

Comparative Study on Degradation Methods of Per- and Polyfluoroalkyl Compounds in Water

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Abstract. This article aims to explore the degradation methods of per- and polyfluoroalkyl compounds (PFASs) in water bodies, and analyze the principles, advantages and disadvantages of different degradation methods and their application effects in different types of water bodies. In view of the wide application, long half-life, high mobility and potential harm to the ecological environment and biological health of PFASs, it is of great significance to study their effective degradation methods. By reviewing the existing literature, this article lists several major PFASs degradation methods, such as photocatalysis, activated carbon adsorption, and advanced oxidation, and compares their performance characteristics, which provides a scientific basis for the control of PFASs pollution in water bodies.

Keywords: per- and polyfluoroalkyl compounds, degradation methods, comparative study.

1. Introduction

Various forms of water on the Earth's surface are constantly transforming into each other, circulating between land, oceans and the atmosphere in gaseous, liquid and solid forms. Water on the earth's surface migrates on the surface and its adjacent spaces (troposphere and shallow underground layers) through morphological transformations, such as evaporation, precipitation, infiltration, surface flow and underground flow, etc.

With the rapid increase of global population, the shortage of global fresh water resources is gradually becoming apparent. According to United Nations statistics, global freshwater consumption has increased approximately 6-7 times since the beginning of the 20th century, which is twice as fast as population growth. Currently, 1.4 billion people around the world lack safe and clean drinking water.

Globally, water pollution has become a serious environmental problem. This pollution mainly comes from channels such as industrial wastewater, agricultural discharge, urban sewage and solid waste. Among them, pollutants include toxic chemicals, heavy metals, pesticide residues, microplastics, etc., which pose a huge threat to aquatic life and the entire ecosystem. Water pollution has seriously affected the ecosystem and biodiversity. The release of pollutants has destroyed the habitats of aquatic life, broken the ecological balance of water, and even led to the death of many fish and other aquatic animals and plants [1].

Among many pollutants, per- and polyfluoroalkyl substances (PFASs) are a type of synthetic compounds in which all or part of the hydrogen atoms on the carbon skeleton are replaced by fluorine atoms [2]. They are mostly used as surfactants. It is widely used in textile, electroplating, fire protection

and other fields. As a class of persistent organic pollutants, PFASs continue to accumulate in various environmental media. The widespread use of per- and polyfluoroalkyl compounds (PFAS) in various industries has led to their widespread presence in the global air, freshwater supplies and soil, severely affecting ecosystems around the world. Since the production of PFCs, PFC concentration values in contaminated wastewater and groundwater samples worldwide have increased from 0.1 ng/L to more than 1000 mg/L [3]. Toxicological research results show that PFAS has serious toxic effects on the human body and can damage the human endocrine system, immune system, liver, nerves, etc. Currently, many developed countries have restricted or banned the production and use of PFAS-based products. The sources of PFASs in the water environment are shown in Figure 1.

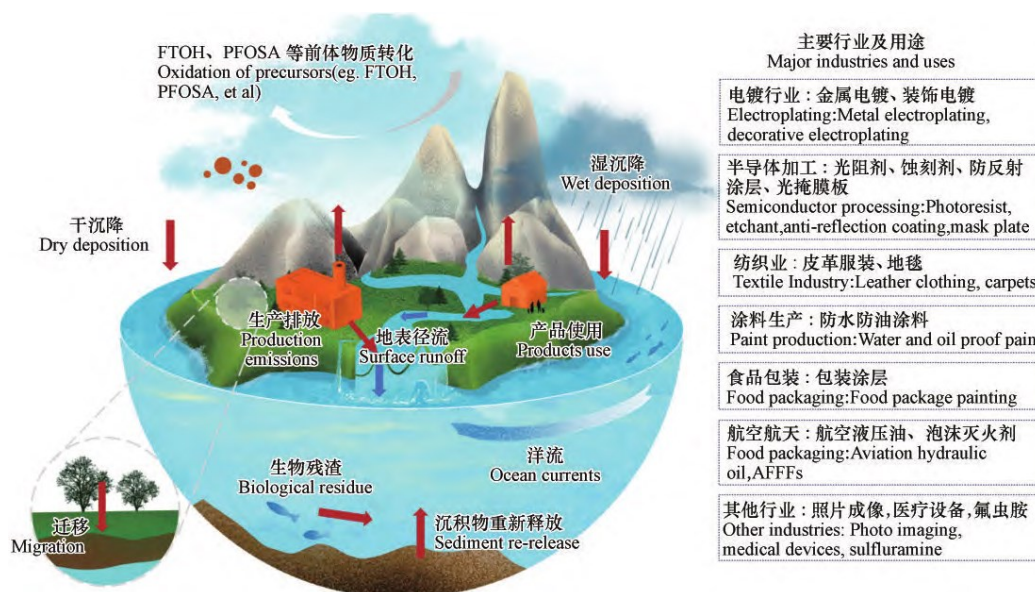


Figure 1. Sources of PFASs in the liquid environment [4]

Among PFAS compounds, the C-F bond is highly polar (bond energy 485kJ/mol). The PFAS structural bond energy is high and is not easily degraded under natural conditions. PFASs are highly stable and difficult to degrade, and can exist in the environment for a long time. And accumulate, posing potential threats to ecosystems and human health [5]. Therefore, studying the degradation methods of PFASs is of great significance for protecting water resources and the ecological environment.

At present, PFASs degradation methods include photocatalysis, activated carbon adsorption, advanced oxidation, etc. Different degradation methods are suitable for water bodies with different pollution conditions. Currently, there are few studies that list and compare the degradation methods of PFASs in different water bodies. This article lists the different degradation methods of PFASs in water bodies. The degradation methods and basic principles are analyzed, and which degradation methods are suitable for different water bodies are analyzed, which provides a basis for the selection of degradation methods for PFASs in sewage in the future.

2. Comparison of PFASs degradation methods

A large number of studies have shown that PFASs have potential biological toxicity, and their presence in the environment will pose a huge threat to human health and ecological security. At present, the two most common long-chain PFASs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been included in the United Nations' "About Us" in 2009 and 2019 respectively. List of persistent organic pollutants controlled by the Stockholm Convention. The water environment is one of the most important fates of PFASs, but due to the high thermal stability and high chemical stability of PFASs, conventional water treatment technologies have been proven to

have little effect on the removal of PFASs [4]. In contrast, some emerging chemical degradation technologies, such as photocatalysis technology and advanced oxidation technology, have attracted much attention because they can achieve direct degradation and removal of PFASs.

2.1. Photocatalysis method

Photocatalytic degradation is a method that uses photocatalysts to promote the decomposition of PFASs under light conditions. The pollutants are mainly degraded through the chemical reaction at the solid-liquid interface between the photocatalyst and the pollutants. The principle of photocatalyst is to absorb sunlight of appropriate wavelength, and the electrons in the photocatalyst's valence band (VB) jump to the conduction band, and generate oxidizing holes in the VB. Electron-hole pairs migrate from the catalyst body to the surface, and most of the electron-hole pairs recombine to produce a photon, which consumes the electrons and holes in the form of light. The remaining electrons and holes react with water and oxygen adsorbed on the catalyst surface respectively to generate active substances, such as hydroxyl radicals, superoxide radicals, etc. Some electrons, holes, and active substances react with pollutants in the water and degrade them. Currently, the photocatalysts that can be used for photocatalytic degradation of PFOS and PFOA mainly include TiO_2 , In_2O_3 and modified catalysts [6]. Wang [7] et al. used oxalic acid as a hole trapping agent and TiO_2 as a photocatalyst to photocatalytically degrade PFOA in a nitrogen atmosphere. According to the Electron Paramagnetic Resonance (EPR) characterization, oxalic acid can be used as the precursor of $\text{CO}_2^{\cdot -}$ in the reaction system, and $\text{CO}_2^{\cdot -}$ is the main active substance in the photocatalytic degradation of PFOA. Panchangam et al. [8] synthesized TiO_2 photocatalyst through sol-gel method and used it for ultrasonic-assisted photocatalytic degradation of PFOA. Under irradiation of deep ultraviolet light with a wavelength of 254 nm, approximately 64% of PFOA was degraded.

The photocatalytic method has the advantages of green environmental protection, high degradation efficiency, and mild conditions. However, the cost of the catalyst is high, and the photogenerated holes and electrons on the catalyst will combine, resulting in low light energy utilization.

2.2. Activated carbon adsorption

Adsorption is one of the most effective methods for removing PFCs, and efficient adsorbents such as activated carbon, resin, chitosan, hydrotalcite, and alumina have been reported. As early as 2005, 3M Company used granular activated carbon (GAC) to remove PFOA with a mass concentration of up to 2 mg/L in water, with a removal rate of 99% [9]. Activated carbon is widely used because of its porous structure and good adsorption performance. For the removal of PFASs in water. Activated carbon is widely used to remove PFASs in water due to its porous structure and good adsorption properties.

Factors affecting the adsorption of PFCs in water by activated carbon include the following aspects:

2.2.1. Influence of activated carbon particle size

Generally speaking, the smaller the particle size of activated carbon, the higher the adsorption rate of pollutants. In terms of removal rate, research by Xiao [10] et al. also proved that the smaller the particle size, the higher the removal rate of PFOS and PFOA.

2.2.2. Influence of pore size and surface chemistry

The pore structure of activated carbon can be roughly divided into micropores less than 2 nm, mesopores 2 to 50 nm, and macropores greater than 50 nm. The pores of activated carbon are the key structure for its adsorption function. Studies have found that PFOS, PFOA, etc. may clog the micropores on the surface of the adsorbent, thereby reducing the adsorption performance of the adsorbent. Deng et al. used the KOH activation method to prepare bamboo-based granular activated carbon (GAC) with larger pore size. The GAC prepared when the KOH/C mass ratio was 4 and the activation temperature was 900°C. When the pH value was 5.0, the activated carbon had an effective effect on PFOS. The adsorption capacity is 2.32 mmol/g, and the adsorption capacity for PFOA is 1.15

mmol/g. The adsorption performance is significantly higher than that of commercially available activated carbon. This is related to the enlarged internal pore size of activated carbon, which is more conducive to the adsorption of PFOS and PFOA [11].

2.2.3. The influence of pH and temperature in the adsorption environment.

pH is an important factor that affects the form of adsorbate in water, and may also affect the surface charge of activated carbon. Research by Yu Qiang [12] shows that compared with neutral environments, activated carbon has a greater adsorption capacity for PFOS and PFOA under acidic conditions with a pH value of 3. The adsorption of PFOA by activated carbon is an endothermic process. Qu [13] and other studies found that there is an optimal temperature for the adsorption amount of PFOA by activated carbon. When the temperature increases from 303K to 313K, the adsorption amount of PFOA increases with the increase of temperature. Gradually increasing, when the temperature continues to rise to 323 K, the adsorption amount of PFOA decreases.

2.2.4. Influence of PFCs structure

The long fluorocarbon chain of PFCs is hydrophobic, and the other end is a hydrophilic group. As the length of the carbon chain of PFCs increases, the hydrophobicity of the carbon chain of PFCs increases. The chain length of PFCs is closely related to the removal effect of activated carbon. The surface of activated carbon is generally non-polar. The longer the chain length of PFCs, the weaker the hydrophilicity, so the adsorption effect of activated carbon is better. Ochoa-Herrera [14] et al. found that the phosphate salinity and the nature of functional groups at 30°C and pH 7.2 affected the adsorption of PFCs, and PFOS was more easily adsorbed, indicating that the substitution of the sulfonic acid group by the carboxyl group and the shortening of the fluorocarbon chain resulted in two. The adsorption of these substances on activated carbon is poor.

Activated carbon technology is one of the most effective methods for removing PFCs. This method is simple to operate and has significant effects. It is especially suitable for the treatment of low-concentration PFASs-contaminated water bodies. However, the cost of regeneration and disposal of activated carbon is high, and its effectiveness in treating water polluted by high concentrations of PFASs is limited. By adjusting the pore structure of activated carbon through appropriate methods, the adsorption effect of activated carbon on PFCs can be improved.

2.3. Advanced oxidation technology

Advanced oxidation technology (AOPs) attacks PFASs molecules by generating strong oxidizing free radicals (such as hydroxyl radicals), causing them to undergo oxidative decomposition. It has the advantages of high degradation efficiency and fast processing speed, and is suitable for various types of water pollution. processing [15]. However, this technology has high equipment requirements and relatively high operating costs. Among drinking water and wastewater treatment technologies based on ultraviolet light, the UVC band (200-280 nm), especially 254 nm UV, is the most widely used and is often used to inactivate pathogenic microorganisms and degrade a variety of organic pollutants in water. However, studies have found that PFASs degrade very slowly under 254 nm UV irradiation. Compared with direct UV photodegradation technology, UV-AOPs generate strong oxidizing free radicals, which can further improve the degradation efficiency of PFOA and PFOS. Hydroxyl radical ($\bullet\text{OH}$) UV/H₂O₂ technology and UV/O₃ technology are the most typical AOPs, which are commonly used to remove various types of refractory organic matter and have relatively mature applications in engineering.

According to the technical characteristics of UV-AOPs and the differences in the degradation mechanism of PFASs, UV-AOPs to remove PFASs, they are divided into homogeneous UV-AOPs that mainly degrade PFASs with free radicals and heterogeneous UV-AOPs that use photo-generated electrons or photo-generated holes to act on PFASs. It has been verified that adding H₂O₂ to the photolysis system is not conducive to the degradation of PFOA. Research by Hassan et al. [16] showed that after adding H₂O₂ to the direct photolysis system at 254 nm, the removal rate of PFOA

decreased from 21.1% to 19.7%. This is due to the special structure of PFASs substances, which makes it almost impossible to destroy them by the $\bullet\text{OH}$ produced in the UV/ H_2O_2 system.

Homogeneous UV-AOPs based on $\bullet\text{OH}$ have obvious limitations in the removal of PFASs. In contrast, the UV/persulfate system generates sulfate radicals ($\bullet\text{SO}_4^-$) with strong oxidizing properties and strong selectivity, can efficiently degrade new environmental pollutants. In recent years, UV/persulfate (mainly PDS) systems have also been proven to have the potential to remove PFASs from water. Hori et al. [17] found that in the presence of $\text{S}_2\text{O}_8^{2-}$, after irradiating PFOA with a 200W xenon lamp (emission wavelength 220--460 nm) for 2 hours, its degradation rate could reach 99.1%. Chain PFCAs can also achieve a considerable degree of defluorination. Compared with 254 nm UV, using 185 nm VUV to activate $\text{S}_2\text{O}_8^{2-}$ can achieve a higher degradation rate of PFASs. For example, Chen et al. [18] found that the degradation rate of $\text{S}_2\text{O}_8^{2-}$ at 185 nm and 254 nm for PFOA was respectively 84% and 65%.

Although PFCAs and perfluoroalkyl sulfonic acids (PFSA) can be removed to a certain extent in the homogeneous UV/AOPs degradation system, they generally require a longer residence time and the defluorination ability is also quite limited. UV-based photocatalytic oxidation technology is a very promising water treatment technology. In recent years, more and more studies have proven that UV/titanium dioxide (TiO_2), UV/indium oxide (In_2O_3) and UV/gallium oxide (Ga_2O_3) Photocatalytic technology can be applied to the degradation of PFASs to achieve low energy consumption and high removal rate. The reaction mechanism of these technologies can generally be summarized as follows: under UV irradiation, photogenerated holes and photoelectrons are generated between the conduction band and valence band of the photocatalytic material. Among them, holes with strong oxidizing properties are the main activity that acts on the degradation of PFASs species.

3. Selection of PFASs degradation methods in different water bodies

PFCs are a type of fluorinated hydrocarbon compounds with extremely high solubility in water bodies. They have potential for persistent environmental pollution, biological toxicity and accumulation, and seriously endanger human health. The treatment of PFASs pollution in water has become a research hotspot for researchers from various countries. Activated carbon adsorption technology has the advantages of low cost, high efficiency and simple operation, but it only achieves the purpose of adsorption and removal and fails to fundamentally degrade PFASs, and subsequent incineration and other treatment methods will cause greater pollution to the environment. It is commonly used For the treatment of PFASs in industrial wastewater; although photocatalysis or advanced oxidation technology can achieve the purpose of degrading PFASs, it has the disadvantages of high reagent and device costs, harsh reaction conditions and secondary pollution. Depending on the degree of water pollution, water quality characteristics, and treatment objectives, appropriate PFASs degradation methods can be selected. For example, for water bodies polluted by PFASs at low concentrations, activated carbon adsorption methods can be given priority; while for PFASs pollution at high concentrations or under complex water quality conditions, photocatalysis or advanced oxidation technology may be needed for treatment. The advantages and disadvantages of the three methods are shown in Table 1.

Table 1. Comparison of advantages and disadvantages of different treatment processes of PFASs

Technology	Advantage	Disadvantage
Photocatalysis	Green environmental protection, high degradation efficiency, mild conditions	High catalyst cost; Photogenic holes and electrons on the catalyst combine to produce light energy Low utilization rate

Table 1. (continued).

Activated Carbon Adsorption	Simple operation, low cost, high efficiency	Physical removal, which simply separates the contaminant from the water, does not eliminate the target contaminant The harmless treatment of fluorine-containing wastewater cannot be completely realized
Advanced Oxidation	Environment friendly, simple operation, fast free radical generation, high mineralization ability	Large quantities of H ₂ O ₂ and iron ionizer are required, and chemical energy consumption is high. Current research direction single one, it mainly focuses on the reduction of PFOA, which is difficult to be applied to the actual industry Wastewater

4. Conclusion

This article reviews the degradation methods of PFASs in water and compares the advantages and disadvantages of photocatalysis, activated carbon adsorption, and advanced oxidation technologies. Through comprehensive analysis of the characteristics and application scope of different degradation methods, it provides a valuable reference for the control of PFASs pollution in water bodies. However, current research still has some limitations, such as degradation efficiency that needs to be improved and treatment costs are high. Therefore, future research should further explore new and efficient PFASs degradation methods and optimize the process parameters of existing technologies to reduce treatment costs and improve treatment efficiency.

The mechanistic processes of some treatment technologies are still not fully studied, which requires further study by researchers; secondly, although existing treatment technologies can degrade PFASs from long-chain molecules into short-chain fluorine-containing compounds, these compounds are still biologically toxic and harmful. , further defluorination treatment is required, and the final products are fluoride ions and carbon dioxide; some treatment methods may have good efficiency in the long-chain degradation step, and some technologies may be very effective in the defluorination rate, which requires further development of joint technology to effectively combine the two; the last key point is that many technologies are currently developed in laboratories. How to further apply them to the actual management of environmental samples requires further improvement and optimization.

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