



Removal of perfluorooctanoic acid and perfluorooctane sulfonate via ozonation under alkaline condition

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HIGHLIGHTS

- ▶ PFOA and PFOS are degraded by O₃ or O₃/H₂O₂ treatment at pH 11.
- ▶ Degradation of PFOA and PFOS by O₃ or O₃/H₂O₂ under alkaline condition is enhanced when the compounds are pretreated by 15 min of ozonation at ambient pH (4–5).
- ▶ PFOA and PFOS removal by O₃ or O₃/H₂O₂ at pH 11 was efficient relative to existing methods in terms of energy and contact time.

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ABSTRACT

The elimination of recalcitrant, ubiquitous perfluoroalkyl acids (PFAAs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) is desirable for reducing potential human health and environmental risks. We here report the degradation of PFOA and PFOS by 85–100% via ozonation under alkaline condition being studied at environmentally relevant contaminant concentrations of 50 µg L⁻¹ to 5 mg L⁻¹, with enhanced removal rates by addition of hydrogen peroxide. Enhanced removal is achieved by ozonation pretreatment for 15 min at the ambient pH (i.e. 4–5), followed by elevation of pH to 11 and continued ozonation treatment for 4 h. The ozonation pretreatment resulted in increased degradation of PFOA by 56% and PFOS by 42%. The results indicated hydroxyl radical-driven degradation of PFOA and PFOS in both treatments by ozone and peroxone under alkaline conditions. Wastewaters from electronics and semiconductor fabrication plants in the Science Park of Hsinchu city, Taiwan containing PFOA and PFOS have been readily treated by ozonation under alkaline condition. Treatment of PFAAs by ozone or peroxone proves to be efficient in terms of energy requirement, contact time, and removal rate.

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1. Introduction

Perfluoroalkyl acids (PFAAs) have been widely used in industrial surfactants, surface coating agents, firefighting foams, additives, and many other products. PFAAs are persistent in the environment; the growing body of knowledge about their toxicities and fate has led to consideration for regulation of certain PFAAs by governments and agencies. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are emitted directly, produced indirectly from oxidation of fluorotelomer alcohols and perfluorooctane sulfonamides in the atmosphere, and/or via biodegradation of their precursors in aquatic and terrestrial environments [1–5]. Due to concerns of their accumulation in the global environment, the manufacture of PFOS

has been banned in the U.S. [6] and their use as a constituent in most consumer products prohibited by the European Commission [7]. Recently, the US EPA included PFOA in its proposed Contaminant Candidate List-3 [8]. The Stockholm Convention has labeled PFOS as a persistent organic pollutant (POP).

Biological methods are unable to degrade PFOA or PFOS, as evidenced by their occurrence in wastewater treatment plant effluents [9–11]. In fact, their concentrations in the effluents are increased due to the conversion of primary PFAAs (precursors) into PFOA and PFOS during biological treatment. Photochemical [12,13], sonochemical [14,15], and combined treatment methods [16,17] have been investigated for the removal of PFOA and/or PFOS with widely varied effectiveness. To date, only sonochemical treatment methods have been reported to achieve complete mineralization of both PFOA and PFOS [15]; other treatment methods merely decomposed PFOA to PFAAs of shorter chain length achieving only partial degradation [18]. The degradation pathways

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involved either electron-transfer (e.g., photochemical methods) or pyrolytic decomposition at cavitation bubbles during sonochemical treatment. Decomposition via hydroxyl radical attack was seen as a minor pathway. However, the observed low removal efficiencies were possibly due to treatment conditions (e.g. low pH) that were not conducive to significant involvement by the hydroxyl radical.

Ozonation has attracted much attention in the water treatment arena because of its ability to oxidize micropollutants including pharmaceuticals and endocrine-disrupting compounds [19]. Only two prior studies have employed ozonation for treatment of PFOA and PFOS with dismal outcomes. Ozonation at $2.6 \text{ g O}_3 \text{ h}^{-1}$ at pH 11 for 2 h failed to degrade 20 mg L^{-1} of PFOS, notwithstanding the use of 30% H_2O_2 along with 15-W UV illumination [20]. In prior studies, the solution pH was adjusted to 11 just before ozonation. In our present study, ozonation at ambient pH (i.e. pH 4–5 after addition of PFAAs) was first allowed for 15 min (hereafter referred to as the “ozonation pretreatment” or simply “pretreatment”), after which the solution pH was increased to 11 and ozonation continued for the remaining duration of treatment. This pretreatment procedure has resulted in a remarkable treatment improvement to those reported by Schröder and Meesters [20] and will be discussed with results obtained in comparable experiments.

Landfill leachates containing PFOA ($65 \text{ }\mu\text{g L}^{-1}$) and PFOS ($30 \text{ }\mu\text{g L}^{-1}$) were subjected to sono-ozone treatment, in which ozonation was first used to attack co-contaminants in the leachate to be followed by sonication as the primary means of removal for PFOA and PFOS [17,21]. However, due to low energy efficiency of sonication for treatment of PFOA and PFOS, treatment alternatives that are energy-efficient and practicable must be developed.

The primary objective of this study is to report a newfound capability of pretreatment and ozonation under alkaline pH for the removal of PFOA and PFOS, pervasive contaminants in the environment. The new method eliminates at high efficiency both PFAA contaminants from wastewater effluents of the Southern Taiwan Science Park (TSP).

2. Experimental details

2.1. Chemicals

Perfluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), and humic acid were purchased from Sigma Aldrich (St. Louis, MO, USA). Tridecafluorohexane-1-sulfonic acid potassium salt (PFHxS), perfluorobutane sulfonate (PFBS), and perfluorooctane sulfonate (PFOS) were purchased from Fluka (Buchs, Switzerland). $^{13}\text{C}_8$ -Perfluorooctanoic acid ($^{13}\text{C}_8$ -PFOA) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Hydrogen peroxide (30%) was obtained from Katayam Chemical Industries (Osaka, Japan) and sodium hydroxide from Nacalai Tesque (Kyoto, Japan). HPLC-grade methanol was purchased from Baker (Phillipsburg, NJ, USA). All chemical standards were of purity >97%. The fluoride standard (99.99%) was purchased from High Purity Standards (USA). Milli-Q water (Millipore) of $18.2 \text{ M}\Omega \text{ cm}$ conductance was used in all experiments.

2.2. Ozonation under alkaline condition

Ozonation experiments were performed in a 1 L glass reactor at 25°C . O_3 gas was supplied by an O_3 generator (OZONIA CFS-1 2G) with O_2 as the feed gas at a flow rate of 4.2 L min^{-1} . The reactor setup is as shown in Fig. 1. Control experiments were conducted that confirmed negligible PFAA adsorption to glass and volatilization. O_3 was first bubbled into the contaminant-containing solution

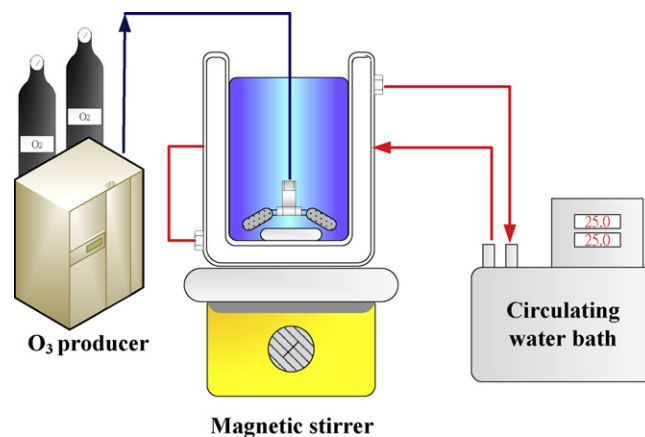


Fig. 1. Schematic of experimental setup.

(PFOS and PFOA at $50 \text{ }\mu\text{g L}^{-1}$ to 5 mg L^{-1}) for 15 min (ozonation pretreatment) at ambient pH (pH 4–5). The solution pH was then adjusted to 11 with a NaOH solution and ozonation continued (hereafter referred to as alkaline ozonation). The gas stream O_3 concentration was controlled by varying the input energy for O_3 generation; the aqueous O_3 concentration was measured by an O_3 analyzer (Orbisphere Laboratories, Switzerland, model 3600) at pH 6–7 and at 11. A typical reaction solution (1 L) containing $50 \text{ }\mu\text{g L}^{-1}$ of contaminants was contacted with $8.7 \text{ g O}_3 \text{ h}^{-1}$ (2.5 wt%); the steady-state aqueous O_3 concentration was 0.3 mg L^{-1} at pH 11 and 3.5 mg L^{-1} around neutral pH, reflecting faster O_3 decomposition at high pH and thus a lower steady-state concentration. For peroxone experiments, the molar ratio of $\text{H}_2\text{O}_2/\text{O}_3$ was varied from 0 to 0.2, while a 0.2 molar ratio was used for all other experiments. Samples were collected at specified intervals (0–4 h) and purged with nitrogen for 5 min to remove residual O_3 . The samples were filtered with $0.22 \text{ }\mu\text{m}$ Chrom Tech nylon syringe filters and stored at 4°C until chromatographic analysis.

2.3. Solid phase extraction (SPE) of Taiwan's science park (TSP) wastewater

The wastewater from TSP located in Southern Taiwan that hosts electronics and semiconductor industries was subjected to alkaline ozonation treatment. Five hundred milliliters of grab TSP wastewater samples were collected and stored in ice-packed coolers. Samples were vacuum-filtered through $0.45 \text{ }\mu\text{m}$ and $0.22 \text{ }\mu\text{m}$ cellulose acetate membrane filters and stored at 4°C until analysis. Two hundred milliliter Oasis HLB cartridges with 6 mL hydrophilic-lipophilic balance purchased from Waters (Milford, MA, USA) were employed for SPE using sample volumes of 400 mL. The SPE procedure and the quality control of this detection method were previously described in detail [22]. Briefly, SPE cartridges were preconditioned with 6 mL of methanol and 6 mL of Milli-Q water. The samples were loaded into the cartridges with a flow rate of $3\text{--}6 \text{ mL min}^{-1}$, rinsed with 6 mL Milli-Q water followed by 6 mL of 30% aqueous methanol, and dried under a nitrogen gas stream for 5 min. The analytes were eluted twice with 3 mL of methanol after drying. The eluates were collected, evaporated to dryness and reconstituted to 0.4 mL with 50% aqueous methanol. The final solutions were filtered through a $0.45 \text{ }\mu\text{m}$ nylon membrane filter before chromatographic analysis. The industrial wastewater samples were subjected to the SPE procedure (detection limits were 0.25 ng/L for PFOS and 0.05 ng/L for PFOA [22]) while other spike samples were injected into liquid chromatographic analysis either directly or after dilution to be within the linear calibration limits.

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