Processes for the removal of perfluorooctane sulfonate (PFOS) from semiconductor effluents

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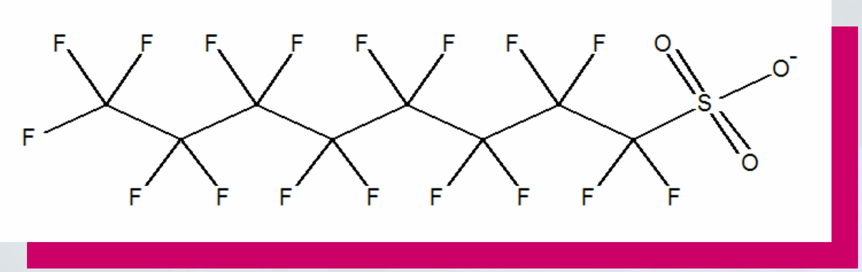
Chemistry

Perfluorinated alkyl surfactants (PFAS)



PFOS [$CF_3(CF_2)_7SO_3^-$]

Properties:

- repeal oil, stain, grease and water
- reduce surface tension better than other surfactants
- work well under harsh conditions

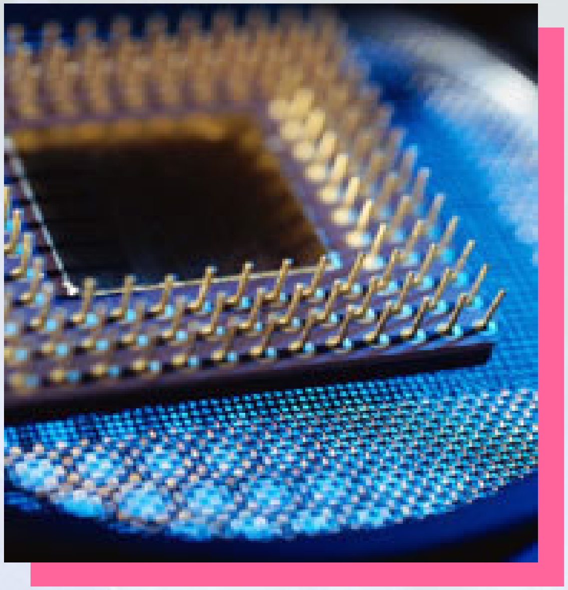
Uses

- Anthropogenic compounds
- Consumer products for > 50 years

Importance

- Photoacid generator (PAG) and surfactant in the photoresist.
- Surfactant in top and bottom antireflecting coatings, TARCs and BARCs

Photolithography and Semiconductor industry

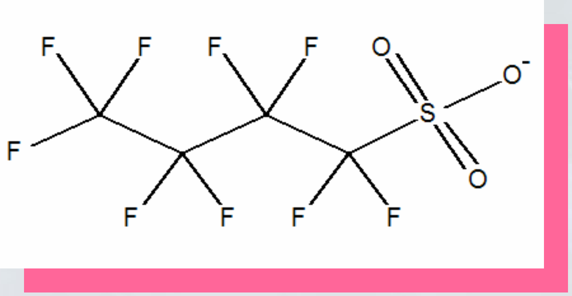


PFOS makes a unique contribution !!!

Regulations

- In 2000 3M announced withdrawal of PFOS and related compounds effective in 2002.
- US EPA issued a proposed Toxic Substances Control Act (TSCA) and Significant New User Rule (SNUR) later in 2002 forbidding the use of PFOS with exemptions for semiconductor industry.
- In January 2006, EPA asked companies to reduce the PFOA emissions by 95% by 2010 and completely eliminated by 2015.
- In April 2006, EPA issued a SNUR to limit the use of 183 perfluoroalkyl sulfonates.

Alternatives



PFBS $[CF_3(CF_2)_3SO_3^-]$

Compound	BCF
PFBS (C_4)	< 1
PFHS (C_6)	59
PFOS (C_8)	3100

Martin et al. (2003) Environ. Tox. Chem. 22:196

Fluorotelomers

$$CF_2 = CF_2$$

$$\downarrow$$

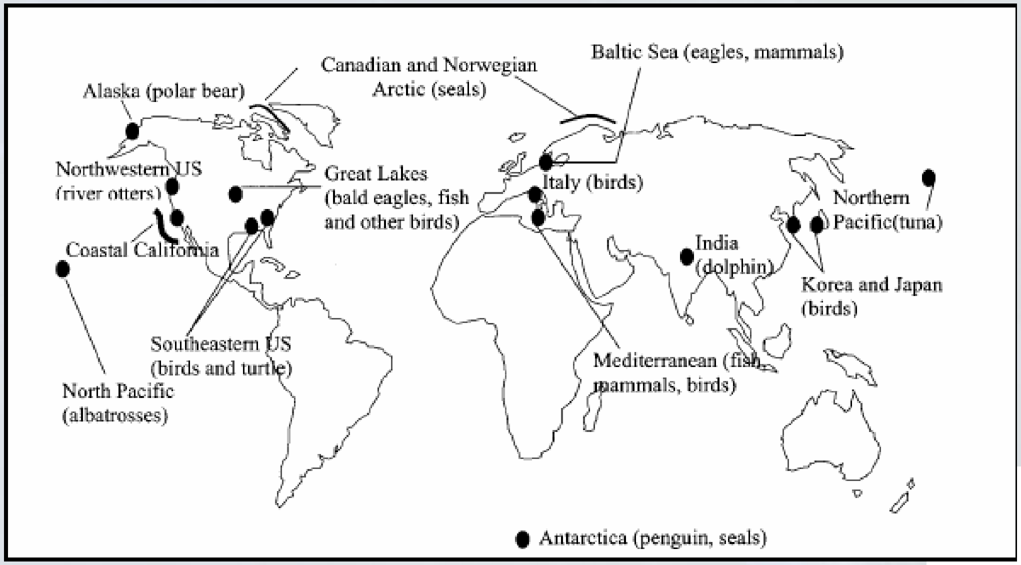
$$C_3CF_2(CF_2CF_2)_n I$$

$$\downarrow$$

$$CF_3CF_2(CF_2CF_2)_nCH_2CH_2I$$

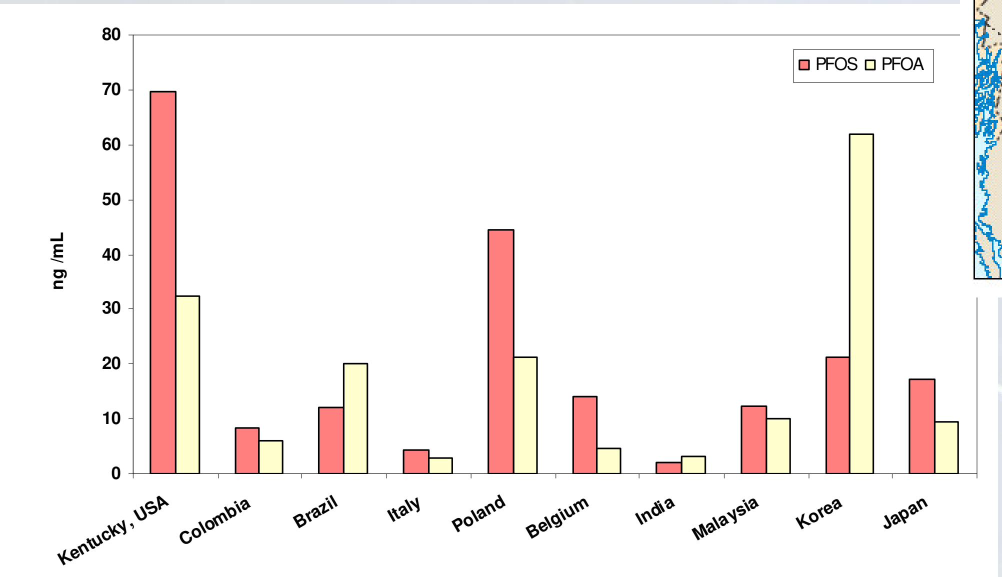
$$\downarrow$$

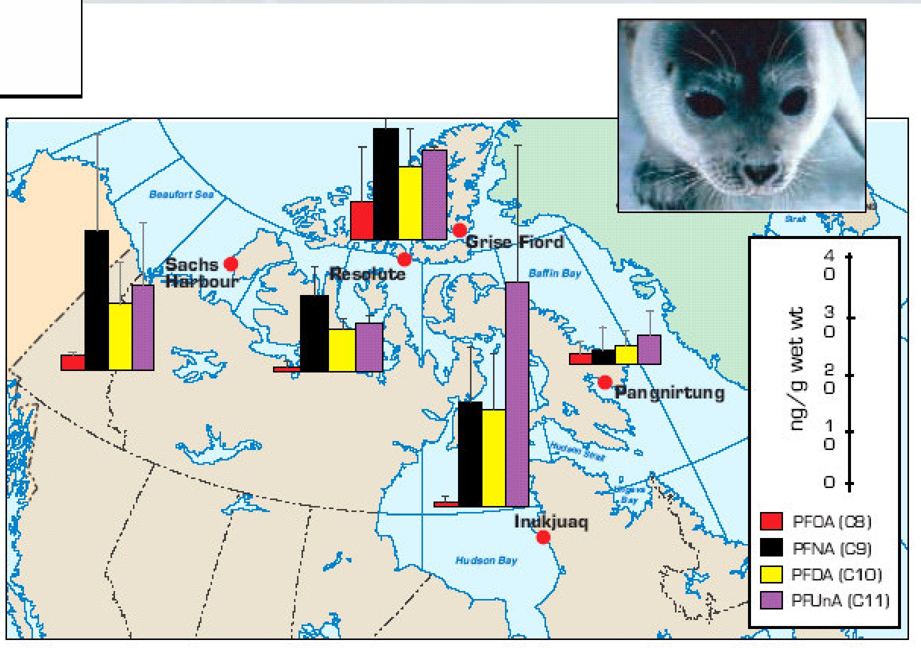
$$CF_3CF_2(CF_2CF_2)_nCH_2CH_2OH$$



Giesy et al. (2001) Environ. Sci. Tech. 35:1339

Kannan et al. (2004) Environ. Sci. Tech. 38:4489





Renner (2004) Science 306:1887

Challenges

- Recalcitrant
  - C-F bond (476 KJ/mol) vs C-H (413 KJ/mol)
  - absence of structures susceptible to electrophilic or nucleophilic attack.
  - perfluorinated tail
- Not known to hydrolyze, photolyze or biodegrade under environmental conditions.
- Long range transport of volatile precursors

PFOS is the ultimate degradation product of PFAS family !!!

Treatments

- Incineration
  - Preconcentration procedures
  - High cost ($3-4/gallon)
- Ion exchange (Lampert et al, 2003)
  - Poor selectivity
- Activated carbon (Lampert et al, 2003)

- Ultrasonic irradiation (Moriwaki et al, 2005)
  - 60% PFOS degradation (argon atmosphere for 60 min)
  - PFOA and short-chain PFAS.
- Zero-valent iron in subcritical water (Hori et al, 2006)
  - 50% F^- release (350 °C for 6 h)
  - CHF_3 in gas phase

Extreme conditions !!!

Objectives

- Develop analytic methods to detect PFOS in environmental samples based on:
  - ^{19}F NMR
  - HPLC-suppressed conductivity ion chromatography

- Evaluate removal of PFOS from semiconductor effluents by:
  - Adsorption onto activated carbon ←
  - Biosorption
  - Reductive dehalogenation ←

Analytical Methods

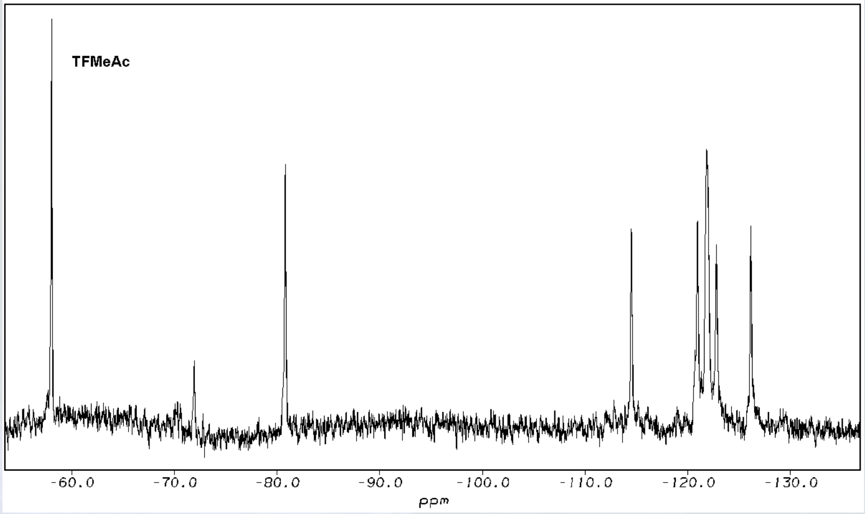
Common analytical techniques (GC/MS, HPLC) cannot be employed.

- HPLC/MS/MS
- Direct injection ESI/MS

Varian Unity-300

HPLC-IC DIONEX 3000

^{19}F NMR



Advantages

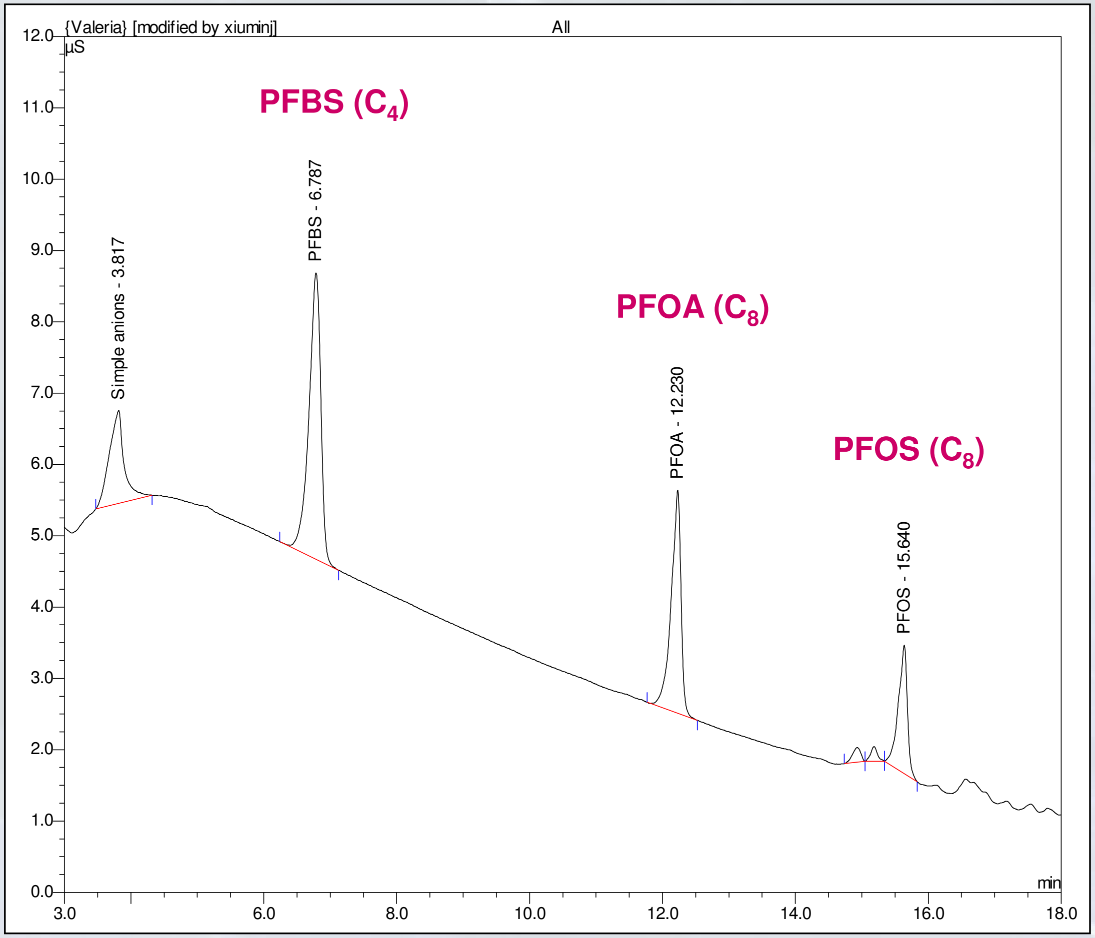
- specificity to fluorine
- changes in chemical shifts
- sharp, well-resolved peaks
- no matrix interferences

Disadvantages

- low sensitivity → SPE
- time consuming

HPLC-IC

Monitor PFOS on a routine basis



Advantages

- Simple, rapid and efficient.
- Short analysis times
- Low-ppm PFOS

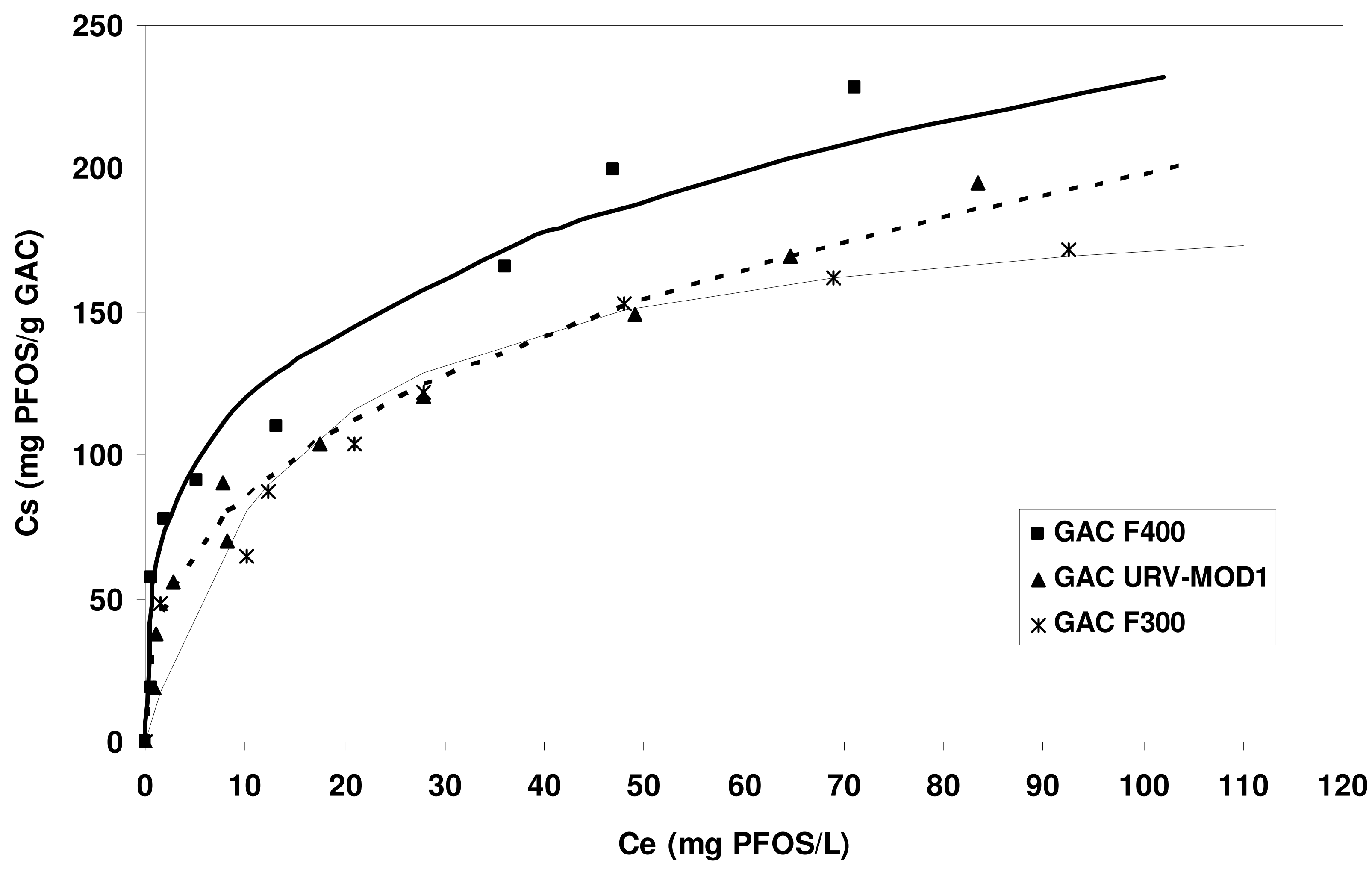
GAC – adsorption isotherms

- Good sorbent material
- Removal of halogenated compounds
- Previous studies on adsorption of PFOS and related substances

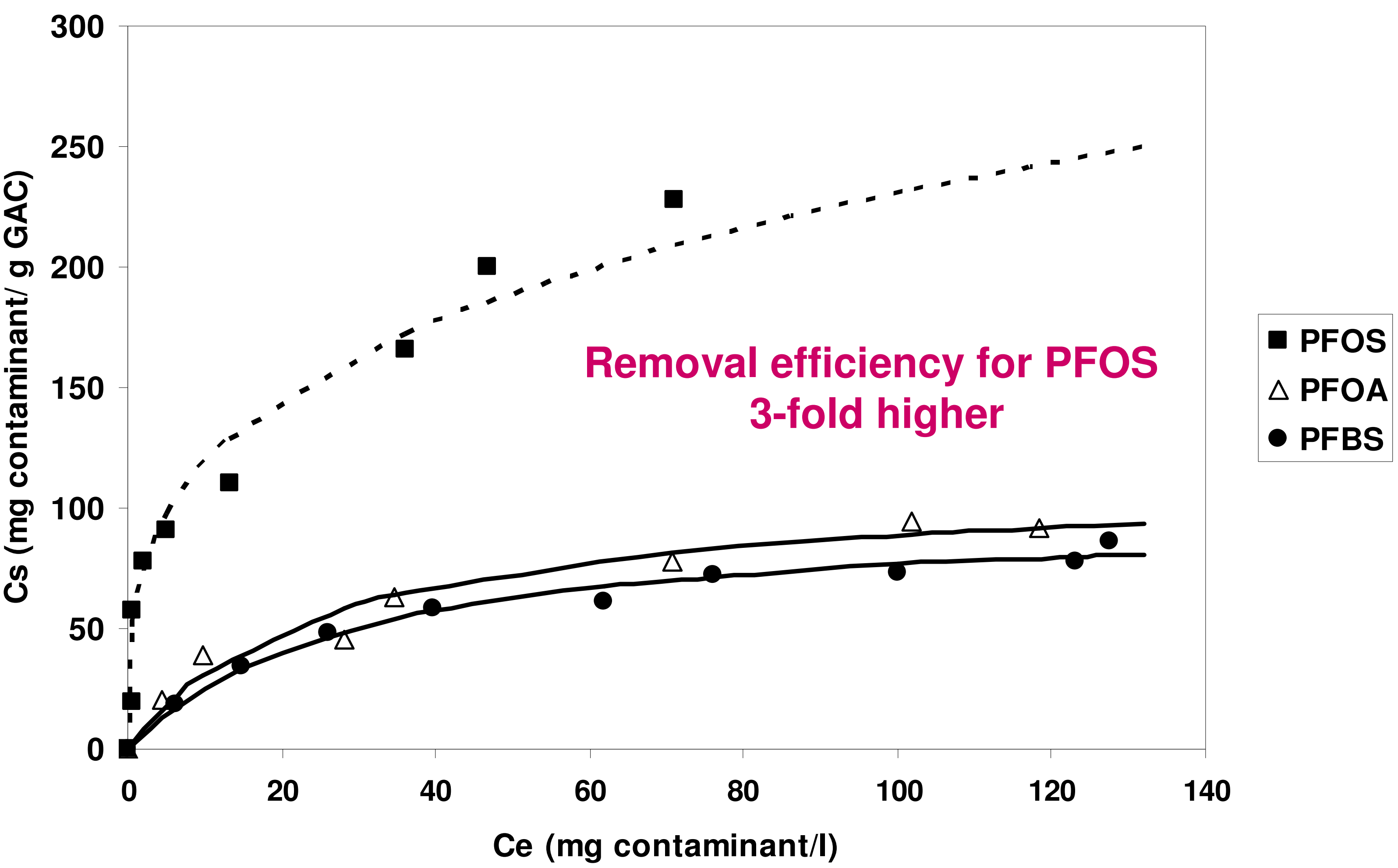
Experimental set-up

- Batch experiments
  - 30ºC , pH 7.2 (48 hours)
- HPLC-IC
- Adsorptive capacity: Langmuir and Freundlich models

Calgon F400 provided higher adsorptive capacity



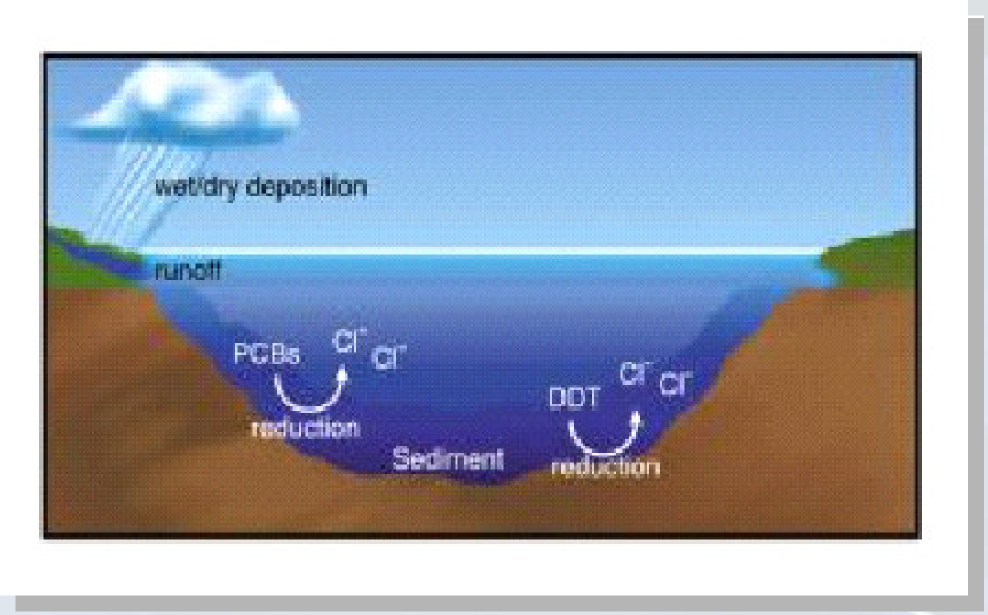
Adsorption isotherms with GAC Calgon F400



Removal efficiency for PFOS 3-fold higher

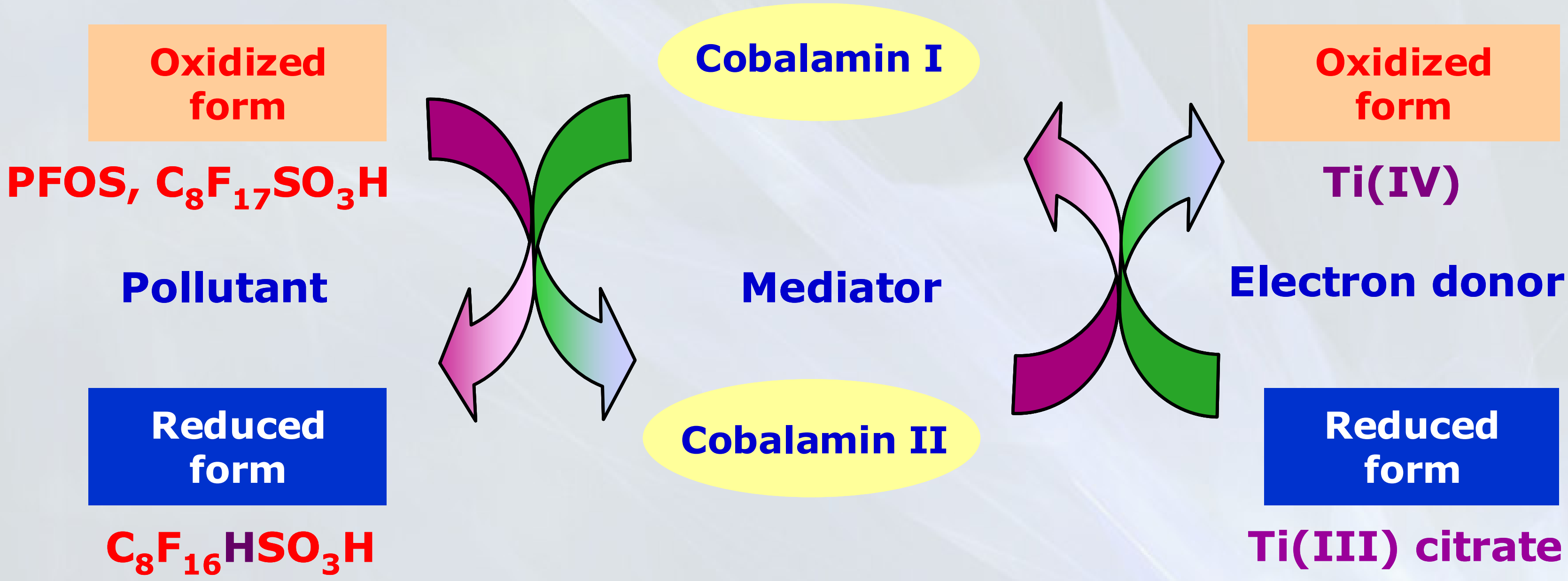
Reductive dehalogenation

$$R\text{–}F + 2e^- + 2H^+ \longrightarrow R\text{–}H + HF$$



Reductive dehalogenation is the main means of degradation of highly halogenated organics. Eg. PCE, PCBs, PBDEs.

Biomimetic Reductive Dehalogenation



Oxidized form

PFOS, $C_8F_{17}SO_3H$

Pollutant

Reduced form

$C_8F_{16}HSO_3H$

Cobalamin I

Mediator

Cobalamin II

Oxidized form

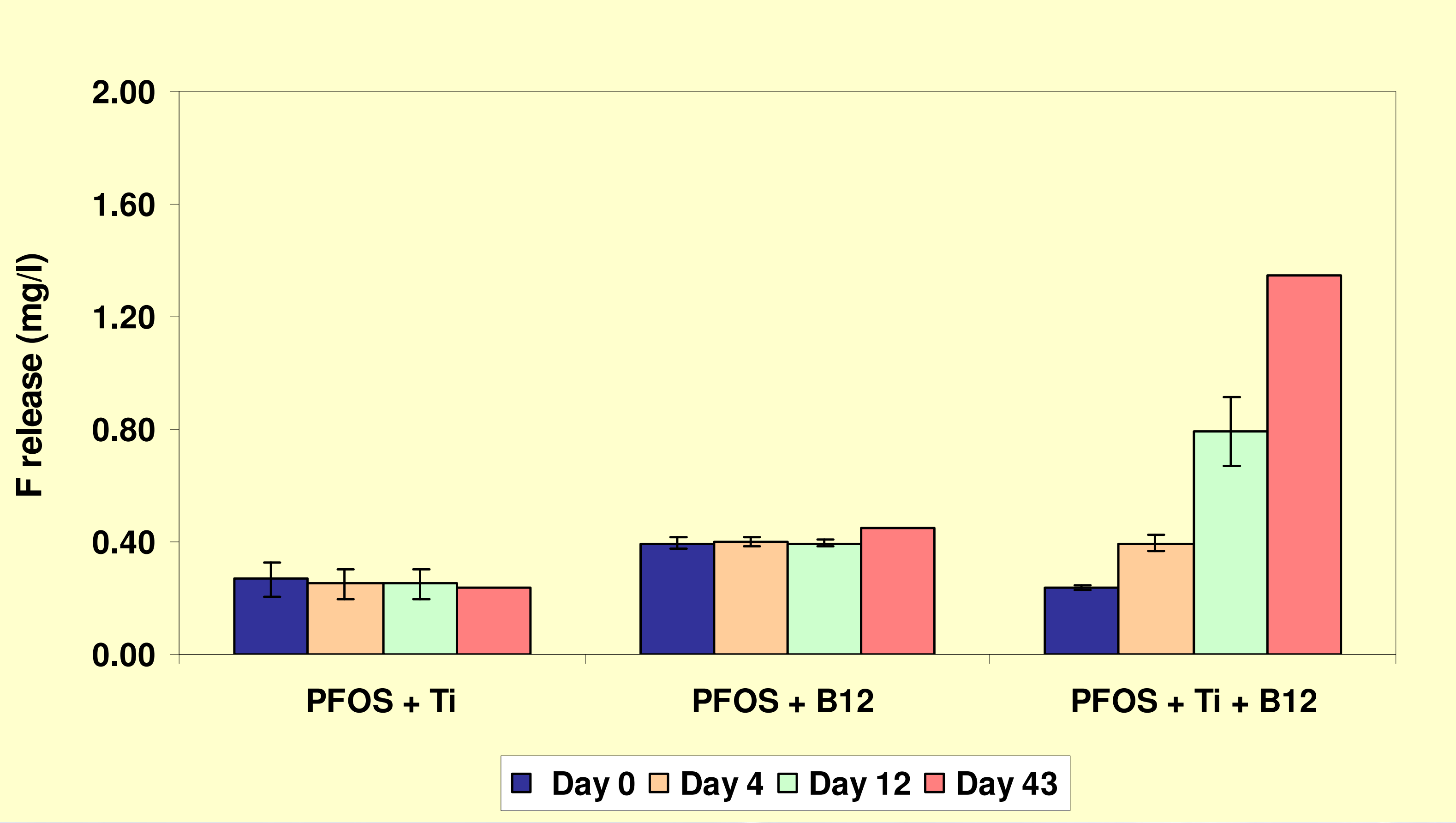
Ti(IV)

Electron donor

Reduced form

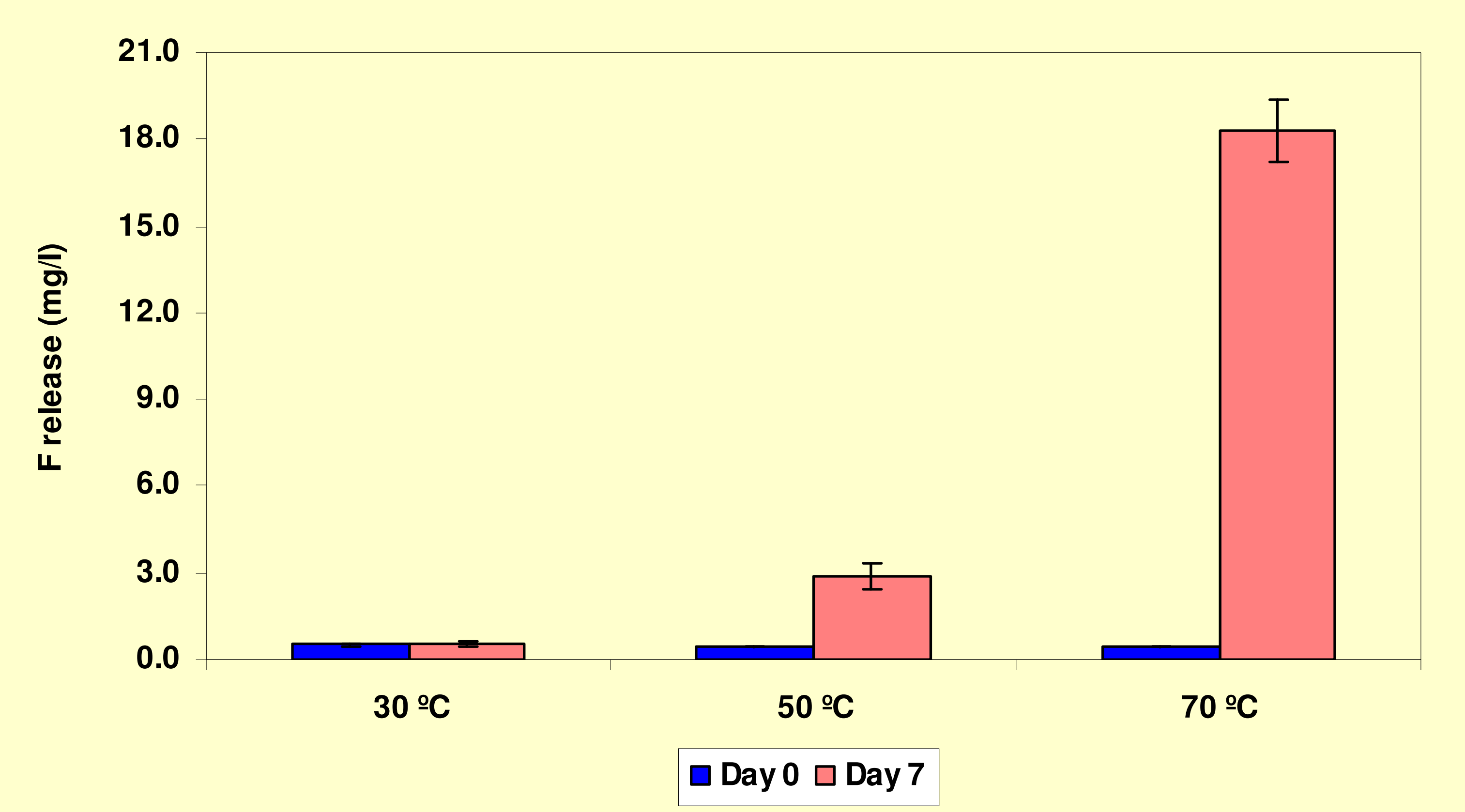
Ti(III) citrate

Biomimetic reductive dehalogenation of PFOS with Ti(III) citrate and cobalamin at 30℃ and pH 7.3

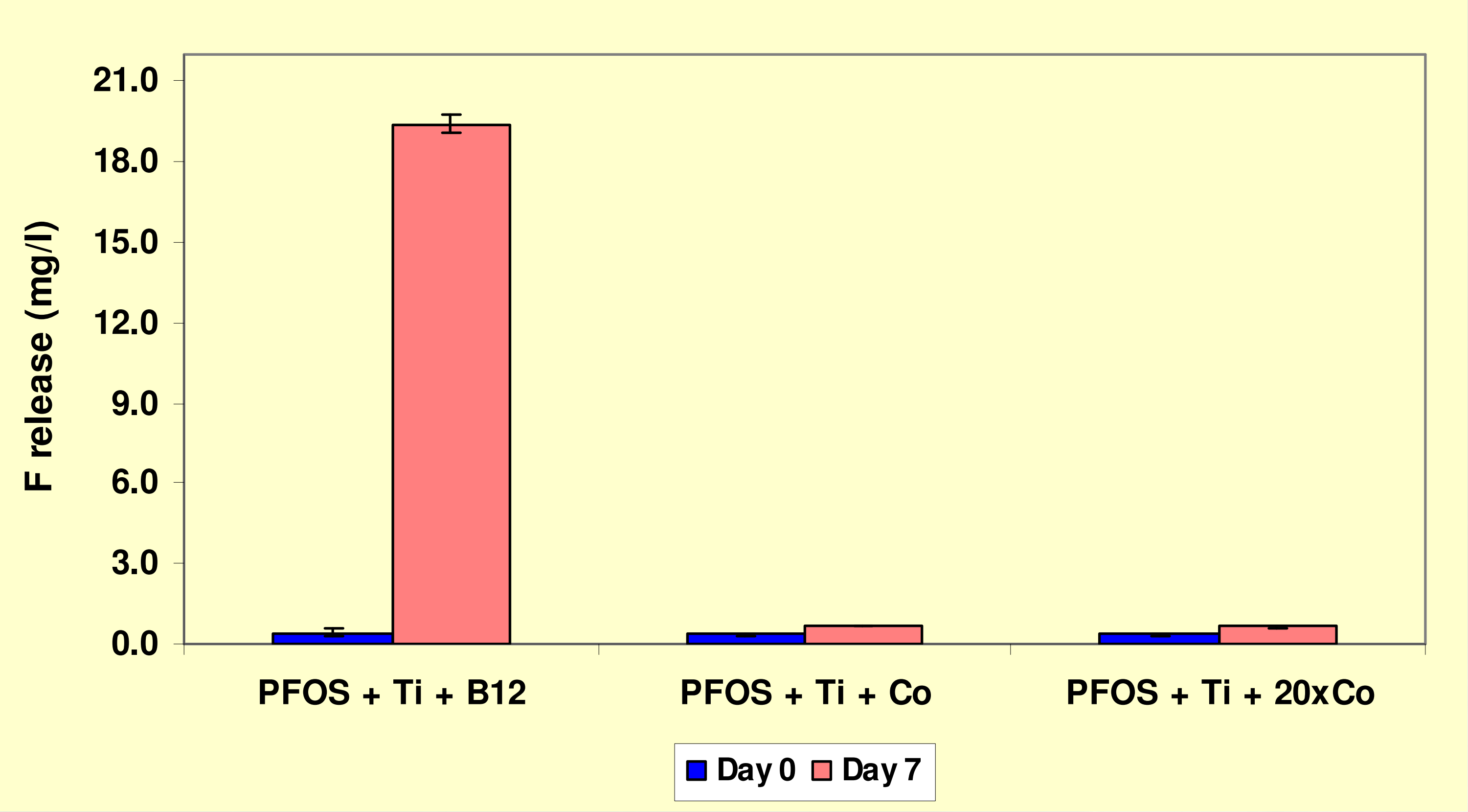


Optimization of kinetics

18 % defluorination corresponding to 3 mol F⁻ / mol PFOS



Cobalamin vs Cobalt



Organometallic enzyme cofactor is responsible for degradation

Conclusions

- Detection and quantification of PFOS in environmental samples by ^{19}F-NMR and HPCL-suppressed conductivity IC (higher sensitivity and short analysis times)

- GAC was shown to be a promise treatment technique for removal of PFOS (high adsorptive capacity at < 1 mg/l)

- PFOS is susceptible to biomimetic reductive dehalogenation by cobalamin/Ti(III) citrate.

- Microbial reductive defluorination of PFOS might be possible

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