DECOMPOSITION OF PERFLUOROOCTANOIC ACID PHOTOCATALYZED BY TIO₂: CHEMICAL MODIFICATION OF THE CATALYST SURFACE INDUCED BY FLUORIDE IONS



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4L PROT

PERFLUOROOCTANOIC ACID

Perfluorooctanoic acid (PFOA) is one of the most largely employed industrial surfactant [1]. Recent studies have shown the presence of high levels of this compound in the environment, particularly in seas and rivers.

PFOA has been found to be bioaccumulative, carcinogen, liver and immune system toxicant and able to exert hormonal effects [2].

PFOA degradation through photocatalytic TiO₂



PFOA is listed as persistent organic pollutant and nowadays US-EPA (Environmental Protection Agency) and EEA (European Environment Agency) are taking action to minimize the emission of PFOA in the environment [3].

EXPERIMENTAL APPARATUS





FLUORIDE IONS BALANCE







FT-IR spectra of titanium dioxide catalyst at different reaction times (*) C-F stretching; (+) COO symmetric stretching.

yield 10 [**F**-] $\eta_{F} =$ 15 · [PFOA] 100 150 200 Time (min) F⁻ yield (%) at different light intensity 35 → W = 75 W/m2 30 —**■**— W = 95 W/m2 25 ۶ 20 **Xield** 15

Time (min)

Ionic Chromatography analyses - Kinetic curves of [F⁻] growth related to PFOA degradation.

CONCLUSIONS

Highest PFOA degradation rates with:

 \blacktriangleright PFOA and its by-products were present on the

Ti 2p region XPS spectra of titanium dioxide catalyst: after 4 h (A); after 9 h reaction (B); after 9 h reaction and after suspension in fluorinated solvent (C).

- [PFOA] < CMC (Critical Micelle Concentration)</p> • $[TiO_2] = 1.00 \text{ g/L}$
- High radiation power, W = 95 W/m²
- > Formation of highly fluorinated and hydroxylated $TiO_{(2-x/2-y/2)}OH_{y}F_{x}$ species on the catalyst surface. These chemical modifications could limit the photocatalytic activity of TiO₂

in the surface first hours catalyst of photodegradation, while after longer reaction times the intensity of FT-IR peaks was evidently decreased.

 \succ A *plateau* in F⁻ yield (%) was reached, working at the optimal degradation reaction conditions; this phenomenon could be related to the chemical modifications of the TiO_2 surface

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