Separation and Purification Technology 87 (2012) 95–100

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

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

ARTICLE INFO

Article history:
Received 26 February 2011
Received in revised form 17 November 2011
Accepted 22 November 2011
Available online 30 November 2011

Keywords:
Perfluorochemicals
PFCs
PFOS
Oxidative degradation
Mn(VII)

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.

© 2011 Elsevier B.V. All rights reserved.

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

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

1383-5866/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2011.11.027

[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 λ < 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° = +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 $3.64 \times 10^{-2}\ d^{-1}$ (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/

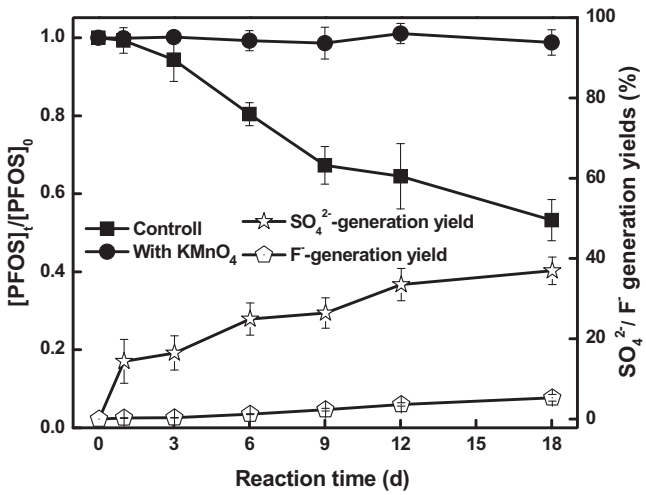

Fig. 1. Oxidative decomposition of PFOS by permanganate and the yields of the mineralization products. Reaction conditions: [initial PFOS] = 100 ppb, [$KMnO_4$] = 1.0 ppm, reaction temperature = 65 °C, and at pH 4.2 with phosphate buffer solution. Bars on symbols represent standard deviations; where absent, bars fall within symbols, which are also applicable in the other figures.

mol), compared to the C–C (99 kcal/mol) and C–F (127 kcal/mol) bonds in PFOS [11]. The oxidation potential of permanganate is 1.7 eV, while the C–F bond in PFOS is the most oxidation resistant bond (E^0 = 3.6 eV) and is difficult to be dissociated by permanganate. Therefore, the first oxidative attack of PFOS by permanganate may have occurred at the C–S and C–C bonds, which released the –CF_2 units and oxidation product of SO_4^{2-} to form the shorter chain perfluoroalkyl sulfonates and perfluorochemical products subject to further transformation reactions such as hydrolysis [13]. While oxidative reactions occurred with carbon mineralization, F^- ions were released with electron transfer from the C–F bonds in the dissociated –CF_2 moiety to permanganate [22].

3.2. Effect of reaction temperature

For organic molecules with high bonding energies in their structures, high energy means, such as ultrasonication, UV light irradiation, and high temperature, are usually needed to overcome the activation energy barrier. Although PFOS can be decomposed by permanganate in relatively mild reaction conditions, the decomposition reaction of PFOS may also be significantly influenced by temperature. The effects of reaction temperature (25, 45, 65, and 85 °C) are demonstrated in Fig. 2, and the results suggest that PFOS decomposition can be effectively facilitated by the increase of reaction temperature. At room temperature, the PFOS decomposition rate was low, with a pseudo-first-order kinetics rate constant of 0.46×10^{-2} d^{-1}. When the temperature was increased to 65 °C, the kinetics rate constant increased to 3.64×10^{-2} d^{-1}, which corresponds to the 46.7% PFOS decomposition after 18 days. Further temperature increase to 85 °C resulted in a higher PFOS decomposition rate (71.7%), with a rate constant of 7.16×10^{-2} d^{-1}. In addition, the activation energy of the decomposition reaction was calculated to be 42.6 kJ/mol based on the experimental data and the Arrhenius equation, $\ln k = \ln A - E_a/RT$, where A is the frequency factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature [23]. This high level of activation energy indicates that reaction temperature is a key factor in enhancing PFOS decomposition by permanganate.

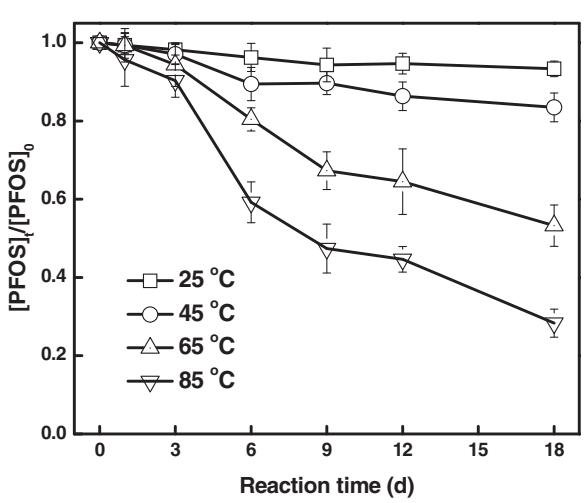

Fig. 2. Effect of reaction temperature on the oxidative decomposition of PFOS by permanganate. Reaction conditions: [initial PFOS] = 100 ppb, [$KMnO_4$] = 1.0 ppm, and at pH 4.2 with phosphate buffer solution.

3.3. Effect of initial permanganate concentrations

The decomposition of PFOS by different permanganate concentrations was carried out at pH 4.2 and 65 °C with 100 ppb of PFOS (Fig. 3A). The initial concentrations of permanganate were 0.1, 0.5, 1.0, 5.0, and 10.0 ppm, and the pseudo-first-order kinetics constants (k) were observed as 2.13×10^{-2}, 2.68×10^{-2}, 3.64×10^{-2}, 4.39×10^{-2}, and 4.48×10^{-2} d^{-1}, respectively. As expected, higher permanganate levels led to larger amounts of PFOS decomposition. The effect of initial MnO_4^- concentration on the kinetics constants is also presented in Fig. 3B, which shows that the k values did not increase linearly with the increase of permanganate concentration, and the excess permanganate did not proportionally enhance the PFOS decomposition, particularly at concentrations higher than 1 ppm. Permanganate reacts with PFOS through the mechanism of electron transfer and, usually, more than one MnO_4^- ion is needed to attack one organic molecule [24]. However, with a much higher MnO_4^- concentration (e.g. more than 10 times than PFOS), the excess MnO_4^- ions may not proportionally increase the effective contact between MnO_4^- ions and PFOS molecules. Therefore, as shown in Fig. 3B, higher permanganate concentrations of 5 and 10 mM did not linearly increase the k values of PFOS degradation. The consumptions of permanganate with different initial concentrations are shown in Fig. 3A, and the result clearly indicates a nearly 1 ppm consumption of permanganate even with a higher initial permanganate concentration, such as 5 or 10 ppm. Therefore, increased permanganate concentration is beneficial for PFOS decomposition, but the practicality and treatment costs also need to be considered. From the result of this work, the optimal molar ratio of MnO_4^- to PFOS is 10/1 when the PFOS concentration is at around the 100 ppb level.

3.4. Effect of pH

In wastewater treatment, pH value may be an important parameter affecting the oxidation rates of organic pollutants. In this study, the oxidative decomposition of PFOS by permanganate was also carried out under a range of different pH conditions between 4.2 and 9.1 controlled by a phosphate buffer. As illustrated in Fig. 4, the PFOS decomposition by permanganate shows strong pH dependence in the tested range. Under neutral to basic pH conditions, the decomposition of PFOS was limited, with merely 13.6% reduction under neutral pH and a corresponding rate constant (k) value of 0.76×10^{-2} d^{-1} (R^2 = 0.904). The oxidative ability of permanganate was effectively enhanced under acidic reaction

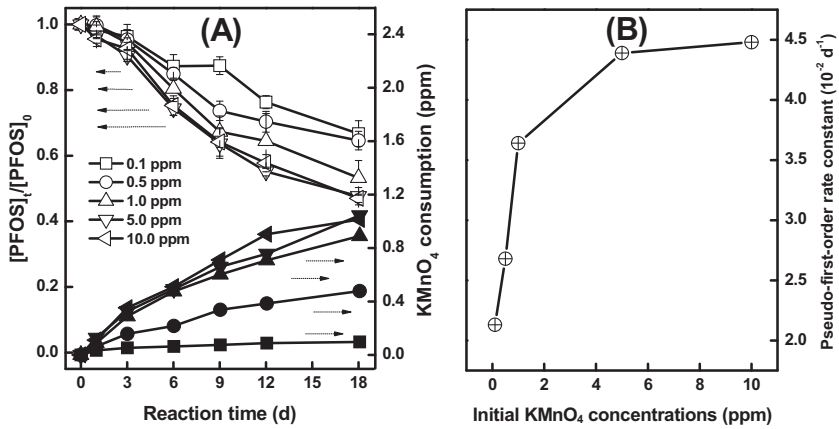

Fig. 3. Effect of initial permanganate concentration on the oxidative decomposition of PFOS: (A) the changes of PFOS concentration (open symbols) and permanganate consumption (solid symbols), and (B) the pseudo-first-order rate constants of PFOS degradation derived from different initial permanganate concentrations. Reaction conditions: [initial PFOS] = 100 ppb, reaction temperature = 65 °C, and at pH 4.2 with phosphate buffer solution.

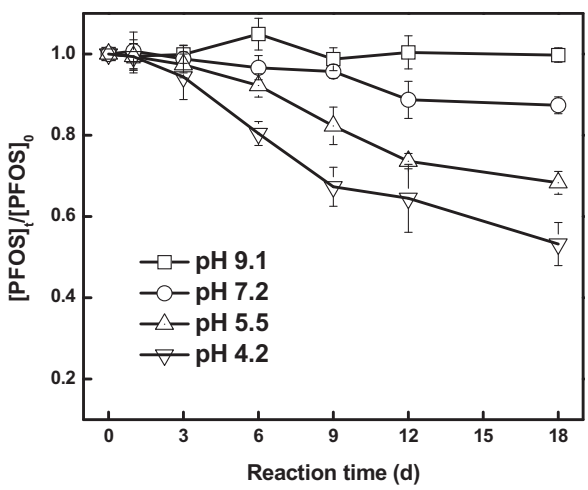

Fig. 4. Effects of pH values (controlled by phosphate buffer solution) on the oxidative decomposition of PFOS by permanganate. Reaction conditions: [initial PFOS] = 100 ppb, [$KMnO_4$] = 1.0 ppm, and reaction temperature = 65 °C.

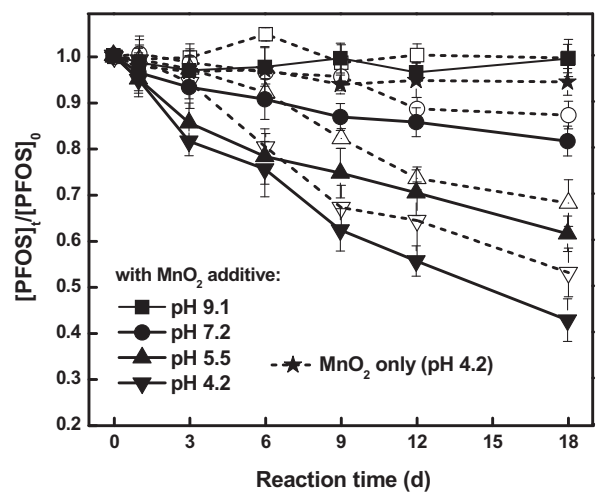

Fig. 5. Effect of 1.0 g/L MnO_2 addition on the oxidative decomposition of PFOS by permanganate. Reaction conditions: [initial PFOS] = 100 ppb, [$KMnO_4$] = 1.0 ppm, and reaction temperature = 65 °C. (The dash lines with open symbols represent the PFOS decomposition without MnO_2 additive at the corresponding pH values).

conditions of pH 5.5 and achieved a PFOS decomposition rate of 31.7% with a k value of 2.16×10^{-2} d^{-1} (R^2 = 0.956). When the pH reached 4.1, the PFOS decomposition rate was further enhanced to 46.8%, with a k value of 3.64×10^{-2} d^{-1} (R^2 = 0.956). The degradation of organic pollutants by permanganate has been reported to show little or even no dependence on reaction pH, because neither hydrogen nor hydroxyl ions can significantly facilitate the cleavage of the C=C double bond under the attack of MnO_4^- [25]. However, for the degradation of PFOS by permanganate, the initial bond cleavage step may occur at the C–C and/or C–S bonds, and thus the higher proton concentration (lower pH) may be favorable for the cleavage of the C–C and/or C–S bonds during the degradation of PFOS.

3.5. Effect of manganese dioxide

As observed from the kinetic behavior of the PFOS decomposition by permanganate, the reaction efficiency was generally lower in the first few days and then increased. Therefore, an autocatalytic process may exist in the oxidative decomposition of PFOS by permanganate, as indicated by the potential acceleration effect of the *in situ* generation of MnO_2 as the reaction progressed. Similar reaction kinetics behavior was also reported in the oxidation of triclosan by permanganate with the adsorption of triclosan on MnO_2 surface through complexes formation [20]. To further investigate the role of MnO_2 in the reaction, we conducted PFOS decomposition experiments by adding δ-MnO_2 powder to the system (Fig. 5). The preparation process and characterization results of the δ-MnO_2 additive were reported in our previous work [26]. Although MnO_2 has been reported with the efficient oxidization of a wide range of pollutants [27–29], our results using δ-MnO_2 alone did not exhibit any decomposition and adsorption capabilities for PFOS, as shown in Fig. 5. However, when MnO_2 was presented together with permanganate, the PFOS decompositions were all observed with higher rates than those only with permanganate at the corresponding pH conditions, particularly at the lower pH range. When the reaction pH was controlled at 4.2, the increase in the PFOS decomposition rate reached around 10%. In our tested pH range, the δ-MnO_2 surface was negatively charged due to its low pH_{pzc} value of 3.33 [26]. Therefore, the electrostatic repulsion between PFOS anion and MnO_2 surface results in the very limited PFOS adsorption on MnO_2 surface as observed in Fig. 5. However, the hydrophobic interaction between the perfluoroalkyl tails and the hydrophobic moieties on mineral surfaces was reported to be responsible for the interaction of hydrophobic

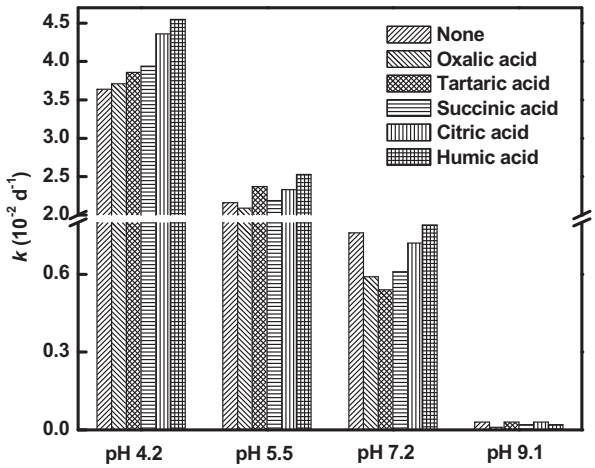

Fig. 6. Effects of organic acids (1.5 mM) on the PFOS decomposition by permanganate at different pH. The reported pseudo-first-order kinetics constants (k) of PFOS decomposition were derived from the reaction period of 18 days. Reaction conditions: [initial PFOS] = 100 ppb, [$KMnO_4$] = 1.0 ppm, and reaction temperature = 65 °C.

matter with minerals of low pH_{pzc} values at about 4 [30,31]. The MnO_2-promoted PFOS decomposition is likely be initiated by this hydrophobic effect, due to the interaction between hydrophobic perfluoroalkyl tails and the low-pH_{pzc} δ-MnO_2 surface. Nevertheless, such hydrophobic interaction mechanism should further be confirmed in the future study [31].

3.6. Addition of organic acids

Permanganate is a powerful oxidant that can decompose a wide range of organic pollutants in water. Thus, the presence of other organic pollutants may reduce the decomposition rate of PFOS due to the competitive reaction with permanganate. Organic acids are commonly found in industrial and domestic wastewater treatments as the degradation intermediates of organic pollutants [32]. With concentrations of 1.5 mM, the effects of five organic acids, i.e. oxalic acid, tartaric acid, succinic acid, citric acid, and humic acid, on decomposing the 100 ppb PFOS with 1.0 ppm permanganate at 65 °C and pH 4.2 were investigated (Fig. 6). It was found that the addition of the organic acids generally did not inhibit the decomposition of PFOS and that, under more acidic conditions, they might even slightly enhance the PFOS decomposition rate. At pH higher than 5.5, the presence of the five organic acids had very little influence on the k values of PFOS decomposition. With the reactions occurring under more acidic conditions, such as at pH 4.2, the k values for FPOS decomposition were observed to be 3.71×10^{-2}, 3.86×10^{-2}, 3.94×10^{-2}, 4.36×10^{-2}, and 4.55×10^{-2} d^{-1} with the addition of oxalic acid, tartaric acid, succinic acid, citric acid, and humic acid, respectively. The reduction of high valent metal oxidants such as Mn(VII) and Fe (VI) are often reported with the generation of highly reactive and unstable reduction intermediates [20]. In the case of decomposing PFOS by permanganate, the oxidizing agents of Mn(IV) and Mn(V) may be formed to further oxidize PFOS. However, these intermediates are also unstable and disproportionate spontaneously [33]. The added organic acids may act as ligands to form Mn complexes and significantly retard the disproportionation and autodecompostion processes of the Mn intermediates [20]. Such mechanisms can increase the decomposition rates of target pollutants, especially for slow oxidation processes like the decomposition of PFOS. Ligands with more complex moieties and higher molecular weights, such as humic acid and citric acid, usually form more stable Mn complexes. Under acidic environments, more active Mn intermediates can be generated, although large quantities of them may still be autodecomposed. Therefore, the PFOS decomposition rate may increase as more Mn intermediates are complexed with organic ligands, as observed at lower pH conditions.

4. Conclusions

PFOS was found to be capable of being oxidatively decomposed by permanganate in water, and the mineralization products of F^- and SO_4^{2-} were detected after the reaction. Increased temperature effectively facilitated PFOS decomposition to obtain higher reaction rate constants. Higher concentration of permanganate generally provided more oxidatively active species for PFOS decomposition, and thus also increased the decomposition rate. The oxidative decomposition of PFOS initiated by permanganate occurred more readily in acidic conditions. In alkaline conditions, PFOS remained stable with the presence of permanganate. However, the PFOS decomposition rate was significantly increased at pH below 5.5. During the PFOS decomposition process, autocatalysis may accelerate the reaction with the MnO_2 that *in situ* formed from the reduction of permanganate, and the experiment of adding MnO_2 into the solution increased the PFOS decomposition rate. Under an acidic environment, the presence of organic acids enhanced the decomposition rate of PFOS with permanganate, which was presumably due to the organic acid complexation with Mn(VII) reduction intermediates. In aqueous solution, organic acids can act as ligands to complex with the reactive Mn intermediates, thereby reducing their disproportionation/autodecompostion processes to prolong their treatment effects toward PFOS decomposition.

Acknowledgements

We acknowledge the funding for this research provided by the General Research Fund Scheme of the Research Grants Council of Hong Kong (HKU 716809E) and the National Natural Science Foundation of China (40801086). The authors are thankful to Ms. Vicky Fung, Dr. Bing Li, and Mr. Ke Yu for assisting with the UPLC/MS/MS analysis.

References

[1] J.P. Giesy, K. Kannan, Perfluorochemicals surfactants in the environment, Environ. Sci. Technol. 36 (2002) 146a–152a.
[2] K. Kannan, S. Corsolini, J. Falandysz, G. Fillmann, L.S. Sumar, B.G. Loganathan, M.A. Mohd, J. Olivero, N.V. Wouwe, J.H. Yang, K.M. Aldous, Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries, Environ. Sci. Technol. 38 (2004) 4489–4495.
[3] W. Kim, S. Lee, J. Jung, Integrated assessment of biomarker responses in common carp (*Cyprinus carpio*) exposed to perfluorinated organic compounds, J. Hazard. Mater. 180 (2010) 395–400.
[4] E. Hoehn, M.H. Plumlee, M. Reinhard, Natural attenuation potential of downwelling streams for perfluorochemicals and other emerging contaminants, Water Sci. Technol. 56 (2007) 59–64.
[5] M.H. Plumlee, J. Larabee, M. Reinhard, Perfluorochemicals in water reuse, Chemosphere 72 (2008) 1541–1547.
[6] C.D. Vecitis, H. Park, J. Cheng, B.T. Mader, M.R. Hoffmann, Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), Front. Environ. Sci. Eng. China 3 (2009) 129–151.
[7] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals (OH/O^-) in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886.
[8] H.F. Schroder, R.J.W. Meesters, Stability of fluorinated surfactants in advanced oxidation processes – A follow up of degradation products using flow injection–mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry, J. Chromatogr. A 1082 (2005) 110–119.
[9] Q. Yuan, R. Ravikrishna, K.T. Valsaraj, Reusable adsorbents for dilute solution separation. 5. Photodegradation of organic matter compounds on surfactant-modified titania, Sep. Purif. Technol. 24 (2001) 309–318.

[10] C. Baudequin, E. Couallier, M. Rakib, I. Deguerry, R. Severac, M. Pabon, Purification of firefighting water containing a fluorinated surfactant by reverse osmosis coupled to electrocoagulation–filtration, Sep. Purif. Technol. 76 (2011) 275–282.
[11] P. Wardman, Reduction potentials of one-electron couples involving free-radicals in aqueous-solution, J. Phys. Chem. Ref. Data 18 (1989) 1637–1755.
[12] H. Hori, A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, S. Kutsuna, H. Kiatagawa, R. Arakawa, Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant, Environ. Sci. Technol. 39 (2005) 2383–2388.
[13] H. Hori, Y. Nagaoka, M. Murayama, S. Kutsuna, Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water, Environ. Sci. Technol. 42 (2008) 7438–7443.
[14] Y.C. Lee, S.L. Lo, P.T. Chiueh, D.G. Chang, Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate, Water Res. 43 (2009) 2811–2816.
[15] Y.T. Tsai, A.Y. Lin, Y.H. Weng, K.C. Li, Treatment of perfluorinated chemicals by electro-microfiltration, Environ. Sci. Technol. 44 (2010) 7914–7920.
[16] Y.C. Lee, S.L. Lo, P.T. Chiueh, Y.H. Liou, M.L. Chen, Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation, Water Res. 44 (2010) 886–892.
[17] H. Hori, E. Yayakawa, H. Einaga, S. Kutsuna, K. Koike, T. Ibusuki, H. Kiatagawa, R. Arakawa, Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches, Environ. Sci. Technol. 38 (2004) 6118–6124.
[18] C.M. Kao, K.D. Huang, J.Y. Wang, T.Y. Chen, H.Y. Chien, Application of pottasium permangante as an oxidant for in situ oxidation of trichloroethylene-contaminated groundwater: A laboratory and kinetics study, J. Hazard. Mater. 153 (2008) 919–927.
[19] R.H. Waldemer, P.G. Tratnyek, Kinetics of contaminant degradation by permanganate, Environ. Sci. Technol. 40 (2006) 1055–1061.
[20] J. Jiang, S.Y. Pang, J. Ma, Oxidation of triclosan by permanganate (Mn(VII)): Importance of ligands and in situ formed manganese oxide, Environ. Sci. Technol. 43 (2009). 8626-8331.
[21] R. Ma, K. Shih, Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong, Environ. Pollut. 158 (2010) 1354–1362.
[22] Y. Wang, P. Zhang, G. Pan, H. Chao, Ferric ion mediate photochemical decomposition of perfluorooctanoic acid (PFOA) by 254 UV light, J. Hazard. Mater. 160 (2008) 181–186.
[23] F.B. Li, C.S. Liu, C.H. Liang, X.Z. Li, L.J. Zhang, The oxidative degradation of 2-mercaptobenzothiazole at the interface of β-MnO_2 and water, J. Hazard. Mater. 154 (2008) 1098–1105.
[24] D. He, X. Guan, J. Ma, X. Yang, C. Cui, Influence of humic acids of different origins on oxidation of phenol and chlorophenols by permanganate, J. Hazard. Mater. 182 (2010) 681–688.
[25] L. Hu, H.M. Martin, O. Arce-Bulted, M.N. Sugihara, K.A. Keating, T.J. Strathmann, Oxidation of carbamazepine by Mn(VII) and Fe(VI): Reaction kinetics and mechanism, Environ. Sci. Technol. 43 (2009) 509–515.
[26] C.S. Liu, L.J. Zhang, F.B. Li, Y. Wang, Y. Gao, X.Z. Li, W.D. Cao, C.H. Feng, J. Dong, L.N. Sun, Dependence of sulfadiazine oxidative degradation on physicochemical properties of manganese dioxides, Ind. Eng. Chem. Res. 48 (2009) 10408–10413.
[27] X. Li, C. Liu, F. Li, Y. Li, L. Zhang, C. Liu, Y. Zhou, The oxidative transformation of sodium arsenite at the interface of α-MnO_2 and water, J. Hazard. Mater. 173 (2010) 675–681.
[28] H. Zhang, W.R. Chen, C.H. Huang, Kinetic modeling of the oxidation of antibacterial agents by manganese oxides, Environ. Sci. Technol. 42 (2008) 5548–5554.
[29] I. Ferrez, M. Carballa, H. Noppe, H. de Brabander, N. Boon, W. Verstraete, Influence of manganese and ammonium oxidation on the removal of 17α-ethinylestradiol (EE2), Water Res. 43 (2009) 77–86.
[30] R.L. Johnson, A.J. Anschutz, J.M. Smolen, M.F. Simcik, R.L. Penn, The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces, J. Chem. Eng. Data 52 (2007) 1165–1170.
[31] C.Y. Tang, Q.S. Fu, D. Gao, C.S. Criddle, J.O. Leckie, Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces, Water Res. 44 (2010) 2654–2662.
[32] A.T. Quitain, M. Faisal, K. Kang, H. Daimon, K. Fujie, Low-molecular-weight carboxylic acids produced from hydrothermal treatment of organic wastes, J. Hazard. Mater. 93 (2002) 209–220.
[33] E. Zahonyi-Budo, L.I. Simandi, Oxidation with unstable manganese (VI) in acidic solution, Inorg. Chim. Acta 237 (1998) 173–175.