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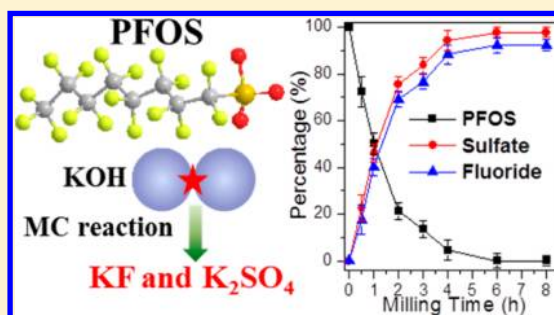
Kunlun Zhang,[†] Jun Huang,^{†,*} Gang Yu,^{†,*} Qiwu Zhang,[‡] Shubo Deng,[†] and Bin Wang[†]

[†]State Key Joint Laboratory of Environment Simulation and Pollution Control (SKJLESPC), School of Environment, POPs Research Center, Tsinghua University, Beijing 100084, P.R. China

[‡]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

S Supporting Information

ABSTRACT: Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have received high concerns due to their extreme persistence, and very few technologies have been reported for their complete destruction. For sound PFCs wastes disposal, mechanochemical method was employed using a planetary ball mill. Potassium hydroxide (KOH) was identified as the best comilling reagent and nearly complete destruction of both PFOS and PFOA was realized. The measured water-soluble fluoride accounted for most of the organic fluorine. The final products of PFOS after treatment were shown to be KF and K₂SO₄ by XRD analysis. The mass ratio between PFOS and KOH significantly affected the fluoride recovery but not for PFOS destruction and the sulfate recovery. The gradual formation of sulfate and fluoride reveals that the degradation of PFOS is initiated with the dissociation of the sulfonate group. FTIR spectra further showed the disappearance of the –CF₃ and –CF₂– groups with the generation of sulfate. The cleavage of C–F bonds in PFOS and the formation of fluoride ion were also identified by XPS spectra. On the basis of these results, possible reaction pathways were proposed. The approach was also successfully applied for the destruction of PFOS and PFOA homologues with different chain lengths.



INTRODUCTION

Perfluorinated compounds (PFCs) and related derivatives have been widely used for decades in a variety of industrial and consumer products, including surfactants, lubricants, firefighting foams, and coatings (e.g., carpet, textiles, paper, leather).^{1–3} Among them, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were the most commonly used and have been frequently detected in the environment, wildlife, and humans from urban to remote areas.^{4–6} They have received wide concerns because of their toxicity, environmental persistence, and bioaccumulation.^{7–9} As a result, PFOS was listed as a persistent organic pollutant in Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) for strict restriction in 2009. Also, PFOA is currently being phasing out according to the US EPA.¹⁰ Between 1970 to 2002, more than 26 500 tons of PFCs solid wastes or byproducts were generated and partly or largely deposited in landfills around production sites.^{3,11} The sound destruction of existing PFCs solid wastes is becoming a practical need particularly in the frame of global implementation of the Stockholm Convention.

Because of the high energy of carbon–fluorine bonds (C–F, 531.5 kJ mol^{–1}), the PFCs are chemically stable and resistant to oxidation, reduction, and biodegradation.^{12–14} Hence, the cleavage of C–F bonds was the most important criteria for PFCs detoxification and persistence elimination.¹⁵ Recently, various approaches including sonochemical, photochemical, subcritical, and electrochemical decomposition of PFOS and

PFOA in aqueous solutions have been investigated.^{16–20} These methods either required harsh reaction conditions, or were incomplete in terms of the PFC's defluorination and destruction, especially for PFOS.¹³ In addition, most studies focused on aqueous systems while little attention has been paid to the destruction of PFCs in solids phase.

As far as the disposal of PFCs wastes is concerned, high temperature incineration (HTI) would be a commonly preferred choice. However, HTI in this case could generate hydrogen fluoride (HF) gas, which is not only toxic but also corrosive to the refractory materials in waste incinerators.²¹ Also, unintentionally produced POPs such as dioxins might also be generated in the combustion process.²² Therefore, it is necessary to seek noncombustion options for the safe disposal of PFCs wastes.

Mechanochemical (MC) destruction refers to the reactions taken place at the chemical surfaces under the impact by mechanic force, in which transient temperature or even triboplasmas can be generated because of the high energy impact between surfaces.²³ Such agitation can produce marked chemical activation resulting in reactions between the reagents and the pollutants.²⁴ MC destruction has been identified as a promising noncombustion technology for the disposal of chlorinated POPs

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containing wastes, in which the unintentionally produced POPs can be avoided.^{25,26} Many examples such as DDT, PCBs, PCDD/Fs, halogenated benzene, and polyvinylchloride (PVC) have been previously reported on MC destruction.^{27–31} However, for the MC destruction of fluorinated POPs, so far very few studies were reported (except one in a national journal),³² particularly in the final products and quantitative explanation of fluoride.

In the present study, MC method was adopted to destroy PFOS and PFOA in a planetary ball mill. Potassium hydroxide (KOH) was identified as the best comilling reagents considering both the destruction of PFCs and the mineralization represented by the recovery of anions (e.g., F^- and SO_4^{2-}). The products from the MC treatment were investigated and the chemical change of C–F bonds was characterized based on which the possible reaction pathway was proposed. Besides, the extended application of this MC method was also evaluated for the homologues of PFOS and PFOA.

EXPERIMENTAL METHODS

Materials. Potassium salt of perfluorooctane sulfonate (PFOS, >98%), perfluorohexane sulfonate (PFHxS, >98%) and perfluorobutane sulfonate (PFBS, >98%), perfluorodecanoic acid (PFDA, >98%), and perfluorododecanoic acid (PFDaA, >97%) were purchased from Sigma-Aldrich Co. (USA). Perfluorooctanoic acid (PFOA, >97% in purity) was obtained from Apollo Scientific Limited (Manchester, England). Potassium hydroxide (KOH, >90%) was purchased from J&K Chemical China Limited (China). The ultrapure water used was produced by a Milli-Q integral water purification system (Millipore, USA).

Ball Milling Experiment. A planetary ball mill (QM-3SP2, Nanjing University Instrument Corporation, China) was used for the experiments. The milling pots with volume of 100 mL and balls with diameters of either 5.5 or 9.6 mm were made of stainless steel. During the ball milling 4.6 g, comilling reagents were mixed with 0.2 g PFCs (PFOS content was increased to 0.8 g in samples for characterization analysis including XRD, FTIR, and XPS) and then put into the pots along with 20 big balls and 90 small balls. The rotation speed of the planetary disk was set as 275 rpm and the rotation direction changed automatically every 30 min. After the milling, all of the samples were collected and preserved in a hermetic and dry apparatus for further use.

Sample Extraction and Instrumental Analysis. Each milled sample (0.050 g) was dissolved in 50 mL ultrapure water with 15 min ultrasonic treatment at 60 °C. The solution was filtered by 0.22 μ m polyether sulfone (PES) filter and then subjected to instrumental analysis for both residual PFCs and soluble inorganic ions.

The residual PFCs were determined by an HPLC system (Shimadzu LC-20AT HPLC with conductivity detector CDD-10A) using a C_{18} reversed phase column (4.6 \times 250 mm, 5 μ m, Agilent) and an automatic sampling system (SIL-20A). The column oven temperature was set as 40 °C. Methanol/0.02 M NaH_2PO_4 (65/35, v/v) was used as a mobile phase with a flow rate of 1.0 mL min^{-1} . The soluble inorganic ions were measured by the ion chromatography (IC, DX-2000, DIONEX Co., USA) equipped with an anion exchange column (IonPac AS4A-SC) and an auto sampling system.

Characterization of the Materials. Besides the chromatographic determinations above, the chemical composition change of the solid samples (representatively PFOS samples) during the MC reactions were also characterized. X-ray diffraction was

conducted using an XRD (Smartlab, Rigaku) with Cu $K\alpha$ radiation at a speed of 6° min^{-1} ranging from of $2\theta = 20^\circ - 80^\circ$. Fourier transform infrared (FTIR) was carried out using Nicolet 6700 (Thermo-Fisher) with the KBr disk method from 200 cm^{-1} to 4000 cm^{-1} . X-ray photoelectron spectrometry (XPS) was conducted using Scanning X-ray Microprobe (PHI Quantera SXM, ULVAC-PHI), in which the binding energy was calibrated using the C (1s) peak as 284.6 eV.

EXPERIMENTAL RESULTS

Comparison of Comilling Reagents. For the assessment and selection of an appropriate destruction media, different comilling reagents were used including CaO, SiO_2 , Fe– SiO_2 (mass ratio 10:1), NaOH, and KOH. They were separately ball milled with PFOS and PFOA for 4 h. The defluorination degree was expressed by recovery of water-soluble fluoride, which was calculated from:

$$\begin{aligned} \text{recovery of fluoride} &= F^- \text{ recovery} \\ &= \frac{\text{measured soluble fluoride ion}}{\text{calculated fluorine from initial PFC}} \end{aligned}$$

The MC destruction efficiency and defluorination results are shown in Figure 1. Although significant removal of PFOS and

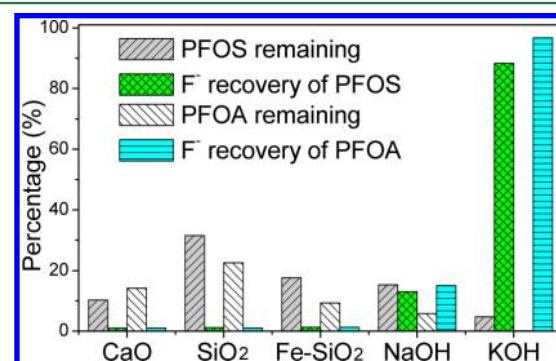


Figure 1. Four hour MC treatment of PFOS and PFOA with different comilling reagents.

PFOA were found when using CaO, SiO_2 , and Fe– SiO_2 , the extremely low fluoride recovery made people doubt whether the mineralization had been really achieved. Co-milling with NaOH achieved enhanced effect but still unsatisfactory. The fluoride recovery was dramatically improved using KOH as comilling reagent (88.3% and 96.7% fluoride recovery respectively for PFOS and PFOA after 4 h ball milling). In this case, both the destruction and the mineralization of PFOS and PFOA have been realized. For the purposes of confirmation, a series of ball milling experiments were further conducted and discussed below.

Effects of Main Factors – Ball Milling Time. The effect of treatment time was first evaluated with the measurement of residual PFOS or PFOA and water-soluble fluoride and sulfate. The sulfate recovery was calculated the same way as fluoride and the results are shown in Figure 2.

As shown in part a of Figure 2, with increased milling time, the remaining PFOS decreased gradually, and the recovery of sulfate and fluoride increased simultaneously. After 6 h ball milling, less than 0.2% of the original PFOS remained and the sulfate and fluoride recovery reached 97.7% and 92.3%, respectively. The high fluoride and sulfate recovery demonstrates the dissociation

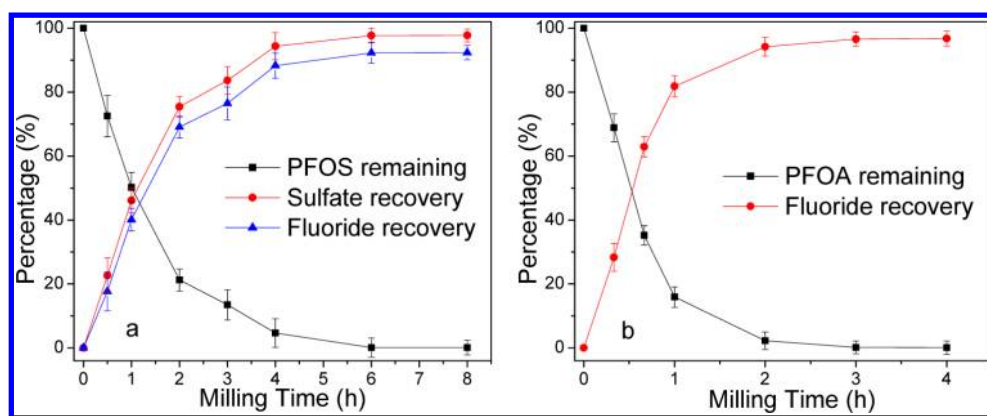


Figure 2. MC treatment of PFOS (a) and PFOA (b) with KOH for various milling time.

of sulfonate and the cleavage of C–F in PFOS showing nearly complete mineralization of PFOS after MC treatment.

During the milling, the recovery of fluoride and sulfate matched up well with the destruction of PFOS and there was no time interval between them as reported for some chlorinated and brominated pollutants.^{33,34} This means a series of dissociation and formation reactions occurred swiftly and spontaneously with few intermediates, which was actually confirmed by the analysis using LC–MS–MS.

However, the destruction of PFOS increased rapidly in the beginning and then slowed down in the later phase of the experiment. This was also observed in the MC treatment of poly vinylidene fluoride (PVDF) with sodium hydroxide reported by Zhang et al. in 2001, in which the author attributed the fact to the agglomeration due to the generation of H₂O.³⁵ In the present study, the agglomeration was also observed in the samples especially after long hours ball milling suggesting the generation of H₂O. The agglomeration of particles with inclusion of PFCs then shielded the reactive surface and resulted in slower reaction speed with prolonged milling.

It is worth noting that the recovery of sulfate was always higher than that of fluoride during the milling, which means the desulfonation reactions take place prior to the defluorination process. It is consistent with the fact that the sulfonate end of PFOS molecule is relatively unstable and reactive,³⁶ and the C–S bonds were usually cleaved first during degradation.¹⁶ Therefore, during the ball milling of PFOS with KOH, the sulfonate group is supposed to be the trigger point, from which the degradation starts to take place.

For the MC treatment of PFOA shown in part b of Figure 2, the destruction and defluorination results of PFOA had similar trend and conclusion as PFOS. After 3 h milling with KOH, PFOA was completely destroyed and more than 97% fluoride was recovered. It should be noted that the destruction of PFOA (100% destruction at 3 h) was much faster than PFOS (99.88% destruction at 6 h) in MC treatment. This is easy to explain because the chemical property of PFOA is not as stable as PFOS and PFOA degrades easily.^{36,37}

To investigate the final products after ball milling, X-ray diffraction (XRD) analysis of PFOS samples was conducted. The XRD spectra of the 0 h mixture and 8 h milled sample are shown in Figure 3 labeled with the pattern of the typical products.

For the 0 h mixture of PFOS and KOH, only the diffraction of hydrated KOH can be found in the XRD spectra. After 8 h milling, quite strong diffraction peaks of potassium fluoride (KF) appeared in the spectra (circled) showing the formation of KF. Again the breakage of C–F bonds can be confirmed as the crystal

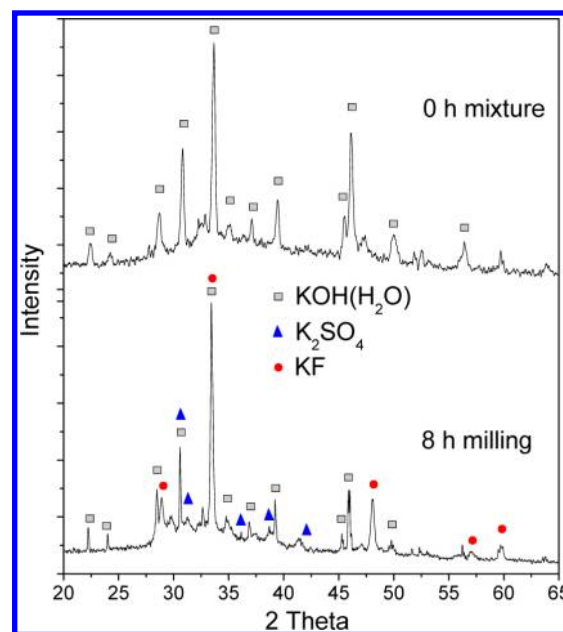


Figure 3. XRD patterns of PFOS sample after ball milling with KOH.

structure of formed KF was clearly illustrated in XRD spectra.³⁸ Besides KF, there were also diffraction signals for potassium sulfate (K₂SO₄) indicating the generation of sulfate. This again demonstrates that PFOS was decomposed into inorganic fluoride and sulfate, corresponding to results above.

Effects of Main Factors – Composition of Inputs.

Previous studies have revealed that the mass ratio between comilling reagents and pollutants was an important factor affecting the performance of MC reactions.³⁹ Experiments based on different mass ratios of KOH and PFOS (from 95:1 to 5:1, total mass stayed 4.8 g) were carried out for 4 h to compare the effects as shown in Figure 4.

Higher mass ratios showed relatively better performance especially in terms of defluorination, where PFOS can be completely destroyed with high recovery of fluoride and sulfate. When the mass ratio was reduced from 95:1 to 5:1, the destruction of PFOS and the recovery of sulfate decreased slightly and then stayed unchanged (over 90%), whereas the fluoride recovery still kept decreasing. For example, with the mass ratio of 5:1, 91.2% of PFOS was destroyed and 86.3% sulfate was recovered after 4 h milling, whereas the recovery of fluoride was only 53%.

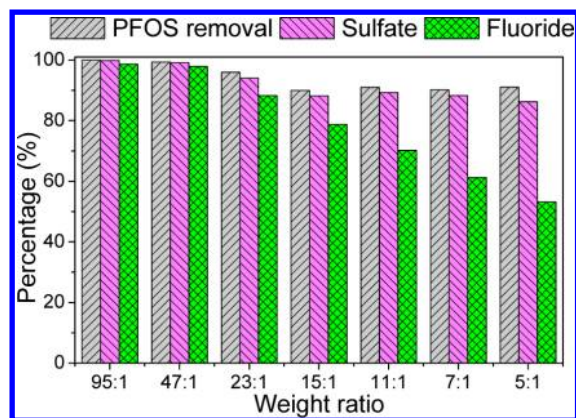


Figure 4. Four hour MC treatment of PFOS using KOH with different mass ratio.

Previous work has shown that the destruction efficiency would drop dramatically with the decrease of mass ratio in MC treatment.³⁹ In this case, the PFOS removal and sulfate recovery did not strictly follow this pattern but the fluoride recovery did. The reason should come from the molecular structure of PFOS and its particular reaction with KOH in which the sulfonate dissociates prior to defluorination. Although the amount of KOH reduced, it was always sufficient for sulfonate dissociation and the reaction could be easily reached. As the content of KOH dropped further, it gradually became the limiting reagent for defluorination and the reaction rate became slower. This uniformity between PFOS removal and sulfate recovery along with the distinct pattern of fluoride recovery also reveals that the MC degradation of PFOS started from the dissociation of the sulfonate group corresponding to the results and descriptions above.

With high mass ratio, high destruction efficiency and rapid reaction can be obtained. But more commingling reagent is needed than that with low mass ratio to destroy the same amount of PFOS. With low mass ratio, the reaction is slower and the destruction efficiency decreases but the total amount of PFOS destroyed in the same batch is even higher than that with high mass ratio (the total amount of PFOS destroyed with different mass ratio is shown in Figure S1 of the Supporting Information). Therefore, for practical application, the MC conditions should be determined after comprehensive considerations of several factors including efficiency demand, reaction time, and the total cost.

Characterization of the Milled Samples. To better understand the chemical change of PFOS in the MC reactions, Fourier transform infrared (FTIR) spectra were recorded to show the variation of functional groups in PFOS as shown in Figure 5.

In FTIR spectra, the typical peak band for PFOS is around 1200–1350 cm^{-1} , which corresponds to the vibrations of the $-\text{CF}_3$ and $-\text{CF}_2-$ group and could be used as the monitor of organic fluorine.^{40,41} The other peak bands shown in 1150–1250 cm^{-1} , 1000–1075 cm^{-1} , and 600–700 cm^{-1} could be assigned to the vibrations of organic sulfonate group ($-\text{SO}_3^-$).^{41,42} During the ball milling of PFOS with KOH, the peak intensity of $-\text{CF}_3$ and $-\text{CF}_2-$ group weakened rapidly after 2 h and nearly disappeared with the extended milling to 8 h. This indicates that these organic C–F bonds were destroyed gradually and the fluorine had been removed from the PFOS molecule by MC force. Similarly, the peak of $-\text{SO}_3^-$ also decreased gradually with the increasing peak of inorganic sulfate (SO_4^{2-}). After 8 h milling,

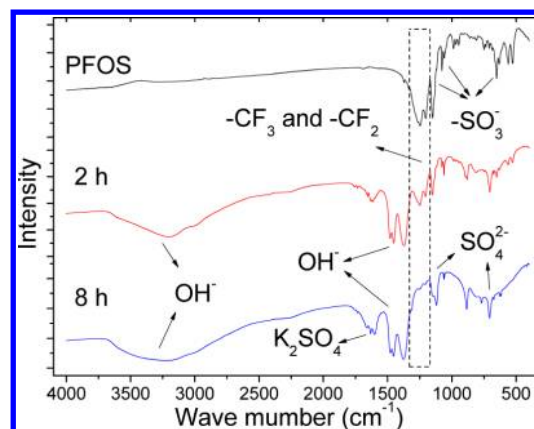


Figure 5. FTIR spectra of PFOS milled samples with different time.

all characteristic peaks of PFOS in FTIR disappeared and the inorganic SO_4^{2-} became the dominating species, demonstrating the destruction of organic fluorine and sulfonate group with generation of sulfate salts.

X-ray photoelectron spectrometry (XPS) was also used to quantify the change of the C–F bonds. The spectra corresponding to the binding energy of F (1s) core electrons are shown in Figure 6. For the 0 h mixture of PFOS and KOH, a

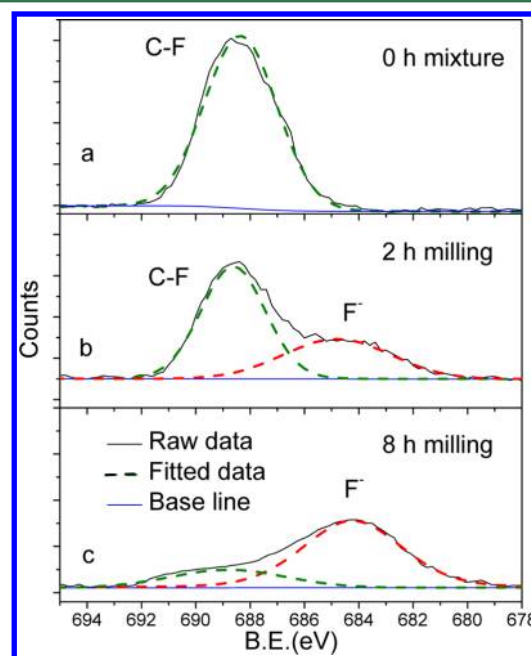


Figure 6. XPS spectra (F1s) of PFOS milled samples with different milling time.

dominant peak was found centered at 689.0 eV (part a of Figure 6), which was attributed to the fluorine bonded to carbon (C–F). After 2 h milling, this peak became weaker and a new peak formed centered at 684.0 eV (part b of Figure 6). This new peak was assigned to the negatively charged monovalent fluorine (F^-) in the F (1s) region.⁴³ After 8 h milling, the C–F peak almost completely disappeared coupled with a significant increase of F^- peak intensity (part c of Figure 6). The weak C–F peak that still existed was attributed to the low mass ratio (5:1) used, and it would totally disappear if higher mass ratio, longer milling time, or higher rotation speed was applied.

The above findings clearly demonstrate that the C–F bonds were cleaved and the organic fluorine was converted into inorganic fluoride indicating the mineralization of PFOS into F^- during the MC treatment.

Proposed Reaction Pathways. According to the results and discussions above, the degradation pathways of PFCs in MC treatment with KOH are proposed in Figure 7. As mentioned,

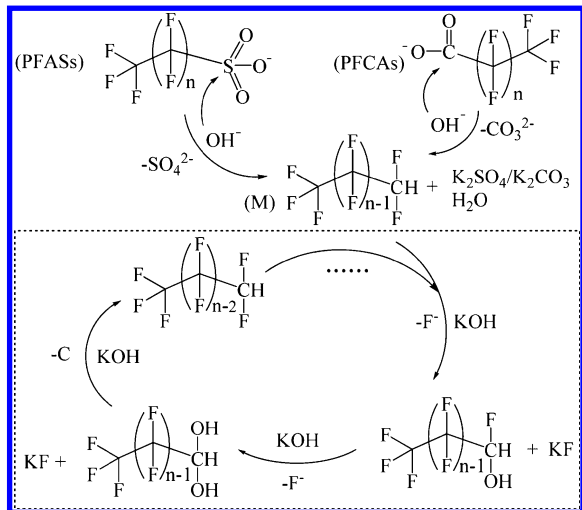
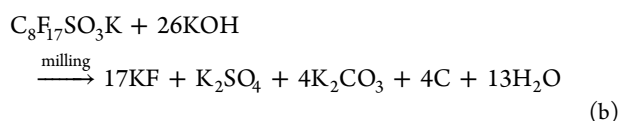
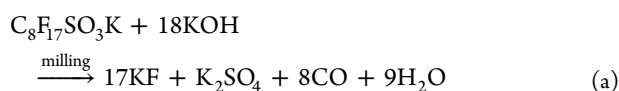


Figure 7. Proposed reaction pathways of PFCs during the milling with KOH.

the sulfonate of perfluoroalkyl sulfonates (PFASs) or carboxylate of perfluorocarboxylic acids (PFCAs) is comparatively labile and easy to be attacked. The sulfur or carbon atom at this polar end are bonded to many electron withdrawing groups (e.g., $C_nF_{2n-1}-$, $=O$, $-OH$), which make it easy for them to bond with nucleophilic groups such as hydroxide. During the ball milling, the sulfonate or carboxylate of PFCs was first nucleophilically attacked by hydroxide and subsequently dissociated from the PFC molecule, transforming into sulfate or carbonate. This result was confirmed by the IC determination. Afterward (shown in the dotted frame in Figure 7, further confirmation needed), it is inferred that the fluorine atoms at the end of the remaining perfluoroalkyl group were then nucleophilically replaced by hydroxide with fluoride yielded, after which a degraded perfluoroalkyl intermediate with one less carbon would be produced. Then this sequential degradation continues until the PFCs was totally mineralized affording fluoride as the final degradation products. It should be stated that further study is needed for the mechanisms on nucleophilic substitution of fluorine and the species of perfluoroalkyl intermediates.

Besides fluorine and sulfur, the fate of the carbon in PFCs molecules during MC reactions should also be discussed in spite that it has few environment relevance. Taking PFOS for example, normally the MC destruction should follow either equations below (eqs a and b)



However, in our experiment, there was no gas phase product detected and, unlike other MC reactions, there was either no generation of elemental carbon observed in the Raman spectra.⁴⁴ It is worth mentioning that the milled samples remained white and could be completely dissolved. This indicates that neither CO nor elemental C was generated and the reactions should not strictly follow the two equations above.

Considering the FTIR spectra (Figure 5), in which the peaks of carboxyl group (~ 1600 , 1400 cm^{-1}) and carbonyl (~ 1400 , 870 cm^{-1}) group were shown, the final form of carbon should be some carbon-containing compounds that can be dissolved in alkaline solution. It is not one pure compound with only one base but a mixture consisting of different chemical bases, similarly confirmed by Zhang et al. in the MC destruction of PVDF using NaOH.³⁵

Application Trials for Homologues of PFOS and PFOA.

After the successful destruction of PFOS and PFOA, this MC method using KOH as comilling reagent was also applied to destroy the homologues of PFOS and PFOA, including perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS), perfluorodecanoic acid (PFDA), and perfluorododecanoic acid (PFDoA). PFHxS and PFBS are the substitutes of PFOS and produced in bulk amounts today, whereas PFDA and PFDoA increased in biota and humans in the past decade revealing their contemporary use and relevance. The decomposition efficiency and ions recovery of them after 4 h ball milling with KOH (mass ratio 4.8 g: 0.2 g) were shown in Figure 8. All of

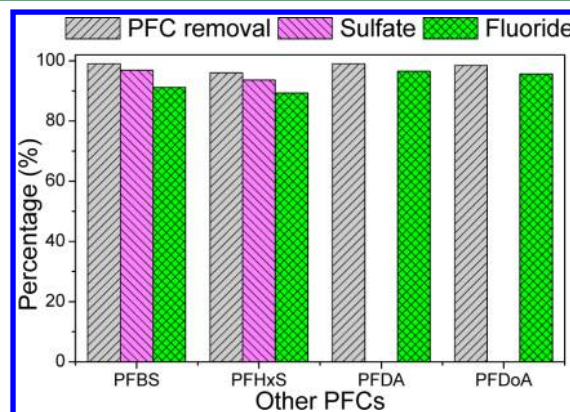


Figure 8. Four hour MC treatment of other PFCs by ball milling with KOH.

the homologues of PFOS and PFOA were destroyed efficiently with high recoveries of sulfate and fluoride. Therefore, the MC method is not only applicable for PFOS and PFOA but also promising for other solid phase PFCs including some emerging alternatives to PFOS and PFOA in the market.

■ ASSOCIATED CONTENT

Supporting Information

Total amount of PFOS destroyed with different mass ratio. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +86 10 6278 7137, fax: +86 10 62794006, e-mail: yg-den@mail.tsinghua.edu.cn (G.Y.); huangjun@tsinghua.edu.cn (J.H.).

Notes

The authors declare no competing financial interest.

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