA/cm$^2$)$^{-1}$ (L)] | 267 x 10$^{-5}$ | 6.6 x 10$^{-5}$ | 25 x 10$^{-5}$ | 46 x 10$^{-5}$ | |

Chaplin, B. P. et al. *Environmental Science & Technology Letters* **2019**, *6*, 504-510.



MF-ELFlow



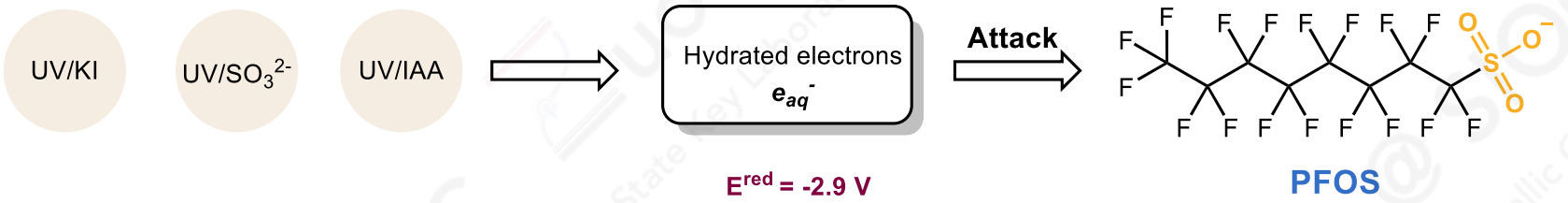

**Reduction: E < -1.3 V**

**Oxidation: E > 2.0 V**

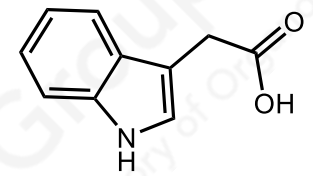
Park, H. et al. *Photochem Photobiol Sci.* **2011**, *10*, 1945-1953.

# Photodegradation of Polyfluorooctane Sulfonate

## Photodegradation of polyfluorooctane sulfonate *via* hydrated electrons

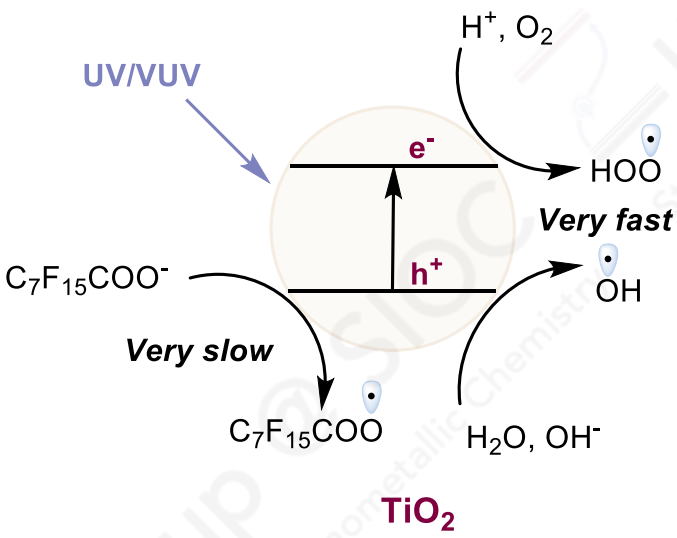



## Degradation mechanism



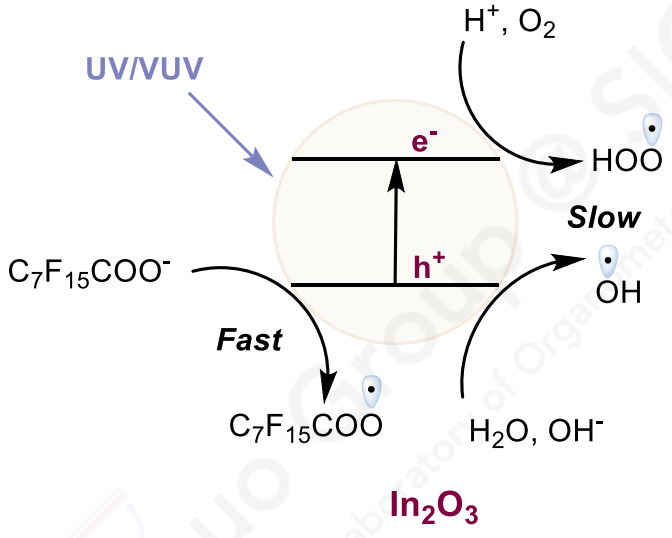
# Photodegradation of Polyfluorooctane Sulfonate

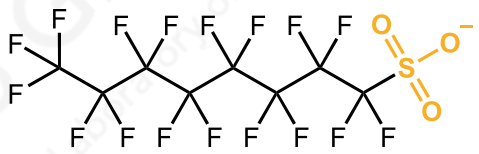
## Photodegradation of Polyfluorooctane sulfonate by semiconductor




PFOA √

PFOS □



**PFOS** 0.019 mM

254 nm UV lamp (5 W)

SiC/GQDs

$SO_2$, $C_nH_{2n+1}COO^-$

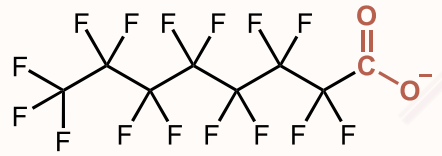
- **Removal rate 88.5%**
- **k = 0.098 $h^{-1}$**
- **$T_{1/2}$ = 7.2 h**

**GQDs**: **G**raphene **Q**uantum **D**ots

*Niu, J. et al. Chemical Engineering Journal* **2017**, *323*, 406-414.

# Photodegradation of Polyfluorooctanoic Acid

## The first photodegradation of polyfluorooctanoic acid



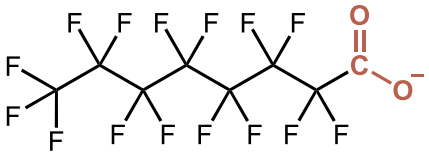
**PFOA** 1.35 mM

220-460 nm xenon-mercury lamp (200 W)

$H_2O$

$CO_2$, $F^-$, $C_nF_{2n+1}COO^-$

| Entry | Conditions | degradation rate/% | $F^-$ recovery/% | $CO_2$ recovery/% |
|---|---|---|---|---|
| 1 | $O_2$(0.48 MPa), 24 h | 44.9 | 14.9 | 29.3 |
| **2** | **$O_2$(0.48 MPa), 72 h** | **89.5** | **33.5** | **52.4** |
| 3 | Ar(0.48 MPa), 24 h | 43.2 | 11.8 | 10.3 |
| 4 | $H_2O_2$ + $O_2$(0.48 MPa), 24 h | 35.5 | 11.3 | 15.1 |
| **5** | **$[PW_{12}O_{40}]^{3-}$ + $O_2$(0.48 MPa), 24 h** | **100** | **82.4** | **77.7** |
| 6 | $[PW_{12}O_{40}]^{3-}$ + Ar(0.48 MPa), 24 h | 7.7 | 2.6 | 4.2 |



Conditiona of **entry 5**

$H_2{}^{18}O$

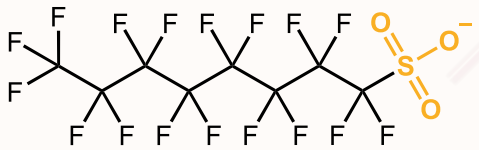
$C^{16}O_2$ + $C^{16}O^{18}O$ + $C^{18}O_2$

**4.1%** **7.6%** **88.3%**

Hori, H. et al. *Environmental Science & Technology* **2004**, *38*, 6118-6124.

# Photodegradation of Polyfluorooctane Sulfonate

## The first photodegradation of polyfluorooctane sulfonate

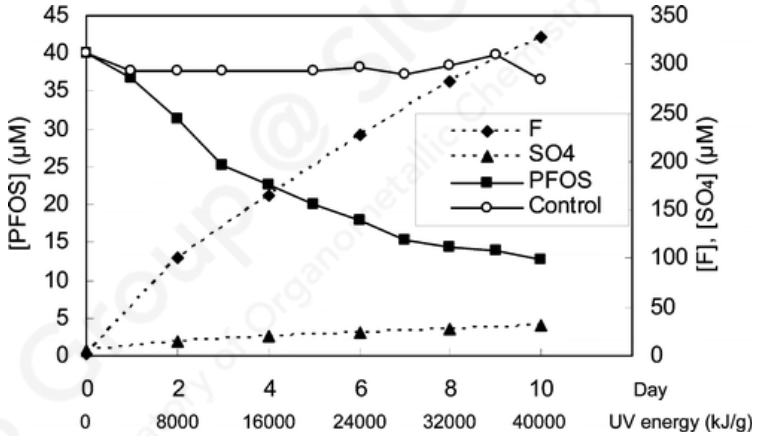


**PFOS** 0.04 mM

254 nm low-pressure mercury lamp (32 W)

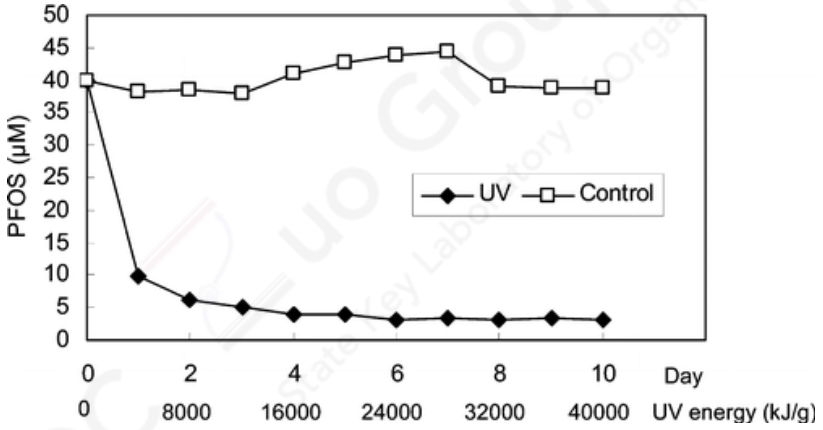
$N_2$, solvent

$SO_4^{2-}$, $CO_2$, $F^-$, $C_nF_{2n+1}COO^-$




**in $H_2O$, 36-46 °C**

**k = 0.13 $d^{-1}$**



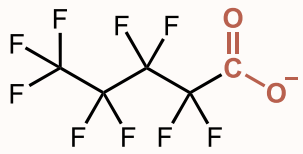

**in alkaline 2-propanol, 38-50 °C**

**k = 2.0 $d^{-1}$**

Yamamoto, T. et al. *Environmental Science & Technology* **2007**, *41*, 5660-5665.

# Photodegradation of Polyfluorooctanoic Acid *via* $Fe^{3+}$

## Photodegradation of short-chain perfluorocarboxylic acids *via* $Fe^{3+}$



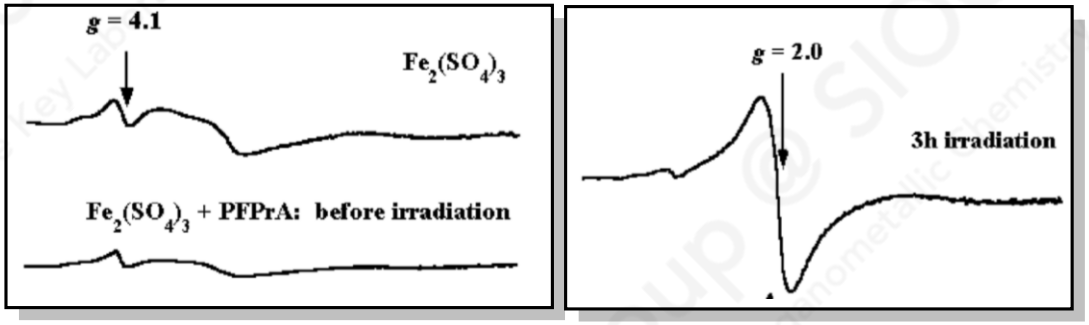
**PFPeA** 67.3 mM

220-460 nm xenon-mercury lamp (200 W)
$Fe_2(SO_4)_3 \cdot 7.5H_2O$
$O_2$(0.49 MPa), $H_2O$, 24 h

$CO_2$, $F^-$, $C_nF_{2n+1}COO^-$

| Entry | Conditions | degradation rate/% | $F^-$ recovery/% | $k/10^{-2} \cdot h^{-1}$ |
|---|---|---|---|---|
| **1** | **5 mM $Fe^{3+}$** | **64.5** | **69.2** | **4.26** |
| 2 | without $Fe^{3+}$ | 24.3 | 12.1 | 1.18 |
| 3 | Ar(0.49 MPa) | 35.6 | | |
| 4 | 2.5 mM $Fe^{3+}$ | 49.2 | | |
| 5 | $Fe(ClO_4)_3 \cdot 6H_2O$ | 71.2 | | |
| 6 | $FeCl_3 \cdot 6H_2O$ | 24.3 | | |

### ESR spectra

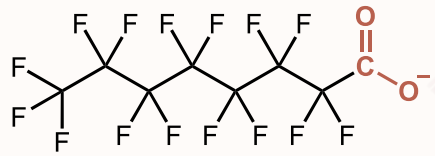



**$Fe^{3+}$–PFPrA complex**

Hori, H. et al. *Chemosphere* **2007**, *68*, 572-578.

# Photodegradation of Polyfluorooctanoic Acid *via* $Fe^{3+}$

## Photodegradation of perfluorooctanoic acid *via* $Fe^{3+}$



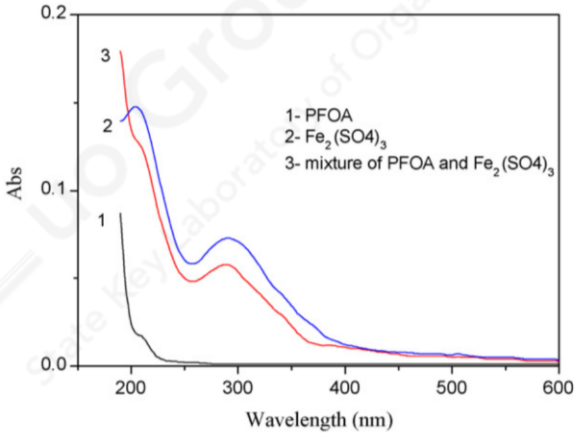

PFOA 0.048 mM

254nm low-pressure mercury lamp (32 W)
$Fe_2(SO_4)_3$, $O_2$
$H_2O$, 4 h

$CO_2$, $F^-$, $C_nF_{2n+1}COO^-$

| Entry | Conditions | degradation rate/% | $k/min^{-1}\cdot10^{-3}$ | $t_{1/2}$/min |
|---|---|---|---|---|
| **1** | **50 μM $Fe^{3+}$** | **77.8** | **6.5** | **107** |
| 2 | without $Fe^{3+}$ | 4.2 | 0.2 | 4333 |
| 3 | 30 μM $Fe^{3+}$ | 72.2 | 5.3 | 132 |
| 4 | 80 μM $Fe^{3+}$ | 80.2 | 6.7 | 103 |
| 5 | 50 μM $Cu^{2+}$ | 7.4 | | |
| 6 | 30 μM $Fe^{2+}$ | 68.8 | | |

**UV–vis spectra**

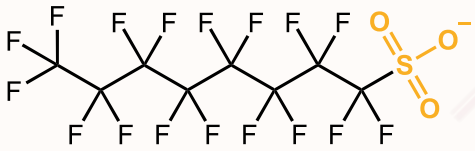



$Fe^{3+}$– PFOA complex $\xrightarrow[\text{LMCT}]{\text{UV}}$ $Fe^{2+} + CO_2 + {}^{\cdot}C_7F_{15}$

Zhang, P. et al. *J. Hazard. Mater.* **2008**, *160*, 181-186.

# Photodegradation of Polyfluorooctane Sulfonate via $Fe^{3+}$

## Photodegradation of polyfluorooctane sulfonate *via* $Fe^{3+}$



**PFOS** 0.02 mM

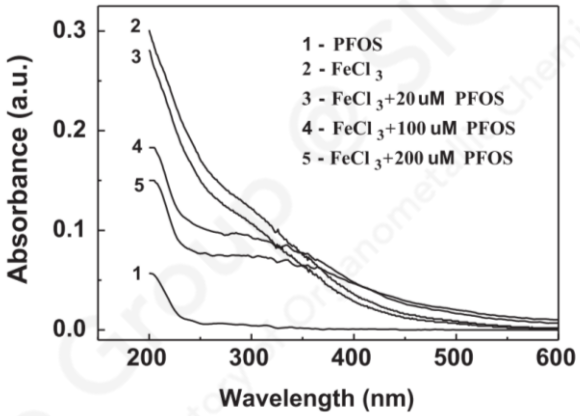
254 nm low-pressure mercury lamp (32 W)
$FeCl_3 \cdot 6H_2O$(0.1 mM), $O_2$
$H_2O$, 72 h

$SO_4^{2-}$, $CO_2$, $F^-$, $C_nF_{2n+1}COO^-$

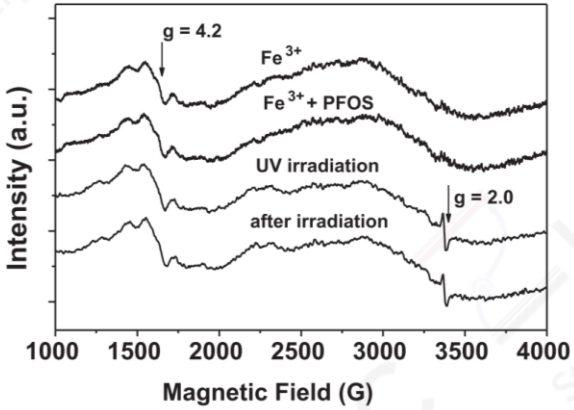
**Degradation rate: 100%**

**k = 1.67 $d^{-1}$**

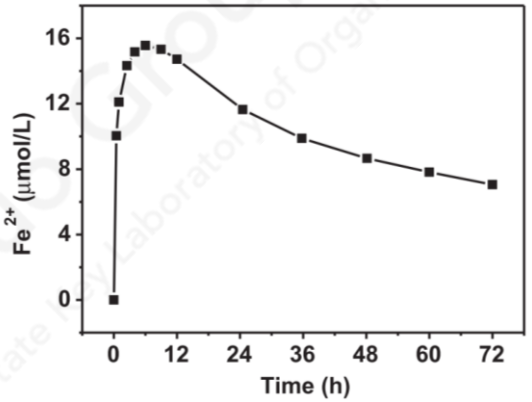
### UV–vis absorption spectra

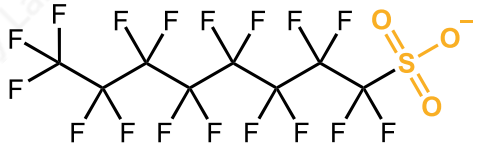



### ESR spectra



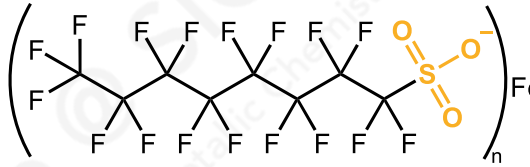

### $Fe^{2+}$



**PFOS**

$Fe^{3+}$



$Fe^{3+}$

**UV**
**LMCT**

$C_8F_{17}SO_3^{\cdot}$

Zhang, P. et al. *J. Hazard. Mater*. **2014**, *271*, 9-15.

# Summary

**Biodegradation**

- Green and sustainable
- Strict condition
- Low efficiency

**Sorption and Removal**

- High efficiency
- Recyclable
- Need to be degraded again

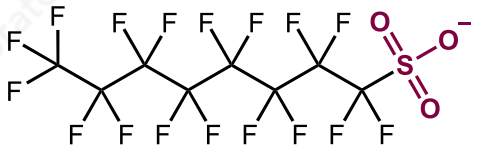
**PFOS**

**Photodegradation**

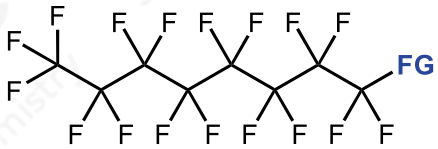
- Green and sustainable
- Multiple by-products

**Advanced Oxidation & Reduction**

- High efficiency
- High energy consumption




PFOS


Drug activity & Functional molecule