



Review

Photocatalytic degradation of perfluorooctanoic acid and perfluorooctane sulfonate in water: A critical review



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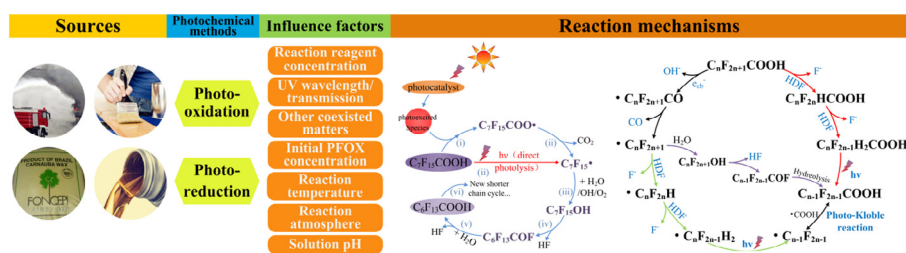
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HIGHLIGHTS

- The photochemical technologies for removing PFOX from water were summarized.
- Characteristics of PFOX photo-oxidation and photo-reduction processes were explored.
- Factors affecting the PFOX degradation and defluorination procedure were discussed.
- The PFOX photochemical degradation mechanisms were elucidated in details.
- The application prospects for PFOX photodegradation were suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are persistent organic pollutants in the environment and have serious health risks, including endocrine disrupting properties, immunotoxicity and developmental effects etc. The photochemical degradation has been proven to be a low-cost, efficient and sustainable technology for the removal of PFOX (X = A or S) in water. At present, most of the investigations have been conducted in ultrapure water and at concentrations much higher comparing to those detected in the real wastewaters. Furthermore, there are few studies about the toxicity of treated water. In this paper, the state of knowledge on the photocatalytic degradation of PFOX, including photo-oxidative and photo-reductive degradation, is reviewed comprehensively. Compared with photo-oxidation, photo-reduction appears to be more suitable for the PFOX removal since it is more favorable for the defluorination of PFOX and further complete mineralization. The effects of key parameters on the photocatalytic degradation and defluorination process of PFOX are commendably accessed, such as light wavelength, photocatalyst concentration, initial PFOX concentration, pH, reaction atmosphere,

Abbreviations: AIX, anion exchange resin; AOPs, advanced oxidation processes; GAC, granular activated carbon; HDF, hydrodefluorination; MWCNTs, multiple wall carbon nanotubes; NOM, natural organic matter; NPNSs, nanoporous nanospheres; PAC, powdered activated carbon; PBS, phosphate buffer solution; PFA, perfluorooctanoic acid; PFBA, perfluorobenzaldehyde; PFBA, perfluorobutanoic acid; PFCA, perfluoroalkyl carboxylic acid; PFCs, perfluorinated compounds; PFHpA, perfluoroheptanoic acid; PFHxA, perfluorohexanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFOX, X = A or S; PFPeA, perfluoropentanoic acid; PFPrA, perfluoropropionic acid; pI_{pzc}, zero point charge; POPs, persistent organic pollutants; TFA, trifluoroacetic acid; TNTs, titanate nanotubes; UV, ultraviolet; VUV, vacuum ultraviolet; WWTPs, wastewater treatment plants.

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temperature, and coexisting organic or inorganic matters. The mechanisms of PFOX photodegradation process are also elucidated in detail. This paper will help to deeply understand PFOX decomposition process and put forward better perspectives in the future for researchers who work in this field.

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1. Introduction

PFOA and PFOS, as typical refractory pollutants, have unique physicochemical properties such as extraordinary thermal, chemical, radiation and biological stability and high surface-active effect [1]. Therefore, PFOX (X = A or S) has been widely utilized in industrial and commercial products in the past decades, including waxes, varnishes, high-temperature lubricants, protective coatings, surfactants and firefighting foams [2–5]. Owing to direct or indirect discharge from the process of manufacture, usage, and disposal, PFOX has been globally detected in the environment, like seawater [6], indoor dust [7], wildlife [8,9] and human blood serum [10–12]. Researchers have confirmed that PFOX has multiple toxic effects including immunotoxicity, hepatotoxicity, developmental toxicity and carcinogenicity [13–16]. Therefore, PFOS was listed in the international Stockholm Convention on POPs as an Annex B substance, and PFOA has been named as a candidate under the same framework [17]. Moreover, it is reported that PFOX can be produced by transforming precursor compounds PFCs during the secondary biological treatment process [18,19]. The concentration of PFOX in WWTPs effluent is often higher than that in influent [20]. So PFOX cannot be degraded effectively in WWTPs.

The chemical formulas of PFOS and PFOA are $C_8F_{17}SO_3^-$ and $C_7F_{15}COOH$, respectively, and their chemical structures are shown in Fig. 1. Since the C–F bond of fluorocarbon is one of the bonds with the strongest bonds energy in nature (approximately 110 kcal/mol), most conventional technologies are ineffective to PFOS and PFOA degradation [21–23]. In general, most refractory pollutants can be degraded by AOPs, for example, using the hydroxyl radicals ($\cdot OH$) to attack the organic compounds via a hydrogen abstraction [24–27]. However, PFOX has no hydrogen atoms to be abstracted so that they could be not attacked by $\cdot OH$. Moreover, the oxidation potential value of $\cdot OH$ (276.0 kJ/mol) is significantly smaller than average C–C bond energy (347.0 kJ/mol), and thus PFOX is inert to $\cdot OH$ attack [28]. Pulse radiolysis experiments

[29] confirmed that the perfluorinated surfactants, compared with hydrocarbon surfactants, remain practically unreactive towards $\cdot OH$. Additionally, the ionic headgroup ($-CO_2^-$ for PFOA and $-SO_3^-$ for PFOS) will inductively reduce headgroup electron density, leading to the decrease of the oxidizability of ionic headgroup. For these reasons, it is difficult to degrade PFOX by conventional AOPs. Rayne and Forest [30] reviewed the methods for degrading perfluorinated acids. However, most of methods exhibit slow kinetic profiles for the degradation of perfluorinated acids, hindering their direct application in conventional low hydraulic residence time systems. Therefore, better methods should be explored to transform them to harmless species under mild conditions.

The degradation methods of PFOX could be grouped into two categories, physical adsorption and redox (Fig. 2). Through physical adsorption, GAC [31] and PAC [32] can partly remove PFOX from wastewater, but their adsorption capacity is relatively weak compared with other high-efficiency adsorbent such as AIX [33]. Meanwhile, the presence of NOM affects the removal efficiency due to the competitive adsorption between NOM and PFOX [34]. Although AIX has the stronger sorption capacity for PFOX than GAC and PAC, its sorption velocity is very slow because of the slow diffusion of PFOX in the porous materials [33]. Besides, the high costs of AIX also become the bottleneck in practical applications. In fact, these physical adsorption methods merely transfer PFOX from water phase to another phase and cannot mineralize them. In order to avoid the secondary pollution, the subsequent destruction process such as incineration is necessary to deal with the adsorbent saturated by PFOX.

Recently, redox, including photochemical [28,35–37], sonochemical [38–43], electrochemical [44–46], radiochemical [47], thermochemical [48], subcritical [49,50] and plasma [51] treatment processes, is becoming a promising technology for PFOX removal due to the complete mineralization. Compared with other redox technologies, photochemical degradation offers an easier operation under mild conditions, and achieves the higher

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