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Photodegradation of perfluorooctane sulfonate in environmental matrices

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ABSTRACT

Effective photodegradation of perfluorooctane sulfonate (PFOS), an environmentally-ubiquitous persistent organic pollutant, in simple aqueous solution has been previously demonstrated. However, photocatalyst usually needs to be added and its application in complicated aquatic environment has not been reported so far. Here, we investigated the photodegradation of PFOS in environmental matrices, including municipal wastewater treatment plant (WWTP) effluent and lake water, and without adding any photocatalyst. A moderate PFOS degradation in the WWTP effluent and lake water was observed, with pseudo-first-order decomposition rate constants of $0.10 \pm 0.02\ h^{-1}$ and $0.16 \pm 0.01\ h^{-1}$ respectively. A further investigation using artificial water solution suggest that the weak alkaline pH and the presence of some dissolved organic matters (e.g., phenol and ammonia) might be important factor accounting for the efficient PFOS decomposition in environmental matrices, while humic acid and the relatively low ionic strength posed negative impacts. This study demonstrates the feasibility of eliminating PFOS pollution by photodegradation approach and may have implications for wastewater deep treatment and environmental remediation.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) had been widely used in industries and in daily lives for decades [1,2]. However, owing to their high developmental toxicity, immunotoxicity, hepatotoxicity, the production and use of some PFASs, e.g., perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), have been restricted in most countries so far [3,4]. Nevertheless, residual PFASs continue to be detected today in the hydrosphere and in wildlife bodies, attributed to their environmental persistence and bioaccumulative nature [4–6]. To eliminate PFAS pollution, advanced treatment processes, such as photochemical [7–10], sonochemical [11], electrochemical [12,13], radiochemical [14] and subcritical [15,16] treatment processes, are commonly used. In particular, photodegradation is recognized as an appealing option, which could hopefully take advantage of the inexhaustible solar energy as a driving force [17] and is environmentally friendly and cost effective.

Our previous study has shown that PFOS could be efficiently photodegraded without chemical dosing, in which process reduction by photo-generated hydrated electrons was the key reaction pathway [18]. This process can be further accelerated by adding alcohol or iodide as the enhancement agent [7,9]. However, all these studies were conducted in simple aqueous solution systems, while the PFOS photodegradation performance in complicated aquatic environment is unknown yet. Many organic and/or inorganic substances in natural water environment could affect photodecomposition of PFOA [19,20]. Among these influential factors, the dissolved organic matters (DOM), which ubiquitously exist in wastewater or natural water environment, may deserve special attention. For instance, humic acids (HAs) was found to promote the solar-driven photodegradation of pharmaceuticals in wastewater treatment plant (WWTP) effluents [21]. However, in another study, HAs and other DOM significantly decelerated the photodegradation of androstenedione owing to physical or chemical quenching of the photochemical degradation intermediates [22]. Furthermore, it was demonstrated that DOM played a dual role of sensitizer and quencher in the photodegradation of tryptophan [23]. Thus, it is reasonable to hypothesize that DOM may also

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pose non-negligible influences on PFOS photodegradation process [15]. To promote environmental application of the PFOS photodegradation process, it is essential to understand how this process would be affected by the various DOM and other coexisting pollutants in environmental matrices.

In this paper, we investigated the photodegradation of PFOS in municipal WWTP effluent, lake water and artificial water. The possible influences of several common coexisting solution components, such as HA, inorganic salts, phenol and ammonia, on this process were evaluated. Our results suggest a high possibility for efficient elimination of PFOS and other oxidation resistant pollutants in environmental matrices by photochemical processes.

2. Materials and methods

2.1. Chemicals

The PFOS potassium salt (>98.0%) was obtained from Tokyo Chemical Industry Co., China. HA (technical grade) and methanol (HPLC grade) were supplied by Sigma-Aldrich Co., USA. All other chemicals (AR grade) were purchased from Sinopharm Chemical Reagent Co., China. All solutions were prepared with deionized water from a water purification system (Millipore Inc., USA).

2.2. Experimental procedures

All the experiments were carried out in a 250-mL photoreaction system as reported previously, where a medium pressure mercury lamp (500 W, GY-500, Beijing Tianmaihenghui Co., China) was used as UV irradiation source (Fig. S1) [18]. In each batch experiment, 200 mL reaction solution was fed into the quartz photoreactor, deoxygenated by purging nitrogen gas for 10 min, and then irradiated internally with mercury lamp for 6 h. The solution temperature was maintained at about 90 °C using water bath. Generally, an aliquot of 2 mL solution was sampled each hour using a syringe. However, in some cases with rapid PFOS decomposition, a shorter irradiation period and more frequent sampling were adopted.

To examine the photodegradation performance of PFOS in environmental matrices, water samples from the effluent of a municipal WWTP and Dushu Lake in Suzhou were used. Prior to the experiment, the collected water samples were filtered through 0.45-μm mixed cellulose ester filter, and then mixed with PFOS potassium salt (37.2 μM) as reaction solution.

In addition, to explore the impacts of other commonly coexisting components in the environmental matrices on the photodegradation process, mixed solutions of PFOS and individual components were prepared and tested. To prepare the artificial water, a PFOS stock solution (37.2 μM) was initially obtained by directly dissolving 80.0 mg PFOS potassium salt in 4.0 L deionize water. Then, a given amount of specific solutes was added into 200 mL PFOS stock solution. In most cases, 6.0 mM potassium dihydrogen phosphate was used as a pH buffer, and the solution pH was adjusted with potassium hydroxide solution (10 M).

2.3. Analysis

Concentration of PFOS and fluoride ions, the decomposition rate constants and the defluorination ratios were analyzed following the methods reported in a previous study [18]. The total organic carbon (TOC) was determined using a TOC analyzer (Elementar Analysensysteme GmbH, Germany). Potassium hydrogen phthalate standard solutions with TOC concentration of 1–100 mg/L were prepared in order to generate the external calibration curve. The solution pH was measured with a pH meter (Delta 320, Mettler Toledo Co., USA) at ambient temperature (20 °C).

3. Results and discussion

3.1. Photodegradation of PFOS in WWTP effluent and lake water

Fig. 1 shows the profiles of PFOS photodegradation in deionized water, phosphate buffer solution (PBS) and two real aqueous matrices respectively. It was anticipated that the various coexisting substances in the environmental matrices might affect the PFOS photodegradation process. Surprisingly, however, similar photodegradation profiles were obtained for the environmental samples and the PBS-buffered solution. Pseudo-first-order decay model was used to describe the PFOS photodegradation kinetics [7,9], and the decomposition rate constants of PFOS in the WWTP effluent and in the lake water were calculated to be 0.10 ± 0.02 h^{-1} (adjusted $R^2 = 0.8035$) and 0.16 ± 0.01 h^{-1} (adjusted $R^2 = 0.9591$), respectively, very close to that in PBS (0.11 ± 0.02 h^{-1}, adjusted $R^2 = 0.8297$).

The carbon–fluorine bonds in PFOS molecules could be partially broken during this photodegradation process [7,18,24]. Thus, the decomposition degree of PFOS anions could be reflected by the defluorination ratios (i.e., the ratio of broken carbon–fluorine bonds to the total). Table 1 shows that the defluorination ratios varied significantly under different test conditions and were independent of the decomposition kinetics. For instance, the defluorination ratio was much lower in the WWTP than in the PBS despite of their similar PFOS decomposition kinetics. It is possible that, although decomposition could still occur efficiently, a complete defluorination may be suppressed in the presence of some dissolved organic matters (e.g., HA and phenol) in the WWTP effluent, leading to low defluorination ratio in this case.

The decomposition rates of PFOS were highly associated with the solution properties. In our study, both the WWTP effluent and lake water had a considerable level of ionic strength and DOM (Table 2), and maintained a weak alkaline pH during the PFOS photodegradation (Table 1).

Our previous study has demonstrated that the PFOS photodegradation were significantly affected by solution pH [18]. Generally, the PFOS decomposition rate decreased significantly with pH descending under acidic conditions, while kept almost unchanged under neutral and alkaline conditions [18]. In this

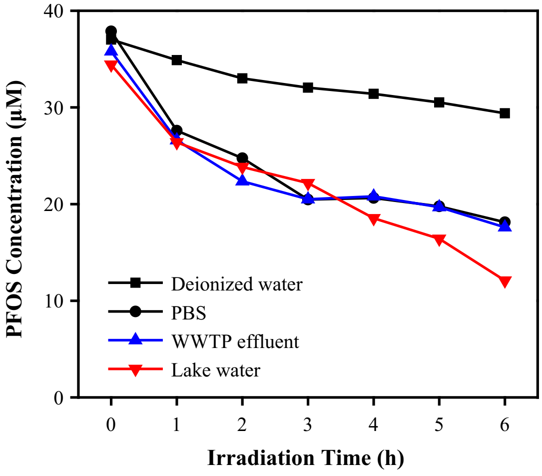

Fig. 1. Photodegradation of PFOS (37.2 μM) in deionized water (initial pH: 7.4, final pH: 4.3), PBS (6.0 mM, initial pH: 8.0, final pH: 7.7), WWTP effluent (initial pH: 7.7, final pH: 7.6) and lake water (initial pH: 8.7, final pH: 7.8).