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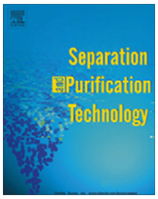

Oxidative decomposition of perfluorooctanesulfonate in water by permanganate

C.S. Liu [a,b], K. Shih [a,*], F. Wang [a]

[a] Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China
[b] Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, China

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ABSTRACT

Experiments were conducted to examine the oxidative decomposition of perfluorooctanesulfonate (PFOS), a widely distributed and highly resistant emerging organic pollutant, by permanganate in aqueous solutions. At 65 °C and pH 4.2, 46.8% of the PFOS was decomposed by permanganate, with a F^- yield of 5.3% and a SO_4^{2-} yield of 36.9%. The effects of temperature, initial permanganate concentration, and pH on PFOS decomposition efficiency were systematically investigated with batch experiments. Increasing the temperature and initial permanganate concentration effectively accelerated the rate of PFOS decomposition. However, increased pH decreased the PFOS decomposition rate, therefore indicating that a more acidic solution favors the decomposition of PFOS by permanganate. Moreover, the autocatalysis effect was found to accelerate the rate of PFOS decomposition by the *in situ* formed MnO_2 from the reduction of permanganate and, thus, the addition of MnO_2 to the reaction solution also increased the decomposition rate. Under acidic conditions, the addition of organic acids can enhance their complexation with Mn(V) and Mn(VI). Therefore, the duration of the Mn(VII) reduction intermediates, which are highly active and easily disproportionated and autodecomposed, can be further prolonged to facilitate the oxidative decomposition of PFOS.

1. Introduction

Perfluorochemicals (PFCs), such as perfluorooctanesulfonate (PFOS), are used in a wide variety of industrial, commercial, and consumer applications, including as surfactants, lubricants, and pesticides, due to their unique high surface activity, thermal and acid resistance, and hydro- and lipophobic properties. However, PFCs have been found to be environmentally resistant, bioaccumulative, globally distributed and potentially harmful to humans [1]. Studies show that nearly all people, regardless of age and sex, have detectable levels of PFCs in their blood from being exposed to the PFCs contained in food, water, and commercial products or from environments where they have been spilled or released [2]. PFCs are an emerging pollutant and have produced toxicological effects in laboratory animals [3]. Furthermore, in a 2005 draft risk assessment of PFCs, the US EPA stated that it had found "suggestive evidence" of their potential to cause cancer in humans.

Studies have shown that PFCs are able to enter the groundwater and move long distances [4]. It has also been suggested that PFCs are capable of being released into the air, flushed out by rain, deposited in soils or surface water, and of eventually making their way into the groundwater [5]. PFCs are highly recalcitrant because the molecules allow the complete substitution of hydrogen (C–H bond) by fluorine (C–F bond), which is the most electronegative element. The fluorine will retain its electrons at all cost and reduce the oxidizability of the ionic headgroup ($-SO_3^-$ for PFOS), because it reduces the headgroup electron density [6]. Owing to its potential toxicity to humans, the development of technology for the oxidative decomposition of PFCs in wastewater has the potential to be highly beneficial and has received increasing attention.

Advanced oxidation technologies (AOTs) have been extensively studied and are seen as the most promising technologies for the removal of persistent organic pollutants. With the highly oxidative potential, the generated hydroxyl radicals by AOTs generally attack organic molecules through the H-atom abstraction to form water [7]. However, as PFCs contain no hydrogen to be abstracted in environmentally relevant pH conditions, they are thus relatively inert to AOTs [8]. In fact, the decomposition resistance of PFCs to conventional AOTs is evidenced by the use of PFOS as a surfactant to increase the adsorption of organic pollutants on TiO_2 to obtain the accelerated AOT effects [9,10]. Owing to the high decomposition resistance of PFCs, different forms of exogenous energy, such as ultrasonic waves, UV light, or heat, have been introduced to initiate and accelerate the PFC decomposition. For example, persulfate was employed for the oxidative degradation of PFCs, because the generated sulfate radicals have a one-electron reduction potential of 2.3 eV, making persulfate a strong direct electron transfer oxidant [11]. To obtain efficient PFCs decomposition, photolysis

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* Corresponding author. Tel.: +852 2859 1973; fax: +852 2559 5337.
E-mail address: kshih@hku.hk (K. Shih).

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[12], thermolysis [13], microwaves [14], electrochemical [15], or a combination of different forms of exogenous energy [16] were used for generating sulfate radicals. Highly efficient photocatalysts, such as $H_3PW_{12}O_{40}$ and TiO_2, were also tested for PFC decomposition under UV light irradiation. However, the harsh reaction conditions (e.g. efficient at pH <2 and light $\lambda < 390$ nm) with $H_3PW_{12}O_{40}$ and TiO_2 were only capable of decomposing PFOA, not PFOS [17]. Although stronger forms of energy, such as direct photolysis, ultrasonic waves, and pyrolysis, can lead to PFC decomposition under certain special reaction conditions, the decomposition rates were generally still found to be low [6]. To minimize the need for energy in wastewater treatments, the exploration of other PFC decomposition techniques without intensive energy input is a timely and important task.

Chemical oxidation involving permanganate ($KMnO_4$) is efficient, owing to its high reduction potential ($E^\circ = +1.7$ V) and selective oxidizing character for specific organic pollutants [18]. Permanganate is a strong oxidizing agent and has been known to react with electron-rich moieties through several reaction pathways, including electron exchange, hydrogen abstraction, and direct oxygen transfer [19]. Because of its comparative stability, ease of handling, relatively low cost, and pH-independent effectiveness, permanganate has been widely used for *in situ* chemical oxidation to remediate contaminated soil and wastewater [20]. This study aimed to evaluate the application potential of permanganate for the oxidative decomposition of PFOS in water. The decomposition kinetics of PFOS by permanganate and the main PFOS mineralization products were determined. Furthermore, different reaction conditions, i.e. initial concentration of permanganate, temperature, and solution pH, were investigated to explore the optimal PFOS decomposition conditions by permanganate. Finally, the role of manganese dioxide, which is usually derived from the permanganate reduction product, and the effects of common organic acids on the oxidative decomposition of PFOS by permanganate in wastewater plants were also evaluated.

2. Materials and methods

2.1. Chemicals

Perfluorooctanesulfonate (PFOS, $C_8F_{17}SO_3H$, 98%) was purchased from Sigma–Aldrich Co. (St. Louis, MO, USA), and sodium permanganate ($KMnO_4$, >99%) was purchased from Guangzhou Chemical Industry (Guangzhou, China). The optima grade methanol and ammonium acetate used for preparing the mobile phase in the liquid chromatography tandem mass spectrometry (LC/MS/MS) analysis were obtained from Fisher Scientific (Pittsburgh, PA, USA) and BDH Chemicals (Poole, UK), respectively. The phosphate buffer solution was purchased from Fisher Scientific and the other analytical grade chemicals were obtained from BDH Chemicals. Eighteen MΩ cm water obtained from a Milli-Q water purification system was used to prepare the reaction solutions and the mobile phase in the LC/MS/MS analysis.

2.2. Reaction procedures

PFOS stock solution (10 ppm) was prepared with 18 MΩ cm water and then stored in a refrigerator (4 °C) before used. The reactions were conducted in batch experiments in sealed polypropylene copolymer (PPCO) test tubes (40 mL), due to their superior non-sorption property. The reaction solutions were prepared by introducing appropriate amounts of PFOS stock solution into the phosphate buffer solutions, and the initial PFOS concentrations were controlled at 100 ppb. The reaction pH was kept constant by the buffer solution, together with the adjustment by 0.5 M NaOH or 0.5 M HCl, if necessary. After being heated to the preset target temperature, the reaction was initiated by adding the corresponding amounts of $KMnO_4$ solution and then kept at the constant temperature. When the designated reaction time was reached, a test tube was sampled and quickly cooled to room temperature by cold water (4 °C). Before being mixed with 3.5 mL methanol [21], 0.5 mL ascorbic acid (1 M) was added to the 1.0 mL sample to remove any potential Mn(VII) or Mn(IV) remaining in the solution. The solution sample was then filtered through a 0.2 μm Whatman inorganic membrane (Kent, UK) before LC/MS/MS analysis. Furthermore, the concentrations of sulfate and fluoride ions generated from the reactions were also determined by ion chromatography (IC) analysis. Control sets of the experiments were performed in the absence of permanganate, and each experiment was conducted in triplicate.

2.3. Analytical procedures

The concentrations of PFOS were measured with a Waters Acquity ultra-performance LC/MS/MS system (UPLC/MS/MS) equipped with a 50 × 2.1 mm Waters BEH C18 column (1.7 μm particle size) and tandem quadrupole mass spectrometers (Milford, MA). Further details of the system modification and measurement procedures, such as PEEK tubes being substituted for transferring the solvents and samples in the UPLC system, the installation of an in-line isolator column, column temperature, and flow rate, etc., were provided in our previous work [21]. The generations of fluoride and sulfate ions were determined by a Dionex ICS-90 IC (Sunnyvale, CA), with a mobile phase of 1.0 mM $NaHCO_3$–8.0 mM Na_2CO_3 aqueous solution at a flow rate of 1.0 mL/min, in which the quantitative detection limits of fluoride and sulfate ions were found to be 8.0 and 5.0 μg/L, respectively. Such results were obtained from the equation of $C_{\min} = C_s\,(3H_n/H)$, where $C_{\min}$ is the detection limit; C_s is the detected concentrations of targeted ions; H_n is the reference noise; and H is the peak height of the targeted ions. The concentration of permanganate in water was determined by measuring its absorbance at 525 nm with a UV–Vis spectrophotometer (UV-160A, Shimadzu, Japan).

3. Results and discussion

3.1. PFOS decomposition by permanganate

The decomposition of PFOS by permanganate was first investigated by using 1 ppm of permanganate with 100 ppb of PFOS at 65 °C in the sealed test tubes. PFOS is highly thermally stable and the concentration of PFOS was essentially unaffected by the heating over the reaction time (Fig. 1). However, a decrease in PFOS concentration was observed over time with the presence of permanganate and 46.8% of the PFOS was decomposed after 18 days. The decomposition of PFOS followed the pseudo-first-order kinetics, with a rate constant of $3.64 \times 10^{-2}\ \mathrm{d}^{-1}$ ($R^2 = 0.976$). To further confirm the oxidative decomposition of PFOS by permanganate, the concentrations of F^- and SO_4^{2-} generated from the PFOS decomposition were measured. As shown in Fig. 1, the increases in the F^- and SO_4^{2-} yields were accompanied by PFOS degradation throughout the experimental period. The SO_4^{2-} yield, determined by (moles of SO_4^{2-} formed)/(moles of sulfur content in initial PFOS), was found to be 36.9% and the F^- yield, determined by (moles of F^- formed)/(moles of fluorine content in initial PFOS), was much lower with the value of 5.3%, after 18 days. The yield of SO_4^{2-} represented the mineralization of sulfur from PFOS and the result was lower than that of the PFOS decomposition rate (46.8%). This indicated that the decomposition of PFOS did not only occur at the bond of C–S, even though this bond is the most thermally unstable (86 kcal/