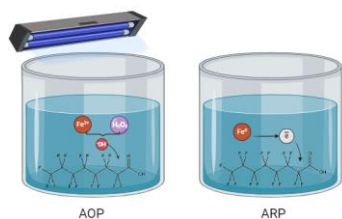


Degradation of polyfluorinated substances by oxidative and reductive process

David Luiz Arruda da Silva¹, Raquel Fernandes Pupo Nogueira¹. (1) São Paulo State University (UNESP), Institute of Chemistry, 14800-060 Araraquara, SP, Brazil.

POSTER
Ph.D. Student: N
Journal: NONE



Polyfluorinated substances are organic pollutants which are very resistant to conventional wastewater treatments processes. Advanced Oxidative and reductive process generate hydroxyl radicals and hydrated electrons, respectively, which may promote pollutants degradation. In this scope, the present study evaluated the photo-Fenton process with iron salts and reductive process using zero valent iron (ZVI) under anoxic conditions to degrade perfluorooctanoic acid (PFOA). For a period of 300 minutes of experiment, the photo-oxidative process proved to be more efficient than reductive process, achieving rates close to 55% degradation and 7% defluorination.

Introduction

Polyfluorinated compounds are substances with carbon chain linked to fluorine atoms. These compounds were listed as new persistent organic pollutants (POPs) at the Stockholm convention. The production of per and poly fluoroalkyls (PFAS), the main representatives of this class, began in 1940^[1]. Since then, these substances are used in many products such as cosmetics and automobile, and mainly as precursors in the manufacture of Teflon. The strong C-F bond (536 kJ mol^{-1}) is one of the characteristics that makes PFAS molecules difficult to degrade. Conventional treatment processes cannot eliminate PFAS, while physical removal require a post treatment^{[2],[3]}.

Given the structural character of PFAS, an oxidative and reductive processes were compared to evaluate the feasibility of degradation of perfluorooctanoic acid (PFOA), mediated by hydroxyl radicals, generated in a photo-Fenton process, and e_{aq}^- generated by zero valent iron (ZVI) under anoxic conditions, respectively.

Material and Methods

Degradation experiments were performed in 250 mL of ultrapure water enriched with 10 mg L^{-1} PFOA. In photo-Fenton oxidative process, the degradation experiments were carried out with H_2O_2 10 mmol L^{-1} , comparing iron II/III salts and ferrioxalate complex (FeOx) at a concentration of 0.2 mmol L^{-1} . In addition, magnetite as a catalyst, at a concentration of 0.125 g L^{-1} was also evaluated for comparison. In the reductive process, ZVI 200 mesh at 0.125 g L^{-1} and 0.250 g L^{-1} , under N_2 flow 1 L min^{-1} were compared. All experiments were carried out at pH 3.0. Degradation efficiency of PFOA was monitored using high performance liquid chromatography (HPLC) coupled to DAD detector (210 nm) and defluorination was monitored using potentiometry with fluoride selective electrode.

Results and Discussion

It was observed that under the conditions applied,

photo-Fenton oxidation using soluble iron achieved much higher efficiency than the reductive process using ZVI (Figure 1).

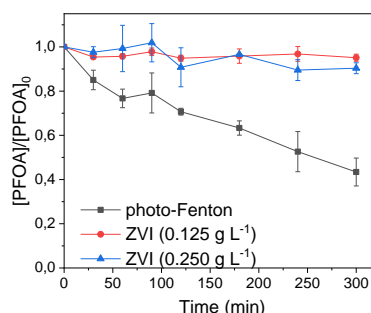


Figure 1: PFOA degradation in photo-Fenton and ZVI process. Oxidative conditions: $0.2 \text{ mmol L}^{-1} \text{ Fe(II)}$, $10 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$, under UVC irradiation; Reductive conditions: 0.125 or 0.250 g L^{-1} ZVI under N_2 flow 1 L min^{-1} ; In both cases PFAS: 10 mg L^{-1} ; pH 3.0.

It has been reported that hydroxyl radicals generated in photo-Fenton process may attack PFOA to remove the carboxylic head^[4]. In the case of reductive processes, the hydrated electrons are responsible for the cleavage of C-F bond^[4]. However, Lyu and coworkers^[5] showed that part of electrons generated are consumed by other species in the reaction medium, decreasing its efficiency for PFOA degradation, even when the ZVI concentration was doubled.

Irradiation induces charge transfer between HOMO and LUMO orbitals weakening the C-F bond by stretching^[6] favoring the attack of hydroxyl to the carboxylate head of the molecule in the photo-Fenton oxidative process. Therefore, UVC irradiation was crucial for degradation, in the absence of which no oxidation occurred. However, UVC irradiation alone did not lead to significant degradation of PFOA as well as UVA (Figure 2).

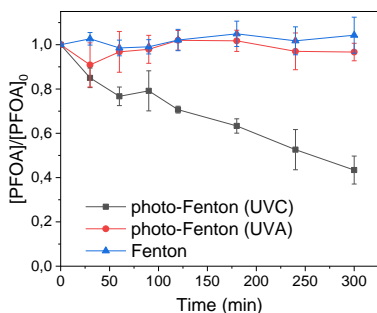


Figure 2: Comparison between photo-Fenton process with UVC irradiation, UVA irradiation and without irradiation. Conditions: PFOA 10 mg L⁻¹, Fe²⁺ 0.2 mmol L⁻¹, H₂O₂ 10 mmol L⁻¹, pH 3.0.

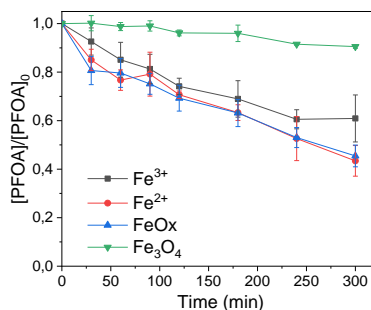


Figure 3: PFOA degradation in photo-Fenton process varying the iron source. Conditions: PFOA 10 mg L⁻¹, iron 0.2 mmol L⁻¹, H₂O₂ 10 mmol L⁻¹, UVC irradiation and pH 3.0.

Considering the positive results of photo-Fenton process, other sources of iron were used to catalyze the decomposition of hydrogen peroxide into hydroxyl radicals to compare with the photo-oxidative process using iron II salt (Figure 3). Magnetite was applied with the aim of degradation PFOA without generating iron sludge. However, there was no successful degradation with heterogeneous process using Fe₃O₄.

Considering that the fluoride generated can complex Fe³⁺ ions (log K = 5.18) interfering with the availability of iron for the Fenton process, the ferrioxalate complex was used as iron source for generation of Fe²⁺ under irradiation^[7]. Degradation using FeOx and Fe(II) were very similar and slightly more efficient than degradation using Fe(III) (Figure 3).

The data obtained when comparing the iron sources, indicated that under the conditions tested, the use of soluble iron can be more efficient than heterogeneous degradation using a magnetite as catalyst. Moreover, the processes with soluble iron resulted in only 7% defluorination (25 μmol L⁻¹) after 5 h, concentration eight times lower than the concentration of iron salt used, resulting in no significant interference of fluoride in the degradation process which was similar using iron salts and FeOx.

Conclusions

This study showed that the degradation of perfluorooctanoic acid occurs through the oxidative process at higher extent than the reductive process, under the conditions experienced. Furthermore, the photo-Fenton process for PFOA degradation was not efficient under mild conditions such as the use of UVA irradiation, requiring the application of the more energetic UVC irradiation. The heterogeneous process was not feasible for the degradation of such recalcitrant contaminant as PFOA.

Acknowledgments

CNPq and CAPES.

References

- [1] Viberg. H, Erikson. P, Perfluorooctane sulfonate and perfluorooctanoic acid. In Reproductive and Developmental Toxicology, Academic Press, 2017, p. 811.
- [2] Da Silva-Rackov. C. K. O, et al, Applied Catalysis B: Environmental, v.192 (2016), p. 253.
- [3] Dadashi Firouzjaei. et al. Environmental Chemistry Letters, v.20 (2022), p. 661
- [4] Alalm. G, M, Boffito. D. C. Chemical Engineering Journal, v. 450 (2022), part 4
- [5] Lyu. X. J, et al, Scientific Reports, v.5 (2015), p.9353
- [6] Yamijala. S. S. R. K. C. et al, Journal of Hazardous Materials, v. 423 (2022), part A.
- [7] Nogueira. R. F. P, et al. Química Nova, v. 30 (2007), p. 400