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INVESTIGACIÓN E INNOVACIÓN EN INGENIERÍA

REVIEW ARTICLE

Perfluoroalkylated Substances as Emerging Contaminants of concern without a viable treatment landscape: Review

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ABSTRACT
Perfluoroalkyl acids (PFAAs) are a group of synthetic persistent chemicals with distinctive properties, such as a high thermal and chemical stability, that make them suitable for a wide range of applications. They have been produced since the 1950s, resulting in a global contamination of the environment and wildlife. They are resistant to biodegradation and have the tendency to bio-accumulate in organisms and bio-magnify in the food chain. Poly and perfluoroalkyl substances (PFASs) have been widely used in many industrial and consumer products. This research presents the problems associated with PFASs emerging pollutants (Emerging Contaminants, EC), their effects on the environment due to bioaccumulation, detection methods and the conventional and non-conventional technologies with which they are treated. A review of the most relevant studies of recent years was carried out. It was found that conventional technologies based on adsorption are widely used, mainly with activated carbons, with pollutant removal efficiencies of up to 95%. However, other technologies such as supercritical fluids and membranes are not sufficiently effective, so more efficient alternatives are required. Advanced oxidation technologies were found to be a valid sustainable option for the treatment of these contaminants.

Keywords: Advanced oxidation processes, Bioaccumulation, Conventional treatments, Perfluoroalkyl acids.

Sustancias perfluoroalquiladas como contaminantes emergentes preocupantes sin un panorama de tratamiento viable: revisión

RESUMEN
Los ácidos perfluoroalquílicos (PFAA) son un grupo de sustancias químicas sintéticas persistentes con propiedades distintivas, como una gran estabilidad térmica y química, que los hacen adecuados para una amplia gama de aplicaciones. Se producen desde la década de 1950, lo que ha provocado una contaminación global del medio ambiente y la fauna. Son resistentes a la

How to cite this article: L. Manrique Losada, M. Mueses, "Perfluoroalkylated Substances as Emerging Contaminants of concern without a viable treatment landscape: Review", *Ing-Nova*, vol. *3*, no. 1, pp. 48-60, ene. 2024. https://doi.org/10.32997/rin-2024-4677

Received 19 de diciembre de 2023
Reviewed: 28 de diciembre de 2023
Accepted: 10 de enero de 2024

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Editor: Miguel Ángel Mueses. Universidad de Cartagena-Colombia.

Universidad Editorial Universitaria de Cartagena

biodegradación y tienen tendencia a bioacumularse en los organismos y biomagnificarse en la cadena alimentaria. Las sustancias poli y perfluoroalquiladas (PFAs) se han utilizado ampliamente en muchos productos industriales y de consumo. Esta investigación presenta los problemas asociados a los PFASs contaminantes emergentes (CE), sus efectos en el medio ambiente debido a la bioacumulación, los métodos de detección y las tecnologías convencionales y no convencionales con las que se tratan. Se realizó una revisión de los estudios más relevantes de los últimos años. Se constató que las tecnologías convencionales basadas en la adsorción son ampliamente utilizadas, principalmente con carbones activados, con eficiencias de eliminación de contaminantes de hasta el 95%. Sin embargo, otras tecnologías como los fluidos supercríticos y las membranas no son suficientemente eficaces, por lo que se requieren alternativas más eficientes. Las tecnologías de oxidación avanzada resultaron ser una opción sostenible válida para el tratamiento de estos contaminantes.

Palabras clave: Ácidos pefluoroalquilicos, Bioacumulación, Procesos avanzados de oxidación, Tratamientos convencionales.

1. Introduction

Perfluoroalkyl acids (PFAAs) are a group of synthetic persistent chemicals with distinctive properties, such as a high thermal and chemical stability, that make them suitable for a wide range of applications. They have been produced since the 1950s, resulting in a global contamination of the environment and wildlife. They are resistant to biodegradation and have the tendency to bio-accumulate in organisms and bio-magnify in the food chain [1].

Poly and perfluoroalkyl substances (PFASs) have been widely used in many industrial and consumer products. They have been detected ubiquitously in ambient water along with other environmental matrices, and their adverse effects on aquatic organisms have been a subject of active investigation. PFAA toxicity appears to be influenced by the sex and developmental stages of aquatic organisms, but not significantly by exposure route. PFAA-induced aquatic toxicity could be classified as metabolism disturbance, reproduction disruption, oxidative stress, developmental toxicity, thyroid disruption, etc. At the molecular level, these responses can be initiated by key events, such as nuclear receptor activation, reactive oxygen species induction, or interaction with a membrane, followed by a cascade of downstream responses. PFAA-induced toxicity involves diverse metabolic processes, and therefore elucidating crosstalk or interactions among diverse metabolic pathways is a challenging task [2].

Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA) are the most representative of a rising class of persistent organic pollutants perfluorochemicals and considered as environmental contaminants which are very persistent in the environment [3]. PFASs are potential reproductive and developmental toxicants and are considered to be endocrine disrupters. These compounds have been found with greater frequency in fish and other seafood compared to other food groups [4]. Research pertaining to exposure of humans to per- and polyfluorinated alkyl substances (PFASs) has received considerable public and regulatory attention in recent years. Although several studies have reported exposure to PFASs by populations in North America and western Europe, such information is still scarce in Latin America, including Brazil. The studies suggest that blood concentrations of PFASs and their effect on fetal growth in pregnant women, for example [5].

The chemical stability of the PFASs molecules is due to the elemental characteristics of the fluorine atom, which admit replacing an alkyl chain by a perfluoroalkyl or polyfluorinated chain in a molecule or polymer. The physicochemical properties and combinations thereof of poly and perfluoroalkyl substances (PFASs) include, extreme hydrophobic and lipophobic character; thermal and chemical stability in extreme conditions; remarkable aptitude to self-assemble into sturdy thin repellent protecting films. Other properties include unique spreading, dispersing, emulsifying, anti-adhesive and levelling, dielectric, piezoelectric and optical properties, leading to numerous industrial and technical uses and consumer products. However, that PFASs with seven or more carbon-long perfluoroalkyl chains had disseminated in air, water, soil and biota worldwide, are persistent in the environment and bioaccumulative in animals and humans, raising serious health and environmental concerns. Further use of long-chain PFASs is environmentally not sustainable. Fluorosurfactants become less effective and less efficient, provide lesser barrier film stability, etc. On the other hand, they remain as persistent in the environment as their longer chain homologues [6].

Recent studies of perfluoroalkylated substances in different place of the word have focused on the toxicity of long chain PFASs, such as PFOS or PFOA, which have been demonstrated to cause an array of developmental and behavioral effects. However, less is known about low molecular weight PFASs and alternatives [7]. In the Table 1, we show the most important reports about the problematic with this substances.

Table 1. Main studies about PFASs around the word.

Study	Country/Region	Ref.
The contamination of tiger sharks (Galeocerdo cuvier) and bull sharks (Carcharhinus leucas) by legacy persistent organic pollutants (POPs) and emerging organic contaminants was investigated in specimens from Reunion Island (Southwest Indian Ocean) in 2018 and 2019. Contamination levels were determined in the muscle of adult individuals of both sexes in relation to biological and trophic parameters. The results show that organic contaminant levels in the studied species were lower than those of other shark species in the Southern Hemisphere, related to the limited urbanization and industrialization of Reunion Island.	Southwest Indian Ocean	[8]
Perfluoroalkyl substances is a growing class of contaminants in the Arctic environment, and include the established perfluorinated sulfonates (PFSAs; especially perfluorooctane sulfonate (PFOS)) and carboxylic acids (PFCAs). PFSAs and PFCAs of varying chain length have been reported to bioaccumulate in lipid rich tissues of the brain among other tissues such as liver, and can reach high concentrations in top predators including the polar bear. PFCA and PFSA bioaccummulation in the brain has the potential to pose neurotoxic effects and therefore we conducted a study to investigate if variations in neurochemical transmitter systems i.e. the cholinergic, glutaminergic, dopaminergic and Gabaergic, could be related to brain-specific bioaccumulation of PFASs in East Greenland polar bears. Results support the hypothesis that PFAS concentrations in polar bears from East Greenland have exceeded the threshold limits for neurochemical alterations.	East Greenland/Artic	[9]

The Greenlandic Inuit have high blood concentrations of environmental persistent organic pollutants (POPs) (15 perfluoroalkylated substances (PFASs)). High concentrations have been associated with age, smoking and consumption of marine mammals. Studies have indicated that exposure to POPs during pregnancy may adversely affect fetal and child development. To assess geographical differences in diet, lifestyle and environmental contaminant exposure among pregnant women in Greenland, blood samples and questionnaire data were collected from 207 pregnant women in five Greenlandic regions (North, Disco Bay, West, South and East). PFASs were significantly associated with PCBs and OCPs in most of the regions. In the North region, PFASs were associated with both selenium and mercury. The detection of POPs and heavy metals in maternal blood indicates fetal exposure to these compounds possibly influencing fetal development.	Greenland/Artic	[10]
On the Antarctic environment the investigations were done, too, using concentrations of 9 organophosphate esters (OPEs), 16 perfluoroalkylated substances (PFASs) and 17 polycyclic aromatic hydrocarbons (PAHs) in summer 2016. Occurrence and profiles of the indicators of OPEs, PFASs and PAHs, as well as air mass back-trajectory analysis provided direct evidences of human activities on Concordia station and posed obvious impacts on local environments. Nevertheless, the exchange processes among different environmental matrices may drive the long-range transport and redistribution of the legacy and emerging Organic contaminants from coast to inland in the Antarctic.	Antarctic Region	[11]
The presence of PFASs in three European countries (Belgium, Italy and Spain) was evaluated including perfluoroalkane sulfonic acids (PFSAs), perfluoroalkyl carboxylic acid (PFCAs) and perfluoroalkane sulfonamides (PFOSAs). The three countries presented similar PFAS levels ranging from 3.13 to 155 ng/g, but in all cases PFCAs concentrations were higher than those obtained for PFSAs (2.30, 1.76 and 2.68 ng/g). The previously published data exhibited an increase in perfluorobutanesulfonate (PFBS) concentrations in Belgian and Italian house dust. Main findings revealed a positive association between PFOS concentrations and the building edification age, which could highlight a decrease in the use of this chemical in Europe. Similarly, perfluorohexanesulfonate (PFHxS) levels correlated with the percentage of the floor covered by textiles. Homes located in industrial sites showed higher PFCA levels compared to urban or agricultural locations, revealing the industrial processes as a potential source of these chemicals in Europe.	Belgium, Italy and Spain/Europe	[12]
In Reus (Spain), the prenatal exposure study to perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in a cohort of pregnant women was done. These chemicals were biomonitored in maternal plasma during the first trimester of pregnancy, at delivery, and in cord blood. The dietary exposure of PFOS and PFOA was estimated by using questionnaires of food frequency and water intake, as well as data on food levels previously reported in the same area. In addition, the exposure through air inhalation and indoor dust ingestion was also calculated. Traces of PFOS were found in all samples in the trimester and at delivery, and almost in all cord blood samples. Transplacental transfers of PFOS and PFOA were estimated to be around 70% and 60%, respectively.	Tarragona County/Catalonia /Spain	[13]

In Antwerp, Belgium bird eggs were used to determine and monitor PFAAs levels in the terrestrial environment. The concentrations and composition profile were stableshed of 12 PFAAs (4 perfluoroalkyl sulfonic acids (PFSAs) and 8 perfluoroalkyl carboxylic acids (PFCAs) in the eggs of great tits (Parus major) collected at a fluorochemical plant close to Antwerp (from 1 to 70 km). The PFSA concentrations measured were among the highest ever reported in eggs with median concentrations of 10380 ng/g (extrapolated), 99.3 ng/g and 47.7 ng/g for PFOS, PFHxS and PFDS respectively. Furthermore, the median concentration of 19.8 ng/g for PFOA was also among the highest ever reported in bird eggs.	Antwerp, Belgium	[14]
A retrospective cohort study has been developed including all singleton live births reported in the Veneto Region Birth Registry between 2003 and 2018 to mothers living in the contaminated and in a control area. We estimated the association between mothers' area of residence and severe Small for gestational age (SGA) using crude RR (and 95% CI) and stepwise logistic regression, including all the maternal characteristics. The occurrence of severe SGA was 3.44% in the contaminated area and 2.67% in the control area. The findings suggest that living in a contaminated area by PFAS plays a role in affecting fetal growth and support the hypothesis that PFAS exposure is a risk factor for SGA.	Veneto/ North-East of Italy	[15]
The report of PFASs levels in human milk, infant formulas and baby food (dry cereals and pots) from the Valencian Community (Spain) in order to evaluate the infant exposure to these substances through the diet was done. The results show that perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA) were in all the samples of the four selected matrices (except PFOA in one sample of dry cereal baby food). This study does not report the effect of these substances on the human health.	Valencian Community/Spain	[16].
In a case study based on prospective data from Danish women, the main effect of exposure of serum perfluoroalkylated substances (PFASs) on the risk to breast cancer was analized. The study population consisted of 178 breast cancer cases and 233 controls (tabnulliparous and frequency matched on age) nested within the Danish National Birth Cohort (DNBC), which was established in 1996-2002. Serum levels of 10 perfluorocarboxylated acids (PFCAs), 5 perfluorosulfonated acids (PFSAs) and 1 sulfonamide (perflurooctane-sulfonamide, PFOSA) were measured. The results indicate that the exposure to these substances can development of breast cancer.	Denmark/Europe	[17]
In the Swedish population, 17 PFASs were measured, of which the vast majority lacks human health risk assessment information using the Hazard Index (HI) approach. Swedish biomonitoring data (blood/serum concentrations of PFASs) were used and two study populations identified: 1) the general population exposed indirectly via the environment and 2) occupationally exposed professional ski waxers. The results showed that PFASs concentrations were in the low ng/ml serum range in the general population, reaching high ng/ml and low µg/ml serum concentrations in the occupationally exposed. The risk characterization showed no concern for hepatotoxicity or reproductive toxicity in the general population except in a subpopulation eating PFOS-contaminated fish, illustrating that high local exposure may be of concern. For the occupationally	Sweden/Europe	[18]

exposed there was concern for hepatotoxicity by PFOA and all congeners in combination as well as for reproductive toxicity by all congeners in combination, thus a need for reduced exposure was identified. Concern for immunotoxicity by PFOS and for disrupted mammary gland development by PFOA was identified in both study populations.		
This this study considered effects of PFAs on Frenche metropolitan population with internal exposure due of high consumers of fresh water fishes. The results showed that analyses of blood serum samples provided the internal concentration of 14 PFAS, considering only molecules for which the detection frequency were above 80% in blood were considered, i.e., PFOS, PFOA, PFHxS, PFNA, PFHpS, and PFDA. For PFOS, the results obtained showed high concentration of these sustances confirmed an over-exposure of the individuals and the high risk for the health.	France/Europe	[19]
The objective of this study was to assess the levels of poly- and perfluoroalkyl substances (PFASs) in different compartments of the Tana Lake (water, sediment, and fish muscle tissue), and its implications for human exposure. The results showed higher PFAS concentrations in piscivorous fish species (Labeobarbus megastoma and Labeobarbus gorguari) than non-piscivorous species (Labeobarbus intermedius, Oreochromis niloticus and Clarias gariepinus) and also spatial distribution similarities. The relative risk (RR) indicates that the consumption of fish contaminated with perfluorooctane sulfonate (PFOS) will likely not cause any harmful effects for the Ethiopian fish eating population. However, mixture toxicity of the sum of PFASs, individual fish consumption patterns and increasing fish consumption are important factors to consider in future risk assessments.	Lake Tana/ Ethiopia/ Africa	[20]
In the study, the distribution of metals and PFASs in fish, invertebrates, sediment and water, collected at two different years at multiple important water reservoirs for domestic and industrial purposes, in the aquatic environment near Morogoro, Tanzania, were presented. Furthermore, the possible risks for human health through consumption of contaminated fish and shrimp is analyzed. Concentrations of multiple metals exceeded water and sediment quality guidelines values. Furthermore, PFOS, PBDE and HCB concentrations exceeded biota quality standard values, suggesting an ecological risk caused by these metals and PFASs in the aquatic environment around Morogoro. The results suggest that potential health effects through consumption of contaminated shrimp, and to minor extent fish, are expected.	Morogoro/ Tanzania/Africa	[21]

The concern of many researchers globally regarding bioaccumulation and the risk that these emerging pollutants represent for human life and aquatic animals is evident (Table 1). This problematic has made many researchers focus their research on studying and understanding these substances, therefore the number of publications about PFAS are increased in the last three decade (See Fig. 1).

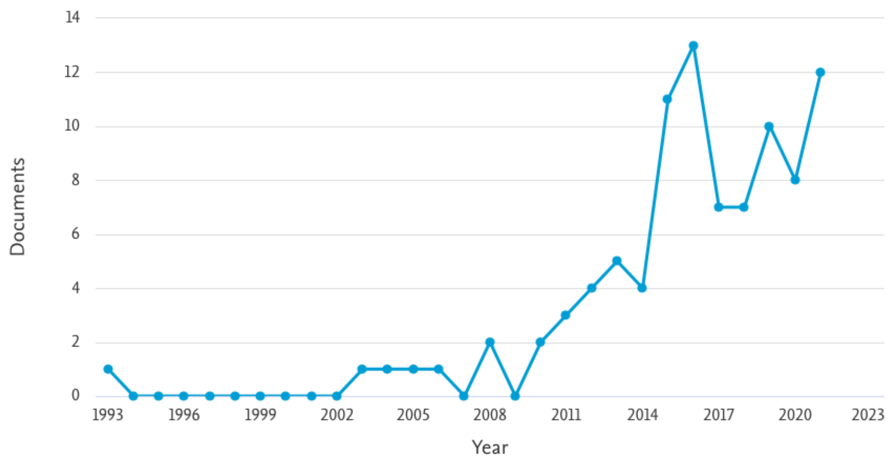

Fig. 1. Number of documents per year for publications about Poly and perfluoroalkyl substances. Source: SCOPUS

The areas of interest of these studies are representative in order to help the environment. In the Figure 2 we present the trends on publications in function of the application area. It is evident that environmental science, chemistry, biochemistry and toxicity are the more important areas between researchers. However, most of the publications and reports are aimed at evidencing the effects of these substances on the health of humans, animals and ecosystems in general; which is very valuable, but it is necessary to establish a solution or treatment route that helps mitigate its effects on the environment, none of them show a possible solution to the problem of PFAs.

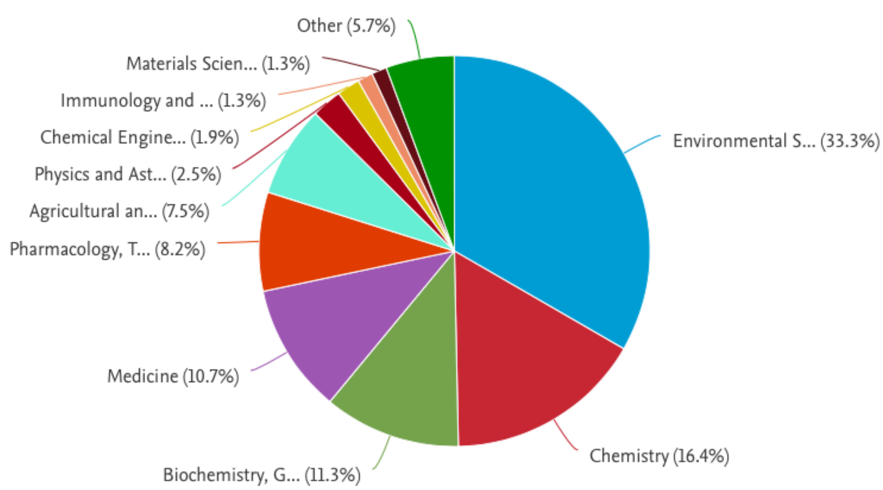

Figure 2. Trends of study of PFAS in function of application areas. Source: SCOPUS

2. Conventional methods of detection of the PFAS

The presence of emerging pollutants in the aquatic environment in relatively small concentrations and the fact that they cannot be removed by conventional water/wastewater treatment processes bring new challenges in terms of adequate selection of technologies from the technical, economic and environmental points of view. Generally, literature discusses emerging pollutants' removal at significant concentrations (such as those in wastewater), while few studies consider their low concentrations occurring in raw water.

PFOS and PFOA blood levels are commonly used as biomarkers of human environmental exposure to these compounds. Many biomonitoring studies indicate 100% detection for PFOS and PFOA thus justifying a concern of possible risk for the most exposed individuals. Many studies addresses the predictive value of hazard quotients (HQs) calculated on the basis of serum PFOS and PFOA in male and female populations of reproductive age. HQs are calculated from the actual biomonitoring results and literature-based animal data linking toxicological outcomes and critical PFOS/PFOA serum levels. Uncertainty factors are applied to reflect interspecies differences and human variability. The HQ approach can help to interpret human biomonitoring data and thus serve as a valuable tool in further risk assessment priority settings and may also be used as a basis for taking decisions in risk management [22].

The most powerful and widely exploited method for this purpose is without a doubt LC/MS/MS, which allows the identification and trace quantitation of all species with detectability and resolution power depending on the particular instrumental configurations. The GC/MS is often employed for the monitoring of volatile fluorocarbons, confirming the formation of radicals in the processes of C–C and C–S bonds cleavage. For the direct monitoring of radicals participating in the reactions of PFCs decomposition, the molecular spectrophotometry is employed, especially electron paramagnetic resonance (EPR). The UV/Vis spectrophotometry as a detection method is of special importance in the evaluation of kinetics of radical reactions with the use of pulse radiolysis methods. The most commonly employed for the determination of the yield of mineralization of PFCs is ion-chromatography, but there is also potentiometry with ion-selective electrode and the measurements of general parameters such as Total Organic Carbon and Total Organic Fluoride [23].

Other technologies to detect long-chained perfluoroalkylated substances (i.e., PFOA, PFDA and PFOS) include the rapid small-scale column testing, activated carbon and fluorescence using UV absorbance, and liquid chromatography/mass spectrometry [24].

3. Conventional treatment

The removal of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from solid matrices has received considerable attention because of the environmental persistence, bioaccumulation, and potential toxicity of these compounds. Several technologies have been developed for PFAS remediation involving two main mechanisms: separation-concentration and destruction. The most widespread in-use technology is adsorption because it is reasonably affordable. Anion exchange resin and synthesized materials are the most effective sorbents having a sorption capacity of 100–2000 mg PFAS/g sorbent, effective within a few hours. The destruction technology such as plasma can also be a promising one for degrading PFAS to below health-based standard in 1 min. However, plasma is costly and not yet ready for full scale application [25].

Adsorption on granular activated carbon usually used to measure which is poorly effective requiring frequent replacement. Application of strong anion exchange resins (Purolite® A520E, A600E and A532E) are developed for the removal of traces of PFOA, PFOS, PFBA and PFBS. This technology is attractive for the possibility of reusing resins after an in-situ regeneration step. A strong relationship between the hydrophobicity of the exchange functional group of the resin and its capacity in removing PFAS exists. The volume of regeneration effluents requiring incineration can be efficiently reduced by more than 96.5% by using reverse osmosis coupled with under-vacuum evaporation [26].

Other technique for treatment of PFAS is the supercritical fluids; the methanol–modified supercritical carbon dioxide (Sc-CO2) is used for extraction and removal of PFOS and PFOA from solid matrices. The optimal conditions for treatment are under a pressure of 20.3MPa and a temperature of 50°C. Extraction time is between 30 and 70min. The extraction efficiencies (with double extractions) are close to 100% for PFOA and 80% for PFOS. The extraction efficiencies for sand are approximately 77% for PFOA and 59% for PFOS [27].

Particular relevance is given to the role of NMs in emerging contaminants (ECs) removal, as conventional remediation methods are not effective, and thus, literature suggests the adoption of membrane-base technology (e.g., nanofiltration), adsorption, and advanced oxidation processes (AOPs) for their removal. It`s because the main issues related to the detection, monitoring, and removal of a heterogeneous class of water pollutants, occurring in the range of concentration between few ng L^{-1} and μg L^{-1} and often referred to as ECs, are addressed by making reference to the use of nanomaterials (NMs) in the aforementioned processes. NMs employed in conservative methods (namely, nanofiltration and adsorption) are essentially nanoporous solids, among which activated carbon materials play a prominent role. Nonconservative methods, i.e., AOPs, seem more promising than conservative ones, as they allow (at least) partial degradation of the pristine pollutants into more biodegradable by-products, which can be further abated by subsequent biological treatments, whereas conservative methods are not enough efficient for the removal of pollutant small quantities and have to be regenerated [28], [29].

4. Advanced Oxidation Process as potential alternative of PFASs

Advanced Oxidation/Reduction Processes (AO/RPs) have become a sustainable alternative for the treatment of water contaminated with emerging pollutants [30], [31]. In spite of the difficult on the monitoring of AO/RPs for the evaluation of the yield and mechanisms of decomposition of perfluorinated compounds (PFCs) (this is mostly due to the formation of hundreds, or even thousands, of both intermediate and final products) the non-selective nature of AOPs is an advantage on the treatment [32]. The considered AO/RPs, involving free radical reactions, include photolytic and photocatalytic processes [33], Fenton/Photo-Fenton reactions [34], sonolysis [35], ozonation [36], application of ionizing radiation and several wet oxidation processes [37].

Mathematical modeling of the PFASs and degradation process can be an alternative for evaluation of the water treatment contaminated with pollutants. The molecular analysis, mechanisms of reaction, photonic efficiency, photoreactors and operational conditions are the main fields for evaluation of degradation process applied of PFAS substances [38].

Conclusions

The problematic associated with PFASs pollutants, their effects on the environment due to bioaccumulation, detection methods and the conventional and non-conventional technologies for treatment were presented. A critical analysis about the effects of these substances present in the water and its influence in human health were evidenced. Advanced oxidation technologies were found to be a valid sustainable option for the treatment of these contaminants as sustainable alternative for degradation and mitigation of the effects in the environment.

Glossary of abbreviatures

PFAA	Perfluoroalkyl acid
PFAAs	Perfluoroalkyl acids
PFASs	Poly and perfluoroalkyl substances
PFOS	Perfluorooctane sulfonate
PFOA	Perfluorooctanoic acid
PFSAs	perfluorinated sulfonates
PFCAs	Perfluorinated carboxylic acids
POPs	Persistent organic pollutants
PCBs	Polychlorinated biphenyls
PAHs	polycyclic aromatic hydrocarbons
PFBS	perfluorobutanesulfonate
PFHxS	perfluorohexanesulfonate
OCPs	Organochlorine pesticides
OPEs	organophosphate esters

Acknowledgement
Authors thanks to Universities of Cartagena and Amazonia for financial support. Prof. Manrique from the Universidad de la Amazonia thanks the financial support provided by MINCIENCIAS COLOMBIA through project No. 82476: "Implementación de estrategias para la recuperación de aguas residuales urbanas basadas en tratamientos solares y convencionales: Caso Florencia Caquetá, mayor centro poblado de la Amazonia Colombiana". Prof. Mueses thanks to Universidad de Cartagena for financial support through project No. 031-2022 “Desarrollo de una herramienta computacional basada en el método Monte Carlo para la caracterización de propiedades ópticas de fotocatalizadores”.

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