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RESEARCH ARTICLE

Thermal defluorination behaviors of PFOS, PFOA and PFBS during regeneration of activated carbon by molten salt

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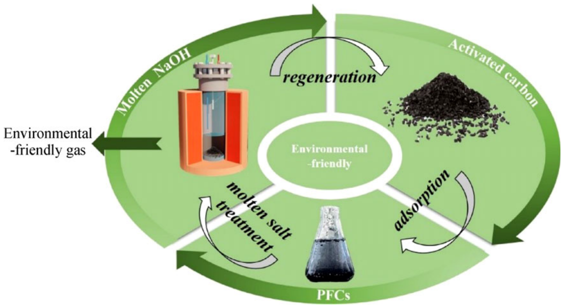
HIGHLIGHTS

- New method of mineralizing PFCs was proposed.
- Activated carbon was regenerated while mineralizing PFCs.
- Molten NaOH has good mineralization effect on PFOS and PFBS.

GRAPHIC ABSTRACT



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ABSTRACT

Current study proposes a green regeneration method of activated carbon (AC) laden with Perfluorochemicals (PFCs) from the perspective of environmental safety and resource regeneration. The defluorination efficiencies of AC adsorbed perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutanesulfonate (PFBS) using three molten sodium salts and one molten alkali were compared. Results showed that defluorination efficiencies of molten NaOH for the three PFCs were higher than the other three molten sodium salts at lower temperature. At 700°C, the defluorination efficiencies of PFOS and PFBS using molten NaOH reached to 84.2% and 79.2%, respectively, while the defluorination efficiency of PFOA was 35.3%. In addition, the temperature of molten salt, the holding time and the ratio of salt to carbon were directly proportional to the defluorination efficiency. The low defluorination efficiency of PFOA was due to the low thermal stability of PFOA, which made it difficult to be captured by molten salt.The weight loss range of PFOA was 75°C–125°C, which was much lower than PFOS and PFBS (400°C–500°C). From the perspective of gas production, fluorine-containing gases produced from molten NaOH-treated AC were significantly reduced, which means that environmental risks were significantly reduced. After molten NaOH treatment, the regenerated AC had higher adsorption capacity than that of pre-treated AC.

1 Introduction

Perfluorochemicals are organic compounds in which all hydrogen atoms linked to carbon atoms are replaced by fluorine atoms. Because carbon-fluorine bonds have a fairly high bond energy that can reach to 533 kJ/mol, Perfluorochemicals (PFCs) have high chemical and thermal stability (Cagnetta et al., 2016). In addition, PFCs have hydrophobic and oleophobic properties and surface activity (Meng et al., 2019). Because of these characteristics, PFCs are widely used in industry, especially in chemical, textile, coating, leather and other industries. However, in recent years, people have become more concerned about the impact of PFCs on the environment and organisms, especially on human health. PFCs are stable and widely used, so they are found in almost all environmental medium and organisms. PFCs

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have been detected in surface water, soil, sediments, human serum and milk, and polar regions (Post et al., 2012). Harada's research showed that, once consumed, there is no active excretion of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) from human body, indicating that these substances are accumulated in the human body (Harada et al., 2005). These substances cause liver toxicity, cardiotoxicity, reproductive toxicity, neurotoxicity, and other potential toxicites (Li et al., 2019b). Therefore, it was critical to develop such a technology which can effectively remove PFCs from the environment.

At present, the removal methods of PFCs in water include physical adsorption, microbiological, electrochemical, Fenton oxidation, ultrasonic, photochemical and photocatalytic methods (Chen et al., 2007; Higgins et al., 2007; Mitchell et al., 2014; Ochoa-Herrera and Sierra-Alvarez 2008; Rodriguez-Freire et al., 2015; Trojanowicz et al., 2019; Wu et al., 2018). Physical adsorption method is the main method for processing PFCs due to its advantages of convenient operation, excellent adsorption performance, low cost and environmental friendliness. Activated carbon has the advantages of large specific surface area, loose and porous internal structure, low cost, etc., making it the most commonly used adsorbent for the treatment of PFCs in environments (Fagbayigbo et al., 2017; Wang et al., 2018). However, there are several associated problems as well in using AC to treat PFCs (Sasi et al., 2021). For example, PFCs in liquid phase are transferred to solid phase and they can not degrade into non-toxic or less toxic forms. Therefore, there is always a risk of secondary pollution. AC loaded with PFCs is often incinerated which will crack large PFCs molecule at high temperatures to produce gaseous PFCs with smaller molecules (such C_2F_6) with greater greenhouse effects (Krusic et al., 2005). Because of their long atmospheric lifetime, gaseous PFCs emissions can permanently alter the radiative budget of the atmosphere (Mahieu et al., 2014). On the other hand, the incineration of AC is also a waste of valuable material and emit a large amount of CO_2. Wang et al adopted waste thermal treatment to mineralize the perfluorinated alkyl substances (PFAS) by calcium compounds (Wang et al., 2015). Xiao et al studied the effect of granular activated carbon on the thermal stability of perfluoroalkyl substances (Xiao et al., 2020). Suehnholz et al applied hydrothermal treatment to regenerate activated carbon loaded with PFOS (Sühnholz et al., 2018). Wang et al adopted mechanochemical method to degrade PFOA by using alumina (Al_2O_3) and potassium persulfate (PS) as comilling agents (Wang et al., 2019).

Molten salt (MS) changes from solid to liquid at high temperature. At the same time, it transforms from ionic crystal to ionic melt at high temperatures. MS has a certain stability at high temperature, high specific heat capacity and electrical conductivity, and can maintain low vapor pressure, low viscosity, high ion migration and diffusion speed in a wide temperature range (Yao et al., 2011). These properties have led to its widespread use in the fields of energy, materials, chemicals and solid waste treatments. MS is usually composed of alkali metal or alkaline earth metal and halide, silicate, carbonate, nitrate, phosphate and so on (Dai et al., 2019a; Hsu et al., 2000). One hand, MS as a strong thermal process can destroy organics while retaining inorganics. It is efficient and feasible for the harmless treatment of Br^-, Cl contained wastes like chlorine-containing pesticides (Dai et al., 2019a), polyvinyl chloride (Dai et al., 2019b), waste printed circuit boards (Flandinet et al., 2012), all of which can not be dehalogenated under normal reaction conditions. Providing sufficient reaction surfaces during a wide temperature range (300 °C–900 °C), molten salt method has a good trapping effect on halogens, which can greatly reduce the generation of halogens containing harmful gases. On the other hand, some MS as reactivated substances has good AC regeneration effects (Olsen and Tomkute, 2013). Therefore, it is meaningful to explore the molten salt regenerating PFCs laden AC. Molten salt can crack PFCs adsorbed by AC, and at the same time it can capture small molecule harmful gases generated by thermal cracking of PFCs.

This paper explored the defluorination efficiencies of three PFCs loaded with activated carbon under molten salts, and studied the effects of reaction temperature, holding time, material ratio and other factors on defluorination efficiency. Meanwhile, the pyrolysis gas before and after the molten salt treatment of PFCs was compared. The adsorption performance of the regenerated activated carbon was evaluated. This study can provide a new method of regenerating AC laden with PFCs without environmental implications.

2 Materials and methods

2.1 Chemicals and apparatus

Perfluorooctanesulfonate (PFOS, 98% purity), perfluorooctanoic acid (PFOA, 96% purity) and perfluorobutanesulfonate (PFBS, 99% purity) were provided by Shanghai Titan Technology Co., Ltd, China. Activated carbon and other chemicals were purchased from Aladdin Industrial Corporation (China) in analytical grades.

The molten salt reaction was carried out in a 50 mL nickel crucible embedded in a high-temperature reaction furnace. The high-temperature furnace was customized from Shengli Instrument Co., Ltd., and the designed maximum temperature was 1500 °C. Actual photo and schematic diagram of the furnace are shown in Fig. 1.

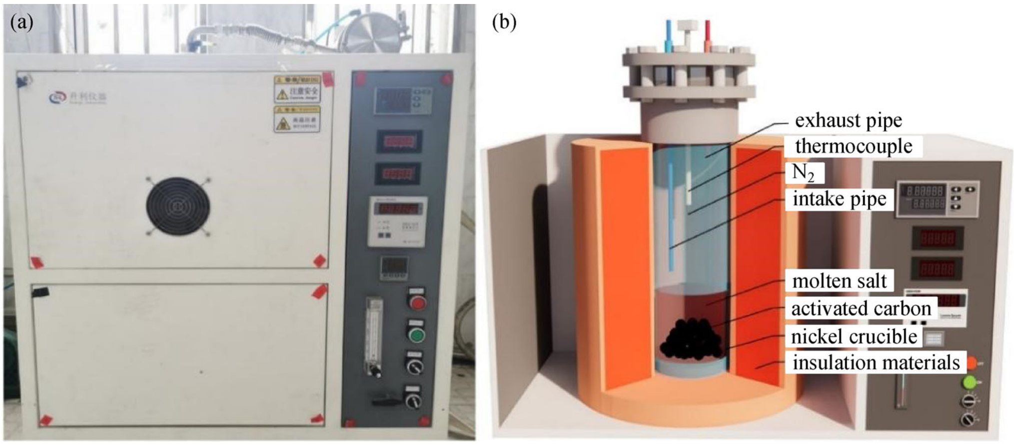

Fig. 1 Actual photo (a) and schematic diagram (b) of the furnace.

2.2 Experimental procedures

2.2.1 Preparation of activated carbon loaded with PFCs

In order to avoid the adsorption of PFCs by glass containers, all the adsorption experiments were performed using polypropylene (PP) material containers (Li et al., 2019a). At first, PFCs solution was prepared with concentration of 500 mg/L. Then, an amount of 2g AC was added into 250 mL flasks containing 100 mL of PFCs solutions. Flasks were placed in orbital shaker at 250 r/min for 48 h at 25 °C. After shaking, AC was removed through filtration and dried in a freeze dryer for 8 h. Liquid chromatography was used to detect the concentration of PFCs in filtrate. The adsorption capacity was evaluated using following equation;

$$q_f = \frac{(c_i - c_f) \times v}{m_{\mathrm{AC}}}, \tag{1}$$

where q_f is the amount of three types of PFCs (PFOS or PFOA or PFBS) adsorbed by AC (mg/g), C_i and C_f are the concentration of the initial and final PFCs solution (mg/L), respectively, V is the volume of PFCs solution (L), and m_{AC} is the mass of AC (g). Calculated adsorption capacity of AC was 25 mg/g for PFOS, 24.98 mg/g for PFOA and 24.98 mg/g for PFBS.

2.2.2 Defluorination and regeneration experiments

2g AC loaded with PFCs was tiled on the bottom of nickel crucible and covered with certain amount of salts. Then, nickel crucible was placed in the furnace and nitrogen gas was inlet to purge the air. The furnace was heated at a heating rate of 10 °C/min till the target temperature was achived and maintained for a specific period of time (referred as residence time from here onward). After heating, the furnace was cooled naturally. High-purity nitrogen which was blown through the furnace was collected at the gas outlet using an air bag, and the composition of collected was analyzed by GC-MS. Residues were dissolved in ultrapure water and AC was collected on filter paper, which were further characterized after freeze-drying. Freeze-dried AC was diluted in 300 mL of deionized water to obtain a salt solution, and then Ion chromatography was used to detect the fluoride ion. The defluorination efficiency of three types of PFCs ($\mathrm{DFE}_{\mathrm{PFCs}}$) was calculated by using following equation

$$DFE_{PFCS} = \frac{m_t(F)}{m_0(PFCS) \times \eta} \times 100\%, \tag{2}$$

where m_0 (PFCs) is weight of PFCs (PFOS or PFOA or PFBS) adsorbed by AC, η is the corresponding weight percentage of fluorine in different PFCs, m_t (F) is the fluorine content in residues.

2.3 Analytical methods

Quantification of PFCs aqueous samples were done using HPLC with conductivity detector (Shimadzu Corporation, Japan). HPLC was equipped with an Agilent TC-C18 column (4.6 mm i.d., 25cm length). The mobile phase was the mixture of methanol and 0.02M NaH_2PO_4 (70/30 for PFOS, 65/35 for PFOA, and 55/45 for PFBS v/v) at 1.1 mL/min flow rate.

A TGA/DSC1/1600HT simultaneous thermal analyzer (Mettle-Toledo, Swiss) was used to study the three PFCs. About 10 mg of PFCs were placed in an alumina crucible, which was then mounted on TGA. The thermogravimetry experiment was conducted between 30°C to 600°C at a constant heating rate of 15°C/min, and the N_2 flow rate was maintained at 30 mL/min.

After the reaction, nitrogen was injected into the inlet pipe, and a 100 mL gas sampling bag made from the aluminum foil composite membrane was used to collect the organic gases. The gas entered GC-MS by a gas sampling valve. The organic gas was analyzed by gas chromatography – mass spectroscopy (GC – MS, Shimadzu Corporation, Japan). The capillary column was a non-polar HP-5ms (30m × 250 μm × 0.25μm). The colunn oven temperature was held at 50°C for 5min, then heated to 100°C at 10°C/min for 1min, finally heated to 280°C at 5°C/min held for a further 20 min. Peaks are identified and confirmed based on the spectrum with the highest similarity in the spectral libraries (NIST mass spectral library). It was trusty when the similarity indexes (SI) of > 80%.

Ion chromatography (IC, ICS-5000 +/900, USA) was used to detect fluoride ion contents. IC was equipped with an IonPac-AS11 Separation column.The sample was transported to In Guard H by pure water to eliminate OH^- interference. Then concentrated F^- through the enrichment column. The flow rate of the KOH eluent was 1.0 mL/min.

The residues in the crucible were characterized by X-ray diffraction (XRD, LabX XRD-6100, Japan) with Cu Kα radiation, operated at 40 kV and 25 mA over an angle of $10° < 2\theta < 80°$, and the scanning velocity was 10°/min.

3 Results and discussion

3.1 Effect of different molten salt systems on defluorination efficiency

There are two prerequisites which need to be considered while choosing molten salt systems. Firstly, the molten salt system used to treat PFCs must remain stable at high temperatures. Secondly, from the perspective of energy consumption and the limitation of the maximum temperature of the equipment, molten salt systems with a relatively low melting point should be selected. The sodium salt has a relatively low melting point and high thermal stability, so three different sodium salts and one alkali that meet the requirements were selected to compare and treat the three PFCs. Figure 2 shows the defluorination efficiencies of NaOH, Na_2SO_4, Na_2CO_3 and NaCl for PFOS, PFOA and PFBS respectively. The heating temperature was 900°C, residence time was 15 minutes, and the mass ratio of AC to salt was 1:5. It was observed that NaOH gasification was intense when the temperature over 700°C, which led to the destruction of AC structure. Therefore, heating temperature was kept at 700°C for NaOH treatments. As shown in Fig. 2, regardless of PFCs type, the defluorination efficiency of molten NaOH was higher than all other three sodium salts. High temperatures provide energy for breaking carbon-fluorine bonds. Higher the temperature, the more breakage of carbon-fluorine bonds (Khan et al., 2020). Maximusm defluorination efficiency of PFCs was observed with NaOH treatment at 700°C, while Na_2SO_4, Na_2CO_3 and NaCl gave their peaks at 900°C. It can be inferred that NaOH has the best defluorination efficiency among these commonly used molten salts. Among other three treatments, molten Na_2CO_3 showed higher defluorination effect on PFCs as compared to Na_2SO_4 and NaCl which can hardly remove fluorine from PFCs. It is speculated that the hydrogen atom of NaOH has hydrodefluorination effect on the carbon-fluorine bonds (Wang et al., 2015).

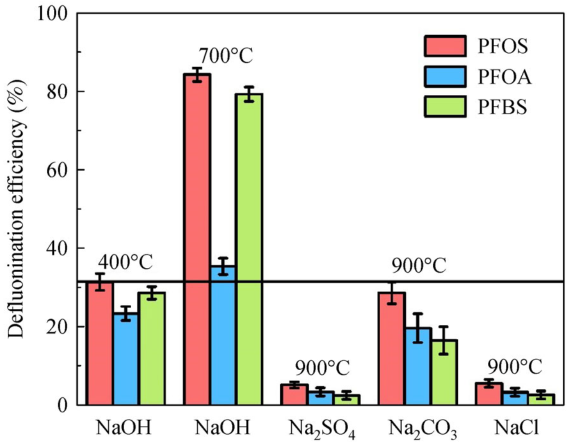

Fig. 2 The defluorination efficiency of NaOH, Na_2SO_4, Na_2CO_3 and NaCl in removing PFOS, PFOA, PFBS.

Among the three PFCs, the defluorination efficiencies of PFOS and PFBS with NaOH were similar (Fig. 2). The defluorination efficiency of PFOA was almost half as compared to other two PFCs with NaOH treatment. Thermogravimetric analyzer (TGA) was used to study the thermal behavior of different PFCs at different temperatures, and to analyze their reaction state with molten salt at different temperatures. Figure 3 describes the weight loss of three different PFCs at different temperatures. Figures 3(a) and 3(c) show that PFOS and PFBS were relatively stable till 400 °C. Both of them had significant weight loss between 400 °C to 500 °C. The weight loss rate slowed down from 500 °C to 550°C, and stabilized after 550 °C without any further significant weight loss. From Fig. 3(b), it can be seen that the thermal stability of PFOA was very low compared with PFOS and PFBS. It can be observed that PFOA began to lose weight at about 75 °C and reached to a steady state at 125 °C. Due to the poor thermal stability of PFOA, maximum weight loss was observed between 75 °C and 125 °C, but this temperature condition is not suitable for NaOH to reach its melting point. As NaOH could not attain its molten state to fully contact with PFOA which might have caused overall low defluorination efficiency for PFOA.

3.2 Factors affecting defluorination efficiency of PFCs treated with molten NaOH

3.2.1 Effect of different temperatures.

Figure 4(a) illustrates the defluorination efficiency of PFCs

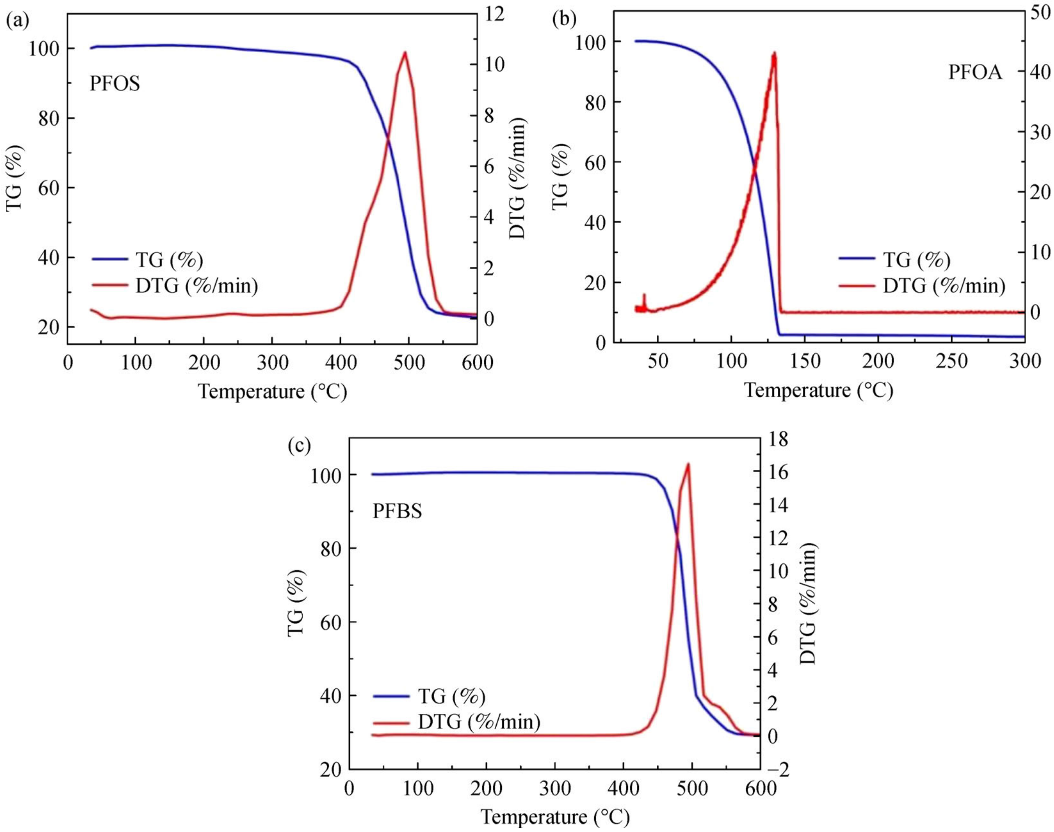

Fig. 3 TG (blue line) and DTG (red line) curves of PFOS (a), PFOA (b) and PFBS (c).

by AC in the presence of molten NaOH at different temperatures. Except temperature, other conditions remained the same i.e. residence time was 15 min and AC mass was 20% of NaOH mass. High temperatures provided energy for breaking carbon-fluorine bonds. Overall, as the temperature of molten NaOH increased, the defluorination efficiencies of the three types of PFCs also increased. Among them, defluorination efficiencies of PFOS and PFBS were more obviously compared with PFOA. It can be observed from Fig. 4(a) that the defluorination efficiencies of both PFOS and PFBS were 0% at 300 °C and reached to about 80% at 700 °C. At 300 °C, NaOH was not in a molten state, and both PFOS and PFBS were in a thermally stable state, which resulted in no effective defluorination reaction occurring at this temperature. At about 318 °C, NaOH began transforming into molten state, which can provide sufficient reaction surfaces. The defluorination efficiencies of PFOS and PFBS started to increase between 300 °C and 400 °C. When temperature increased from 400 °C, PFOS and PFBS were no longer stable and began to gasify. Gaseous materials were trapped by molten NaOH, resulting in a significant increase in defluorination efficiencies of PFOS and PFBS. After 500 °C, the defluorination efficiencies of PFOS and PFBS gradually increased and appeared stable. Defluorination efficiency of PFOA increases from 10% at 300°C to about 30% at 900 °C which was very slow. PFOA began decomposing at 75°C (shown in Fig. 3(b)) and transformed into gaseous state. Therefore, NaOH cannot effectively contact with PFOA, which ultimately leads to its low defluorination efficiency. In general, temperature of 600°C was an optimum temperature which can result in optimum defluorination efficiency to remove three PFCs without consuming much energy.

3.2.2 Effect of residence time on defluorination efficiency of PFCs.

Figure 4(b) shows the effect of residence time on defluorination efficiency of PFCs adsorbed by AC. Heating temperature was set at 600 °C and AC mass was 20% of the NaOH used. It can be observed from Fig. 4(b) that the defluorination efficiencies of all three PFCs increased slowly with increase in residence time. Overall the defluorination efficiencies increased slowly which indicates that the residence time has little impact on defluorination. Considering the defluorination efficiency and energy consumption, 15 min time is the optimum residence time.

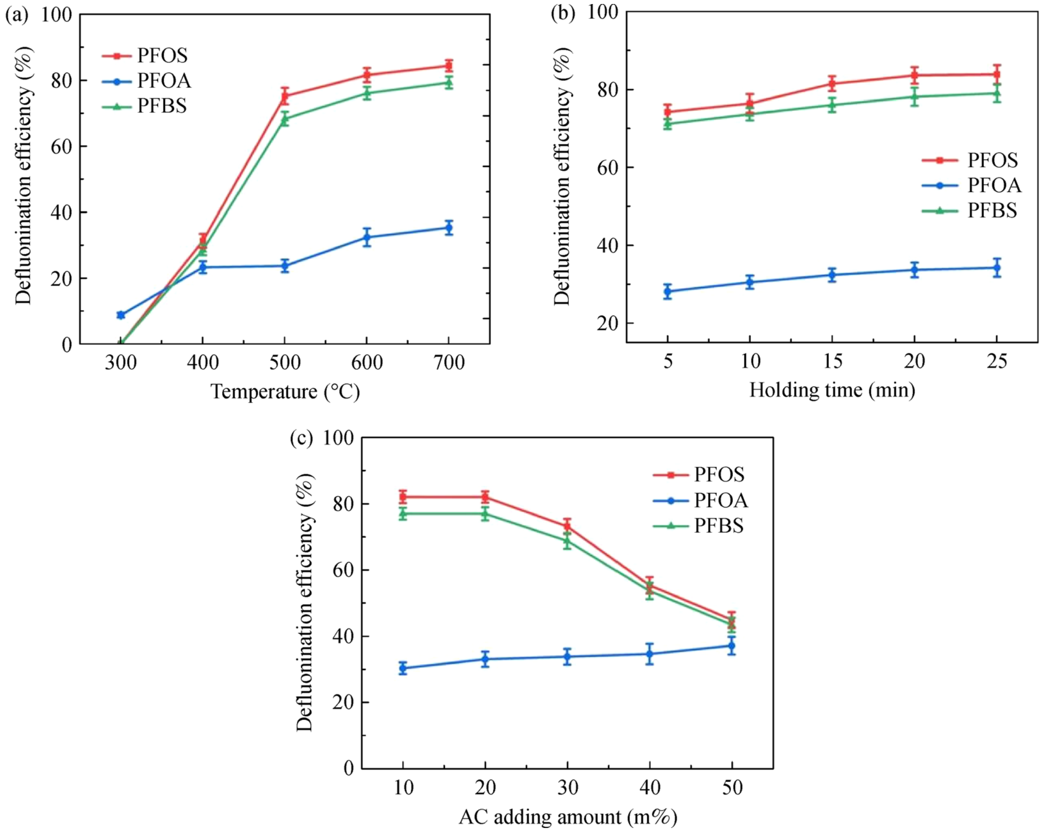

Fig. 4 Effects of temperature (a), residence time (b), and activated carbon amount (c) on defluorination efficiency of PFOS, PFOA and PFBS.

3.2.3 Effect of AC amount on defluorination efficiency of PFCs.

Figure 4(c) shows the relationship between the amount of AC addition and the defluorination efficiency of PFCs. In this part, the heating temperature was kept constant at 600 °C and residence time was 15 min. It was observed that overall defluorination efficiencies of PFOS and PFBS were negatively correlated with the amount of AC. With the increase in AC amount, defluorination efficiency of PFOA increased slightly. Among three PFCs, addition of AC at different ratios had a greater impact on the defluorination efficiency of PFOS and PFBS. However, for PFOA, its effect was minimal. As the amount of NaOH was constant, high ratio of AC to NaOH might cause the insufficient contact surface between NaOH and AC, which might lead to incomplete reaction. Meanwhile, the molten NaOH could not capture the PFCs adsorbed on the AC completely. Due to the low thermal stability of PFOA, molten NaOH could not capture PFOA at lower temperatures. Therefore, the effect of AC addition ratio on PFOA was small. From the given results, the best mass ratio of AC addition was 20%.

3.3 Comparison of gas production before and after NaOH treatment

To characterize the main components of the gases generated, GC-MS was used to analyze the thermally cracked products of PFOS, PFOA and PFBS at 600°C (without NaOH treatment). Results showed that the thermal cracking of these three substances at high temperature did not remove the fluorine element. Long-chain compounds were broken into a short-chain perfluoro compounds (Fig. 5). Particularly, long-chain PFOS and PFOA as shown in Figs. 5(a) and 5(b), respectively, lost one or two carbons to form new perfluoro compounds. It means that CF_4 and C_2F_6, the main pollutants, are generated by this process (Khan et al., 2020). As shown in Fig. 5(c), carbon dioxide was produced with the breakage of carbon chain of PFBS. Similarly, PFBS contained relatively large amount of sulfur, and sulfur dioxide was generated when the carbon-sulfur bonds were broken. For these pollution gases, molten NaOH has good absorption properties which can convert gases to fluorine element which can be mineralized.

High temperature treatment of AC adsorbed PFCs

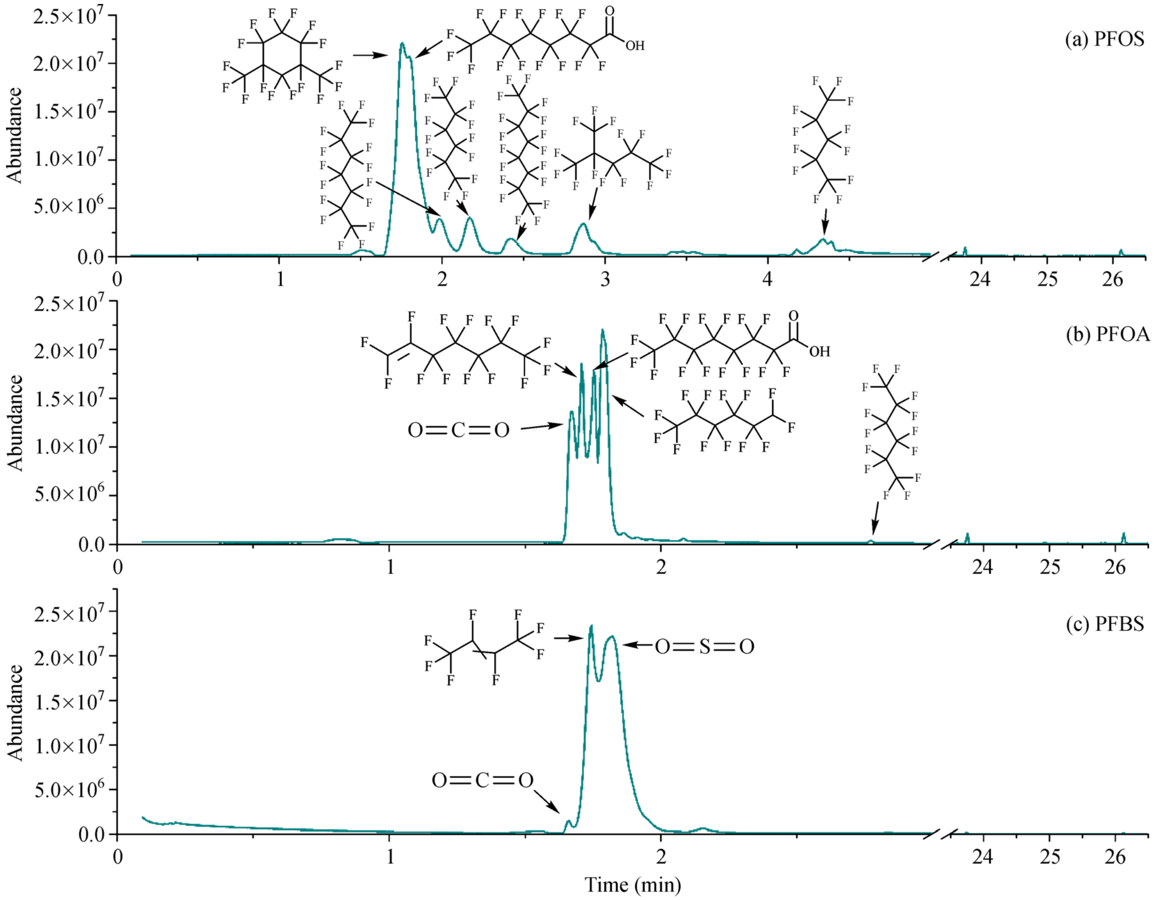

Fig. 5 GC-MS total ion chromatograms of gases generated by pyrolysis of PFOS (a), PFOA (b) and PFBS (c) at 600 °C.

generated different gases which can affect environment greatly. From Fig. 5, it is clear that untreated PFCs were decomposed into various short-chain perfluorinated gas substances at high temperature. For comparison purpose, gas produced at 600°C with 15 minutes residence under 5:1 mass ratio of NaOH and AC was selected. Gases produced are shown in Fig. 6. Compared with Figs. 5(a) and 5(c), the types of fluorine-containing gases were significantly reduced after treating with molten NaOH. At the same time, a certain amount of H_2O and CO_2 was produced. A large proportion of fluoride ions were detected in the salt which indicated that the fluorine gas has been transferred from gaseous to solid salt. Figure 6(b) shows that the treated PFOA still released certain kinds of fluorine-containing gaseous substances. However, comparing with Fig. 5(b), the types of long-chain fluorine-containing substances were reduced, and they were further broken into short-chain fluorine-containing substances. In general, the gas discharged from PFOS and PFBS after molten NaOH treatment has no more threat to environment, while the degree of pollution from PFOA was weakened.

3.4 Characterization of regenerated activated carbon and solid salt

From Fig. S1, three times is an appropriate cycle times. Gas Sorption Analyzer was used to compare the performance of activated carbon before and after molten NaOH treatment (Fig. 7 and Table 1). From Fig. 7(a), it can be seen that in lower relative pressure zone where P/P_0 was less than 0.03, N_2 adsorption capacity of twice regenerated carbon increased sharply with the increase in relative pressure. It shows that the treated regenerated carbon also had a lot of micropores. This curve is a typical type IV isotherm curve. The "H4" type hysteresis loop appeared when the relative pressure P/P_0 was about 0.4–0.9, indicating that the regenerated carbon had mesopores. In addition, there was still adsorption at relatively higher pressures over 0.9, indicating that the regenerated carbon had macropores or slit-type pores. Comparing Fig. 7(b) and Table 1, it can be concluded that the overall pore structure of the regenerated carbon was basically unchanged compared to the original carbon, and the surface area, micropore volume and total

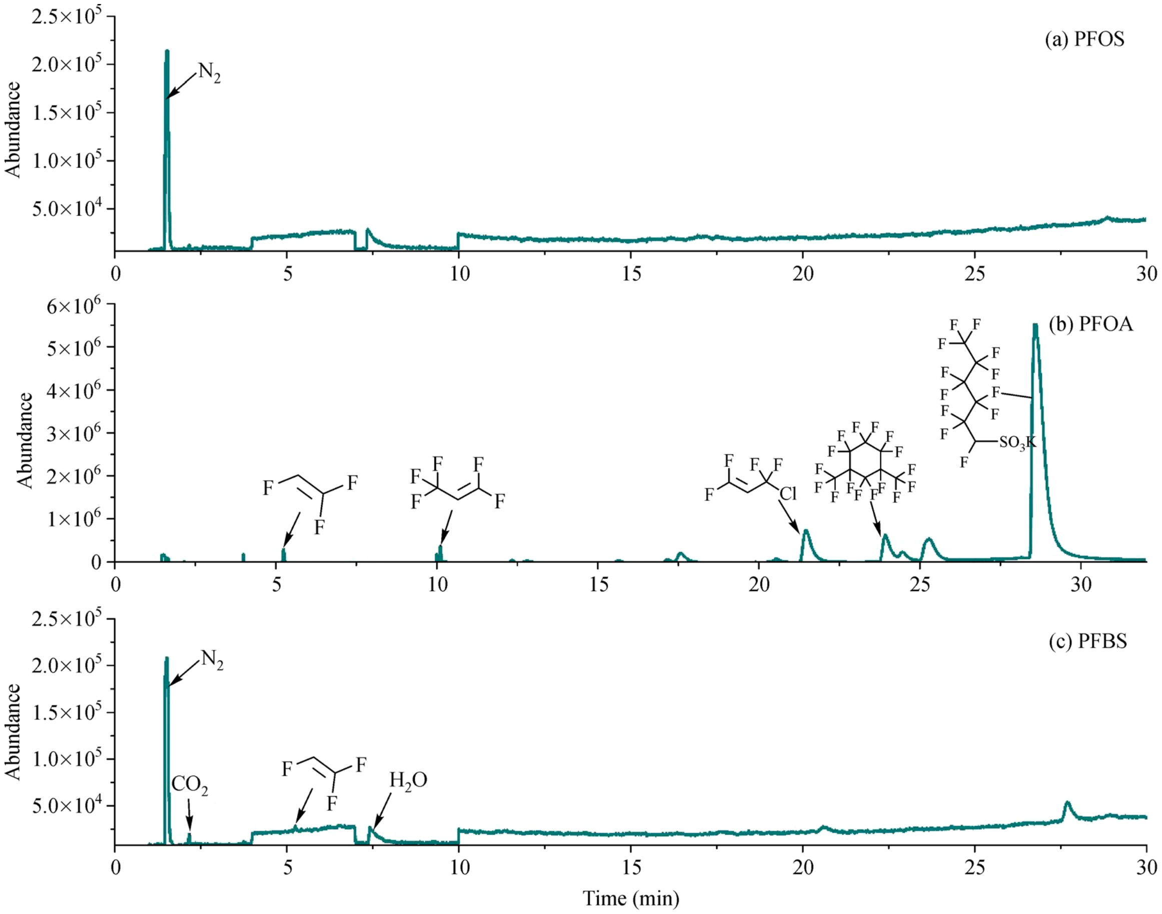

Fig. 6 GC-MS total ion chromatograms of the gas generated by PFOS (a), PFOA (b) and PFBS (c) after treatment with molten sodium hydroxide at 600 °C.

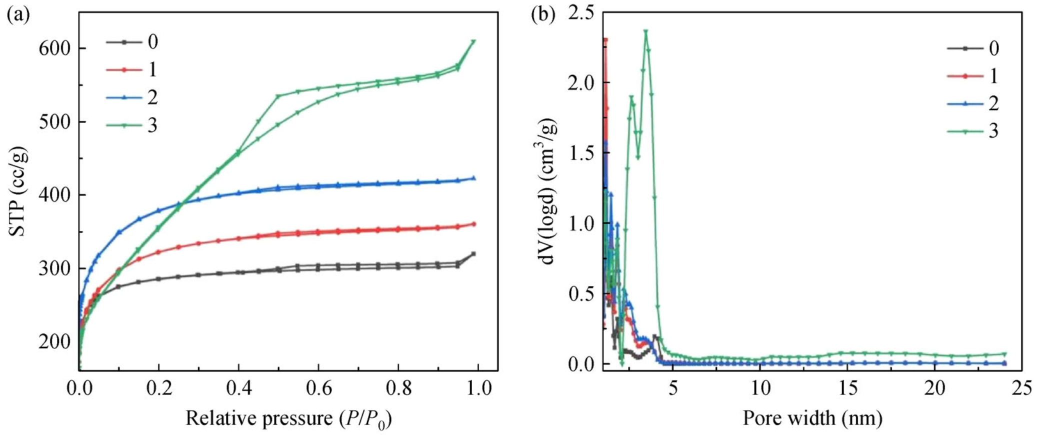

Fig. 7 Adsorption and desorption isotherms (a) and pore size distribution (b) of activated carbon under various regeneration times.

pore volume of the regenerated carbon was slightly increased. It proves that NaOH molten salt has obvious hole making and reaming ability. But after two cycles of reaming, excessive reaming caused the collapse of the hole wall in the entire pore structure. Sodium hydroxide and two cycles had obvious effect as an activator and provided a larger surface area and stronger adsorption performance for the regenerated AC. It can be seen from Fig. S2 that the functional groups on the AC surface after regeneration were not changed.

Table 1 The structural characteristics of activated carbon after several cycles

Cycles	Surface area (m^2/g)	Micropore volume (cc/g)	Micropore area (m^2/g)	Total pore volume (cc/g)
Original	1105.630	0.408	1025.327	0.495
Cycle-1	1142.040	0.426	1048.087	0.506
Cycle-2	1389.729	0.504	1188.700	0.654
Cycle-3	1276.052	0.081	192.994	0.943

For the solid salt collected from the furnace after the reaction, we dissolved the treated salt and detected fluoride ion by ion chromatography. Result showed that carbon-fluorine bonds of PFCs were broken in molten sodium hydroxide. To further determine the composition of the salt after the reaction, mixtures of AC and molten salts were grounded into powder. After drying, XRD was used to determine the main components of the mixture. The XRD pattern of mixture has been shown in Fig. 8. The elemental fluorine is finally converted into sodium fluoride and Na_2CO_3 was generated.

$$2NaOH \Leftrightarrow Na_2O + H_2O \quad (3)$$

$$C + H_2O \rightarrow H_2 + CO \quad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (5)$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \quad (6)$$

It has been reported that carbon-fluorine bonds can be converted to carbon-hydrogen bonds through defluorination and hydrogenation (Douvris and Ozerov, 2008). Defluorination and hydrogenation belong to an organic reaction type, which means that the carbon-fluorine bonds on the substrate are replaced by carbon-hydrogen bonds. It can be seen from Fig. 8 that sodium hydroxide not only plays a role in the defluorination reaction, but also further activates AC. Figure S1 shows the AC weight loss under several regeneration times. The weight loss rate of activated carbon increases sharply after three cycles. It also indicates that AC participates in the thermal reaction, and the specific reaction equation is shown as Eqs. (3)–(6). Meanwhile, after the molten salt regeneration of AC, the generation of Na_2CO_3 was observed as shown in Fig. 8, which confirms that AC involved in the reaction. CO_2 produced by the water gas reaction reacts with Na_2O produced by the NaOH dehydration to produce Na_2CO_3. H_2O as the product of the NaOH dehydration reaction and CO_2 as the product of the water gas reaction were also detected in Fig. 6. Generally, these reactions can be regarded as catalytic reactions in the presence of NaOH. One hand, hydrogen atoms participate dehalogenated in the defluorination and hydrogenation reaction of PFOS in the form of H_2 or H_2O (Lv et al., 2018). On the other hand, they participate in the activation reaction of carbon to produce Na_2CO_3, which increased the specific surface area of AC.

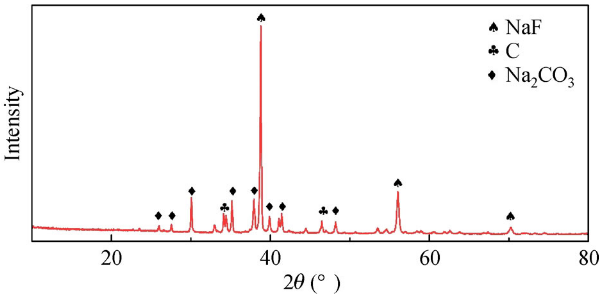

Fig. 8 XRD pattern of the product of PFOS-adsorbed AC treated with molten sodium hydroxide at 600°C for 15 min.

4 Conclusions

The defluorination efficiency of NaOH may be related to the carbon chain length and functional groups of PFCs. Among them, functional groups have a greater influence on the thermal behavior of PFCs, which in turn affect the defluorination efficiency under experimental conditions. Both temperature and heating time promoted the defluorination efficiency of PFCs. XRD patterns indicate that fluorine is finally mineralized and fixed as salt in the form of NaF. It is speculated that hydrogen element in NaOH might have been converted to H_2 or H_2O during the AC pores expansion process, thereby promoting the defluorination and hydrogenation process of PFCs. Molten NaOH acted both as defluorinating agent of PFCs and as an activating agent of AC in this reaction, so as to realize the green regeneration of AC.

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