Chemical Engineering Journal 357 (2019) 698–714

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Application of ionizing radiation in decomposition of perfluorooctanoate (PFOA) in waters

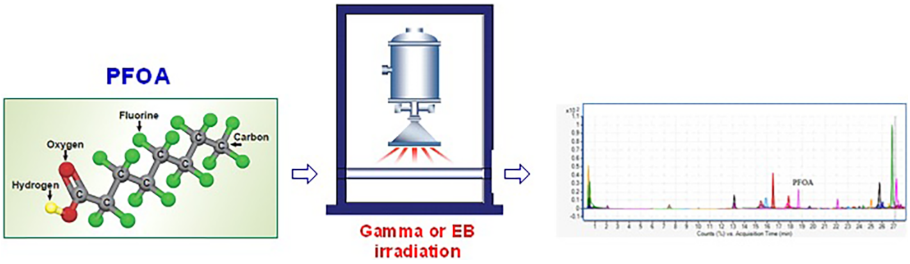
Marek Trojanowicz[a,b,*], Iwona Bartosiewicz[a], Anna Bojanowska-Czajka[a], Krzysztof Kulisa[a], Tomasz Szreder[a], Krzysztof Bobrowski[a], Henrietta Nichipor[c], Juan F. Garcia-Reyes[d], Grzegorz Nałęcz-Jawecki[e], Sylwia Męczyńska-Wielgosz[a], Joanna Kisała[f]

[a] *Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland*
[b] *Department of Chemistry, University of Warsaw, Pasteura 1, 02-092 Warsaw, Poland*
[c] *Institute of Radiation Physical and Chemical Problems, National Academy of Sciences of Belarus, Minsk, Belarus*
[d] *Faculty of Physical and Analytical Chemistry, University of Jaen, Jaen, Spain*
[e] *Department of Environmental Health Sciences, Medical University of Warsaw, Warsaw, Poland*
[f] *Faculty of Biotechnology, University of Rzeszów, Rejtana 16C, 35-959 Rzeszów, Poland*

HIGHLIGHTS

- Gamma and electron beam irradiation effective under reductive conditions.
- Strong effect of dose-rate observed in electron beam (EB) irradiation.
- Support of radiolytic decomposition by formate or nitrate in treated PFOA solutions.
- EB irradiation decomposes PFOA in seconds at initial ppm level.
- A successful kinetic modeling can be carried out based on known rate constants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Perfluorooctanoate
Advanced oxidation/reduction processes
Ionizing radiation
Water treatment

ABSTRACT

It has been demonstrated through the use of both gamma-rays and beam of accelerated electrons (EB) for the radiolytic decomposition of PFOA in diluted aqueous solutions that the most reactive species among the products of water radiolysis are hydrated electrons e_{aq}. The reaction of PFOA with the hydrated electrons takes place with the largest yield in strongly alkaline deaerated solutions.

The PFOA decomposition performed at an initial concentration level of 1 mg/L by γ-irradiation requires the use of absorbed doses below 10 kGy, which, depending on the activity of employed ^{60}Co source, requires 2–3 h irradiation time. Similar results were obtained at pH 12 in the presence and also in the absence of *t*-butanol in the treated solutions. In the case of EB irradiation in a wide range of the absorbed doses (up to 100 kGy), a very pronounced effect of the dose-rate was observed, which can be attributed to various recombination reactions of the products of water radiolysis. A significant improvement in the yield of the PFOA decomposition by EB irradiation can be observed in the presence of trace amounts of nitrate or 100 mM of a formate in the treated solutions. In optimized conditions, about 70–80% decomposition of the initial level of 1 ppm of PFOA can be obtained with an irradiation using 100 kGy absorbed dose, which corresponds to about 5 s treatment with the

---

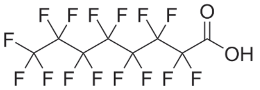
* Corresponding author at: Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland.
E-mail address: trojan@chem.uw.edu.pl (M. Trojanowicz).

https://doi.org/10.1016/j.cej.2018.09.065
Received 17 July 2018; Received in revised form 5 September 2018; Accepted 8 September 2018

use of an employed electron accelerator. The acute toxicity measurements and a kinetic modeling are presented, together with a suggestion of the mechanism of radiolytic decomposition of PFOA.

1. Introduction

Due to high chemical and thermal resistance and large surface tension, perfluoroalkyl compounds (PFCs) are widely applied as industrial detergents, components of fire-fighting foam preparations, impregnating agents for textiles, leather and paper, as well as components of cosmetics and personal care products [1]. Their exceptional chemical inertness was, most probably, the main reason why there has been a lack of interest in them from both environmental and health points of view for many decades. As reported at the beginning of this century, the unexpected observation of their common presence in wildlife, both in urbanized areas and in remote places such as the North Pacific Ocean or Arctic [1], initiated an exponential increase in interest in these compounds. Further intense environmental studies on PFCs conducted by numerous research groups confirmed their common occurrence in the environment [2]. The release from the production of fluoropolymers was assigned to the historical emissions of perfluoroalkyl carboxylic acids, which are one of the most commonly occurring groups of PFCs [3]. Thorough environmental and toxicological studies have shown that they are persistent and bio-accumulative pollutants with numerous adverse effects on human health. The two most commonly occurring species are perfluorooctanoic acid/perfluoro-octanoate (PFOA) and perfluorooctane sulfonic acid/perfluorooctane sulfonate (PFOS) and the first one will be the main subject of this paper.



Perfluorooctanoic acid
(PFOA)

Common occurrence of PFOA in natural waters together with its exceptional stability have triggered wider investigation of PFCs content in drinking water produced with the use of different treatment methods. Early studies of drinking waters in Germany [4], USA [5], China and some other countries [6] have shown that the level of both PFOA and PFOS in numerous places exceeds drinking water guideline values recommended by various regulatory institutions, which are usually in the concentration range between 0.1 and 0.5 µg/L [7]. Recent US Environmental Protection Agency established the health advisory level of the combined concentrations of PFOAs and PFOS in drinking water as 0.07 µg/L [8].

All briefly abovementioned data indicate the need for searching for more efficient methods for the removal of PFCs in water and wastewater treatment technologies for the production of drinking water. It can be also admitted that in the studies of several US full-scale water treatment systems was found, the ozonation, UV-irradiation, UV-H_2O_2 treatment or chlorination is mostly ineffective in the removal of PFCs [9], although the data collected from different sources on the effect of ozonation, carried out together in configuration with various other steps are truly ambiguous [10]. Lack of effectiveness of some Advanced Oxidation Processes (AOPs) can also have an additional cause, which is a potential formation of perfluorinated carboxylic acids (PFCAs) as a result of the oxidation of fluorotelomers occurring in surface waters [11].

Investigations on application of different AOPs and also other advanced reduction processes which can be combined as AO/RPs, for the decomposition of PFCs for environmental purposes and water and wastewater treatment have been carried out from the early 2000s. Their large intensity and diversity is reflected also in several review papers [12–17]. Generally, these methods can be described as processes based on the reactions of target pollutants with free oxidizing or reducing radicals, which are formed in-situ, or with hydrated electrons.

Decomposition of PFOA can be carried out both by radical oxidation and by reduction with hydrated electrons. Some examples of selected AO/RPs, which exhibit particular efficiency among different groups of processes and which have been reported in the literature, are showed in Table 1. Much more information about the developed methods one can find in the above-mentioned reviews. Their comparison is difficult since the initial PFOA concentrations investigated differed in the range exceeding two orders of magnitude. The comparison related to the energy consumption [18] indicates photocatalytic decomposition with In_2O_3 nanoparticles [19], and electrochemical oxidation to be the most favorable [20]. Among all the listed methods, application in the treatment of the real medium such as wastewater was reported only for ozonation in the presence of H_2O_2 [21].

Over the recent decades, an increasing number of applications in the environmental protection can be found for the use of ionizing radiation. Irradiation of target media with the electron beam (EB) obtained from the electron accelerators of different types and power, or gamma-rays from different isotope sources (usually ^{60}Co or ^{137}Cs), can be employed for disinfection of wastewaters and sludges, removal of organic pollutants and heavy metal ions from waters and wastewaters or removal of

Table 1
Application of selected Advanced Oxidation/Reduction Processes for decomposition of PFOA in aqueous media.

Type of AO/RP	Conditions of treatment	Treated media	Initial PFOA concentration, mg/L	Time required for 90% decomposition, min	Rate-constant $^{a)}$, min^{-1}	Reference
Photochemical	254 nm, with sulfite	DW $^{b)}$	8.3	30	–	Song et al. [32]
Photocatalytic	254 nm, with In_2O_3 nanoparticles	DW	30	15	0.158	Li et al. [33]
Ozonation	With H_2O_2, at pH 11	DW, industrial wastewater	5.0	30	0.0716	Lin et al. [21]
Electrochemical	Ti/SnO_2-Sb-Bi electrode	DW	41	90	0.322	Zhuo et al. [20]
Sonolysis		DW	0.10	60	0.041	Vecitis et al. [34]
Fenton	With 0.6 g/L humic acid	DW	41	25	–	Santos et al. [35]
Wet oxidation	With 50 mM persulfate at 80 °C	DW	1.5	~90	0.023	Hori et al. [36]
DC plasma	Plasma generated within gas bubbles	DW	50	N/A	N/A	Yasuoka et al. [37]
Ionizing radiation	γ-irradiation in N_2 saturate solution pH 13	DW	20	~220	0.011	Zhang et al. [30]
	EB, deaerated 0.1 mM phosphate buffer with 20 mg/L nitrate	DW	0.5	0.017$^{c)}$	N/A	Wang et al. [31]

a) Rate-constants for pseudo-first order reaction, b) pure solution in distilled water, c) data for 90% defluorination.
N/A – data are not available.