Effect of initial solution pH on photo-induced reductive decomposition of perfluorooctanoic acid

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Highlights
- The decomposition of PFOA depended strongly on the solution pH in UV–KI system.
- Defluorination of PFOA by hydrated electron enhanced as the increasing of pH.
- Higher pH inhibits the generation of toxic intermediates during PFOA decomposition.
- The concentration of hydrated electron increased with the increase of the initial pH.

Abstract
The effects of initial solution pH on the decomposition of perfluorooctanoic acid (PFOA) with hydrated electrons as reductant were investigated. The reductive decomposition of PFOA depends strongly on the solution pH. In the pH range of 5.0–10.0, the decomposition and defluorination rates of PFOA increased with the increase of the initial solution pH. The rate constant was 0.0295 min$^{-1}$ at pH 10.0, which was more than 49.0 times higher than that at pH 5.0. Higher pH also inhibits the generation of toxic intermediates during the PFOA decomposition. For example, the short-chain PFCAs reached a lower maximum concentration in shorter reaction time as pH increasing. The peak areas of accumulated fluorinated and iodinated hydrocarbons detected by GC/MS under acidic conditions were nearly 10–100 times more than those under alkaline conditions. In short, alkaline conditions were more favorable for photo-induced reduction of PFOA as high pH promoted the decomposition of PFOA and inhibited the accumulation of intermediate products. The concentration of hydrated electron, detected by laser flash photolysis, increased with the increase of the initial pH. This was the main reason why the decomposition of PFOA in the UV–KI system depended strongly on the initial pH.

1. Introduction
Perfluorocarboxylic acids (PFCAs) and their salts have been widely used as emulsifying agents in polymer synthesis, surface treatment in photolithography, paper coatings, waxes and polishes (Kannan, 2011). Some of them, especially perfluorooctanoic acid ($\text{C}_8\text{F}_{15}\text{COOH}$; PFOA), have recently received intense attention due to their persistence and bioaccumulation in the environment. PFOA has been frequently detected in natural waters, sediments, aquatic life and humans (Moody and Field, 1999; Taniyasu et al., 2003; Olsen et al., 2004). Increasing evidence indicates that PFOA is a persistent toxic pollutant that accumulates in higher organisms and presents a serious risk to human health (Kannan, 2011; Post...
et al., 2012). Therefore, developing effective abatement methods to detoxify PFOA under mild conditions is highly desired.

PFCAs exhibit outstanding resistance against chemical and biological degradation. Conventional treatment methods are ineffective for the degradation of aqueous PFCAs since it is inherently recalcitrant to conventional chemical and microbiological treatment (Takagi et al., 2011; Schultz et al., 2006). Several methods have been explored against perfluorocarboxylate pollutants (Hori et al., 2008, 2006). However, severe reaction conditions were needed, such as high temperature and pressure or supercritical conditions.

Thermodynamically, perfluorinated chemicals are more susceptible to reductive defluorination. Photo-reductive decomposition of PFOA in the UV/KI system was reported by our research group (Qu et al., 2010 and Park et al., 2009). In our research, the degradation and defluorination efficiencies were 93.9% and 76.8% at pH 10.0, after 6 h reaction, respectively. It is of practical interest to examine this process under environmentally relevant conditions, since the pH of effluent of semiconductor industry range from 6 to 9 (Currier et al., 2008). Park et al. (2011) have reported that pH had no observable effect on photo-reduction of PFC. The Park’s experiments were completed in an open system, which is different from our case where we conduct in a sealed one. Therefore, the mechanism of the systems and pH effect may be different. It is necessary and essential to carry out the research on the photo-reduction of PFOA in our system at different pH solution. In this paper, the effect of pH on the decomposition of PFOA and the formation of intermediates were also studied. Furthermore, the effect of pH on the transformation mechanism was examined as well.

2. Materials and methods

2.1. Materials and apparatus

Perfluorooctanoic acid (PFOA, ≥90%), perfluoropentanoic acid (PFPeA, ≥94%) and perfluorohexanoic acid (PFHxA, ≥97.0%), perfluoroheptanoic acid (PFHpA, 99%), perfluorobutyric acid (PFBA, 99%), pentafluoroproionic acid (PFPrA, 97%) and trifluoroacetic acid (TFA, 99%) were obtained from Fluka (Milwaukee, WI). HPLC-grade methanol, ammonium hydroxide, ammonium chloride, and potassium iodide were purchased from Sigma–Aldrich. The solvents, sodium chloride, hydrochloric acid, sodium hydroxide and HPLC-grade methanol, ammonium hydroxide, ammonium chloride, sodium chloride, hydrochloric acid, sodium hydroxide and potassium iodide were purchased from Sigma–Aldrich. The solution pH was adjusted by adding hydrochloric acid, potassium hydroxide, ammonium hydroxide and ammonium chloride, and the pH of the solution was measured by a pH meter (Thermo Scientific, ORION 3 STAR).

For details about the reactor, see Supporting Information Fig. S1.

2.2. Photoreductive decomposition of perfluorooctanoic acid

Reductive defluorination of PFOA with hydrated electrons as a bulk reductant under anoxic solutions were examined. Before the reaction, the mixture solution containing 0.025 mmol L\(^{-1}\) PFOA and 0.25 mmol L\(^{-1}\) potassium iodide was purged by pure nitrogen for 30 min in order to remove oxygen from solution. To investigate the pH effect, the photoreductive degradation experiments were carried out at an initial pH ranging from 5.0 to 10.0 adjusted with NaOH or HCl. NH\(_4\)Cl and NH\(_4\)OH mixture solutions were used as buffer when necessary.

2.3. Analysis methods

Concentrations of PFOA and shorter-chain PFCAs including PFHpA(C\(_{6}\)F\(_{13}\)COO\(^-\)), PFHxA(C\(_{6}\)F\(_{11}\)COO\(^-\)), PFPeA(C\(_{4}\)F\(_{9}\)COO\(^-\)), PFPrA(C\(_{3}\)F\(_{8}\)COO\(^-\)) and TFA(C\(_{2}\)F\(_{5}\)COO\(^-\)) were determined by high-performance liquid chromatography/tandem mass spectrometry (HPLC-MS/MS, TSQ™ Quantum Access™, Thermo Finnigan, San Jose, CA, USA). An ion chromatography system (ICS-3000, Dionex Corporation) was used to measure fluoride in the aqueous solution. The fluorinated and iodinated intermediates were determined by a Headspace (HS)-GC/MS system consisting of a gas chromatograph (GC2000, Thermo Fisher Scientific, Inc. Waltham, MA, USA) and a single quadrupole mass spectrometer (Trace DSQ, Thermo Fisher Scientific, Inc. Waltham, MA, USA). The incubation temperature was set at 70 °C for 1 h, 1 mL headspace gas samples were then taken for the GC/MS analysis. Due to the lack of standards for intermediates, peak areas of seven species were used instead of the concentrations in discussion. Detailed information about the LC-MS/MS, IC and HS-GC/MS are provided in the Supporting Information.

2.4. Laser flash photolysis experiments

Laser flash photolysis was used to detect the hydrated electron. An yttrium aluminum garnet (YAG) laser was used as the excitation source (266 nm, 3 ns pulse width, 60 mJ per pulse). The source of analyzing light was a 500 W xenon lamp, which can be brightened 100 times during the detecting period. The laser and analyzing light beam passed perpendicularly through a quartz cell. The transmitted light entered a monochromator equipped with a photomultiplier. The signals were collected using an Agilent

Fig. 1. PFOA decomposition as a function of pH by (a) UV–KI photolysis and (b) direct UV photolysis (without KI) (all experiment repeated 3 times, error bars indicate standard deviation).
54830B digital oscillograph and then transferred to a computer. The sample solutions were deaerated by bubbling with high-purity N₂ (99.99%) for 20 min.

3. Results and discussion

3.1. Effect of pH on decomposition of PFOA

Fig. 1(a) shows the reductive decomposition of PFOA in the presence of potassium iodide at different initial pH values. Control experiments (direct photolysis) were conducted in the absence of KI under otherwise identical conditions (Fig. 1b). From the data in Fig. 1, it was concluded that the reductive decomposition of PFOA depended strongly on the pH. From pH 5.0 to 10.0, the decomposition of PFOA increased with an increase of pH value. For example, after 2 h of reaction, the reductive decomposition of PFOA at pH 7.0 and 10.0 was 74.6% and 97.9%, respectively, while only 9.1% of PFOA was decomposed when the pH was 5.0. The reductive decomposition of PFOA under different pH conditions was fitted with pseudo-first-order kinetics. The decomposition rate constants were listed in Table S1. It is apparent that the rate constant increased with an increase of solution pH. For example, the rate constant at pH 10.0 was 0.0295 min⁻¹, which was 49.0 times higher than that under acidic condition.

In UV/KI system, the aqueous iodides could generate a caged complex (Eqs. (1) and (2)) (Rahn, 1997), which may dissociate into a hydrated electron and an iodide radical (Eq. (3)). Hydrated electron was a strong reductant, which can quickly react with PFOA (Park et al., 2009; Qu et al., 2010). So, there are two different decomposition processes in the UV–KI system, namely reductive decomposition by hydrated electron and direct UV photolysis (Qu et al., 2010). The decomposition rate of PFOA in the UV–KI system increased with the increase of pH value. However, the direct photolysis of PFOA was not dependent on the initial solution pH (shown in Fig. 1b). Therefore, it could be concluded that the pH depended trend of the UV–KI system could be attributed to the hydrated electrons in view of the different effect of pH on the UV–KI system and direct photolysis.

\[ \Gamma^- + H_2O \text{inh}(254 \text{ nm}) \rightarrow H_2O^+ \text{ and } \Gamma^- \]  
\[ \Gamma^- + H_2O \rightarrow (\Gamma^-, e^-) + H_2O \]  
\[ (\Gamma^-, e^-) \rightarrow \Gamma^- + e_{aq} \]  
\[ \Gamma^- + \Gamma^- \rightarrow I_2 \]  
\[ \Gamma^- + I_2 \rightarrow I^- \]  
\[ e_{aq} + I_2 \rightarrow 2I^- \]  
\[ e_{aq} + I^- \rightarrow I^- + I^- \]  
\[ e_{aq} + H_2O^+ \rightarrow H^+ \]  
\[ 3I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O \]  

In order to re-affirm our conclusions, a laser flash photolysis study on the production of hydrated electrons under different pH conditions was carried out. The hydrated electron produced by the absorption of the laser pulse in the various solutions was identified by its characteristic absorption at around 720 nm and by its disappearance through reaction with N₂O saturated solutions (Silva et al., 1998). The production and decay of hydrated electrons in solutions at different pH are shown in Fig. 2. From the data, the conclusion that the production of hydrated electron increased with the increase of the initial pH was easily obtained, which was the main reason why the decomposition of PFOA in the UV–KI system depended strongly on the initial pH value.

This results largely from two facts. Firstly, in the presence of H⁺ or under low pH conditions, hydrated electrons could be quickly converted into H (Eq. (8)) with a rate constant of 2.3 × 10¹⁰ L mol⁻¹ s⁻¹ (Buxton et al., 1988); Therefore, more hydrated electrons would be quenched under acidic conditions than under alkaline conditions.

Secondly, it is believed that higher pH values, specifically above 8.5 could promote the disproportionation of I₂ into I⁻ and IO₃⁻ (Eq. (9)) (Cotton and Wilkinson, 1988), resulting in more iodide ion recycled and less iodine and triiodide generated (Eqs. (4) and (5)). More iodide ion resulted in more hydrated electron produced. Moreover, less iodine and triiodide can decrease consumption of hydrated electron because of their reaction with hydrated electron (Eqs. (6) and (7)) (Rigg and Weiss, 1952). So, disproportionation of I₂, which happens at higher pH values, can increase the concentration of hydrated electron.

The decomposition of monochloroactic acid by hydrated electron enhanced obviously with increasing pH was reported by Li et al. (2012), which is similar with our results in this paper. The pH effect on the reductive decomposition of PFOA and PFOS by hydrated electron was also investigated by Park et al. (2011). While, Park’s paper revealed that the pH has little impact on the observed PFOX reduction kinetics. The difference resulted mainly from the different experimental conditions. For example, an open reactor was used in Park’s experiment, which is different from our case where we conduct in a sealed one in order to avoid reaction of the hydrated electron with O₂.

3.2. Effect of pH on defluorination of PFOA

The higher resistance of PFCs to degradation is attributed to the extreme stability offered by the strong C–F bonds. Therefore, the effect of initial pH on the cleavage of C–F bonds was also investigated in this study.

Defluorination in the UV–KI system and direct photolysis was shown in Fig. 3. In light of the defluorination of direct photolysis being very small, we conclude that it was reductive decomposition by hydrated electron, not direct photolysis, was the main mechanism to cleave C–F bonds in the UV–KI decomposition system. It was reported that reduction of the C–F bond could occur at less than −2.7 V (Park et al., 2009). Hydrated electrons with a reduction
and 85.1% of PFOA degraded under (Eq. (4)) and thus fewer iodide concentrations in reductive photolysis of PFOA.

It was found that defluorination of PFOA in UV–KI system increased with the increase of initial pH value. As shown in Fig. 3, the defluorination efficiency of PFOA at pH 5.0 was only 5.9% after 6 h irradiation, which means that most of the C–F bonds were not cleaved under acidic conditions. While, defluorination of PFOA at alkaline conditions was much higher. For example, after 6 h irradiation, defluorination of PFOA at pH 8.0 and 10.0 were 44.7% and 69.8%, respectively. Obviously, higher pH was preferred for defluorination of PFOA in this UV–KI reductive system.

As discussed above (Section 3.1), more hydrated electrons existed in aqueous solution as the pH increases. So, defluorination of PFOA by hydrated electron enhanced as the increase of the pH. While, hydrogen ions could react with hydrated electrons under acidic condition (Eq. (8)), resulting in the quenching of hydrated electron and formation of hydrogen atom. Hydrogen atom cannot reduce PFOA due to its lower reduction potential (−2.1 V). So, only small parts of C–F bonds can be cleaved under acidic condition.

3.3. Effect of pH on the formation and decomposition of intermediates in reductive photolysis of PFOA

In addition to fluoride, other intermediate products, such as short-chain perfluorinated acids, fluorinated and iodinated hydrocarbons, were also formed during reductive decomposition of PFOA. Effect of initial pH on the formation and decomposition of these intermediates was also discussed in the following section.

3.3.1. Effect of pH on the formation and decomposition of short-chain perfluorinated acids

The formation and decomposition of short-chain perfluorinated acids varied at different pH values. For example, the concentration of PFHpA as a function of irradiation time at different initial pH was shown in Fig. 4. Under acidic conditions (pH 5.0), the concentration of PFHpA increased continuously with reaction time. After 6 h, the concentration of formed PFHpA was greater than 3.9 μmol L⁻¹, which means 15.6% of [PFOA]initial and 85.1% of [PFOA]degraded converted into PFHpA. In acidic solutions, the formed hydrogen atoms and direct photolysis could cleave C–C bonds of PFOA, leading to the formation of shorter chain PFCAs. The shortage of hydrated electron resulted in an accumulation of formed short-chain PFCAs. Such phenomenon was also observed for PFHxA, PFPeA, PFBA, PFPrA and TFA, and the formation and decomposition of these intermediates were shown in Supplementary Information (SI).

As discussed by Park et al., the formation of fluorinated and iodinated hydrocarbons at higher pH values. The logarithm of peak areas of these intermediates after a 2 h reaction at different pH values are shown in Fig. 5. It was clearly noted that the formation of such intermediates decreased as pH increased. As shown in Fig. 5, the peak areas of these species at pH 5.0 were 10–100 times more than that at pH 10.0. Thus, it was concluded that the alkaline conditions could decrease the accumulation of these intermediates and thus effectively reduce the secondary pollution during decomposition of PFOA.

There are two facts which could ascribe to the fewer accumulation of fluorinated and iodinated hydrocarbons at higher pH values. Firstly, there were fewer precursors of these intermediates existing in alkaline solutions. As discussed by Park et al., the formation of such intermediate needed the existence of fluorooalkyl radicals, fluorine and iodide radicals in solutions (Park et al., 2009). More hydrated electrons were generated to attack C–F bonds of PFCAs under alkaline conditions, which reduced the formation of fluorooalkyl radicals. Moreover, under alkaline conditions, I₂ undergo a disproportionation reaction (Eq. (9)), which results in quick reaction of iodide radical to form more I₂ (Eq. (4)) and thus fewer iodide...
radicals existing in solution. Therefore, the formation of fluorinated and iodinated hydrocarbon intermediates under alkaline condition was lower than that under acidic condition. Secondly, the smaller accumulation of these intermediates under alkaline condition may result from the subsequent reduction of C–F and C–I bonds by hydrated electron.

In a word, the result that the concentration of these intermediates decreased with the increase of pH could be attributed to the increase of hydrated electrons as pH increases.

3.4. Effect of pH on transformation mechanism of PFOA

In order to elucidate the effect of pH on the decomposition mechanism of PFOA in the UV–KI system, the decomposition of PFOA in $^{18}\text{O}$-water was conducted at different pH. The electrospray ionization (ESI) mass spectrum of the reaction solution for 90 min is shown in Fig. 5. Peaks at $m/z$ 363 and 367, corresponding to $[\text{CF}_3\text{C}^{18}\text{O}]^{16}\text{O}]$ and $[\text{CF}_3\text{C}^{16}\text{O}^{18}\text{O}^{16}\text{O}]$, were detected at all pH. From the data in Fig. S11(A), it was noticed that the ratio of $[\text{CF}_3\text{C}^{18}\text{O}]^{16}\text{O}]$ to $[\text{CF}_3\text{C}^{16}\text{O}^{18}\text{O}^{16}\text{O}]$ increased with the increase of pH. For example, the ratio of $[\text{CF}_3\text{C}^{16}\text{O}^{18}\text{O}^{16}\text{O}]$ to $[\text{CF}_3\text{C}^{18}\text{O}]^{16}\text{O}]$ was only 1.1 at pH 5.0, while it was 3.4 at pH 10.0.

After direct UV photolysis of PFOA in $^{18}\text{O}$-water, $[\text{CF}_3\text{C}^{18}\text{O}]^{16}\text{O}]$ was found to be the main chemical detected (Hori et al., 2004), which could be formed by the cleavage of the C–C bond between $\text{CF}_3\text{CO}$ and COOH, and the hydrolysis of unstable $\text{CF}_3\text{CO}$ and the hydrolysis of unstable $\text{CF}_3\text{C}^{18}\text{O}$, was the main product of PFOA reduced by hydrated electrons in $^{18}\text{O}$-water, which was attributed to the direct cleavage of C–F bonds and the elimination of $\text{CF}_2$ units (Qu et al., 2010). Thus, the result that the ratio of $[\text{CF}_3\text{C}^{16}\text{O}^{18}\text{O}^{16}\text{O}]$ to $[\text{CF}_3\text{C}^{18}\text{O}]^{16}\text{O}]$ decreased with the decrease of pH means that reductive decomposition by hydrated electron reduced with the decrease of pH among two processes of the UV–KI system.

The cleavage of C–C bonds can be deduced from the detection of short-chain perfluorocarboxylic acids during the decomposition of PFOA (Qu et al., 2010). In order to determine the effect of pH on the cleavage position of PFOA, the photo-induced reduction of MPFOA (1,2,3,4-$^{13}\text{C}$-PFOA) in different pH solutions was carried out. Two facts could be found from data shown in Fig. S11(B).

Firstly, 1,2,3-$^{13}\text{C}$-PFHpA detected at $m/z$ 366 was the main intermediate of MPFOA at all pH values, which means that it is the C–C bond between the carboxyl and perfluoroalkyl group, not that bond between $\text{CF}_3$ and $\text{CF}_2$ group, was the main cleaved position of PFOA at all pH. This result could be deduced from the facts that the bond of C–C between $\text{CF}_3$ and $\text{CF}_2$ group was much stronger than that between the carboxyl and perfluoroalkyl group.

Secondly, the ratio of $1,2,3-$13C-PFHpA ($m/z$ 366) to $1,2,3,4-$13C-PFHpA ($m/z$ 367) increased with the increase of pH. For example, the ratio of $1,2,3-$13C-PFHpA to $1,2,3,4-$13C-PFHpA was 29.7 at pH 5.0, while it was 58.5 at pH 10.0. The result means that the probability of cleavage at the C–C bond between the carboxyl and perfluoroalkyl group enhanced with the increase of pH. The strongest electronegativity of fluorine resulted in the large repulsion between neighboring F atom. Thus, F atoms adjacent to each other stagger angle and was arranged in a spiral around the C chain (Kissa, 2001). The effective shielding of carbon by three fluorine atoms prevents the attack of hydrated electron at the C–C bond between $\text{CF}_3$ and $\text{CF}_2$ group and results in a higher chance of the hydrated electron attacking the C–C bond between the carboxyl and perfluoroalkyl group. Therefore, hydrated electrons could easily attack the C–C bond between the carboxyl and perfluoroalkyl group, resulting in formation of $1,2,3-$13C-PFHpA. The C–C bonds between the $\text{CF}_3$ and $\text{CF}_2$ groups could be cleaved through direct photolysis, resulting in formation of $1,2,3,4-$13C-PFHpA. So, from variation of $^{13}$C labeled intermediates at different pH, it was deduced that, among two process of the UV–KI system, the decomposition by hydrated electron increased with increasing pH. The same conclusion was obtained at the foregoing discussion.

3.5. Evolution of pH in UV–KI photolysis of PFOA

Based on the above discussion, it was concluded that the pH value of the reaction process has a great influence on the reductive photolysis of PFOA. Therefore, it is meaningful to investigate the evolution of the pH value during the decomposition of PFOA. The evolution of the pH value was investigated in detail when the initial pH value was 10.0, which was adjusted by KOH or $\text{NH}_4\text{OH}–\text{NH}_4\text{Cl}$ buffer.

From Fig. S12, it was noticed that the pH changed significantly during the process of PFOA decomposition when the initial pH was adjusted by KOH. The pH value of reaction solution decreased from 10.0 to 7.0 after a 6 h reaction. The decrease of the pH during reaction was due to the consumption of hydroxyl ion by iodine disproportionation reaction (Eq. (9)). While, adjusting the solution by buffer could keep the pH value relatively constant. Fig. S10 shows $\ln(C/C_0)$ as a function of UV irradiation time when the solution was adjusted two ways. Obviously the decomposition of PFOA was promoted greatly by buffer adjustment. Therefore, not only the initial alkaline condition but also keeping the pH value constant was necessary to maintain the higher degradation rate of the reductive photolysis system. Considering the importance of keeping the system under alkaline condition, the buffer adjustment should be taken into account to obtain the higher decomposition efficiency.

During the decomposition of PFOA in KOH adjusted solution, the pH increased to about 10.5 from 30 to 60 min quickly, then decreased to 9.0 after 30 min of irradiation. For comparison, the pH change in the absence of PFOA was studied as well. In the absence of PFOA, the system’s pH value decreased with the irradiation time continuously. Therefore, the pH of KOH adjusted solution increase in the 30–60 min could be attributed to the decomposition of PFOA. The bell-shaped pH change during PFOA decomposition is possibly attributed to the production of intermediates and subsequent consumption of hydroxyl by iodine disproportionation reaction.

4. Conclusion

The effects of the initial solution pH on the PFOA decomposition by UV-induced hydrated electrons were investigated, and several conclusions can be made based upon the experimental results:
(1) The reductive decomposition of PFOA depended strongly on the solution pH in the photo-induced reductive system. Alkaline conditions were more favorable for the reductive decomposition and defluorination of aqueous PFOA by promoting recycling of the iodide ion and inhibiting the quenching of hydrated electrons.

(2) Alkaline conditions reduce the accumulation of intermediates, such as short-chain PFCAs, fluorinated and iodinated hydrocarbons, in reductive photolysis of PFOA. That could be mainly attributed to the increase of hydrated electrons as pH increases.

(3) Keeping the pH value constant during the reaction was also necessary to maintain the high degradation rates of the reductive photolysis. Therefore, buffer adjustment is suggested to obtain higher decomposition efficiency.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.12.046.

References


