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Photocatalytic cleavage of C–F bond in pentafluorobenzoic acid with titanium dioxide-P25

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Abstract

The photocatalytic C–F bond cleavage in pentafluorobenzoic acid (PFBA) with TiO₂-P25 using UV-C light has been investigated under different conditions. Complete cleavage of C–F is observed with TiO₂-P25 under UV-C light irradiation. Oxidants such as IO_4^- , BrO_3^- , $S_2O_8^{2-}$, H_2O_2 and CIO_3^- ions enhance the defluoridation of PFBA. The order of their activities is $IO_4^- > H_2O_2 > S_2O_8^{2-} \approx BrO_3^- > CIO_3^-$. C–F cleavage is also influenced by the addition of inorganic anions and metal ions. The defluoridation intermediates were analyzed by GC-MS technique. \bigcirc 2006 Elsevier B.V. All rights reserved.

Keywords: Pentafluorobenzoic acid; TiO2-P25; Defluoridation; Photocatalysis

1. Introduction

Fluorinated chemicals are prominent xenobiotics used in pharmaceutical, agricultural and other industrial applications due to their thermal stability and enhanced lipophilicity [1,2]. Perfluorinated acids (mainly carboxylic and sulfonic acids) and their derivatives are widely used as emulsifying agents in polymer synthesis, fire retardants, carpet cleaners, paper coatings, surface treatment agents in photolithography, etc. [3–5]. The use of perfluorinated acids has steadily increased and some of them have recently been detected in environmental waters and in animals [6–9]. These perfluorinated acids are quite stable and they have no known natural decomposition [4,5]. Hence the detoxification of these perfluorinated acids under mild conditions becomes essential.

The cleavage of C–F bond of fluorinated compound results in the formation of fluoride ions, which can easily combine with Ca^{2+} to form environmentally harmless CaF_2 . In addition, CaF_2 is a raw material for the production of hydrofluoric acid, which is a starting material for many fluorinated compounds. Hori et al. reported the photocatalytic cleavage of the strong C–F bond (485.3 kJ mol⁻¹) in pentafluoropropionic acid with a water soluble heteropoly acid [H₃PW₁₂O₄₀] photocatalyst [10].

A review of microbial cleavage of the C–F bond had been published [2]. In the recent years, advanced oxidation processes have been developed for the degradation of pollutants in wastewater. In our laboratory we had reported the degradation of dyes by various advanced oxidation processes [11–15]. Heterogeneous photocatalysis using semiconductors such as TiO₂ or ZnO is an attractive advanced oxidation processs [16,17].

In the present work, we have investigated the photocatalytic defluoridation of pentafluorobenzoic acid (PFBA) with TiO₂-P25 using UV-C light and analysed the effect of oxidants, inorganic ions and metal ions on this process.

2. Results and discussion

2.1. Primary defluoridation

Initially the experiments were carried out to test the photodefluoridation with 400 ppm of PFBA under different conditions and the results are shown in Fig. 1. PFBA undergoes self photolysis with 254 and 365 nm light to certain extent. The theoretical amount of fluoride in the compound is 180 mg L⁻¹. After 180 min of 365 nm irradiation of PFBA with TiO₂, 69.2 mg of fluoride ion was released while the catalyst in dark

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Fig. 1. Photodegradability of pentafluorobenzoic acid (PFBA): [PFBA] = 400 ppm; catalyst suspended = 175 mg; airflow rate = 8.1 mL s⁻¹; pH 7; $I_{254 nm} = 2.54 \times 10^{-5}$ einstein L⁻¹ s⁻¹; $I_{365 nm} = 2.08 \times 10^{-6}$ einstein L⁻¹ s⁻¹.

does not facilitate the deflouridation. On irradiation by 254 nm light with TiO₂, 180 mg of fluoride ion was released in 90 min. Complete defluoridation is achieved in 90 min with 254 nm light. The results indicate that PFBA can be effectively degraded in presence of photocatalyst on irradiation with UV-C light. The C-F bond is one of the strongest covalent bonds known. The fluorine atom is larger than the hydrogen atom, so it shields the carbon from attack more effectively than hydrogen atoms. In fluoro carbons C–C bond energy is $334.7 \text{ kJ mol}^{-1}$, whereas C–F bond energy is $485.3 \text{ kJ mol}^{-1}$ [18]. Hence more energy is required to break C-F bond than C-C bond. The release of fluoride ion and carbon dioxide from PFBA on irradiation with 254 nm light in presence of TiO₂ indicates that PFBA can be effectively mineralised into CO₂ and fluoride ions (Eq. (1)). The formation of intermediates before complete mineralisation is discussed in Section 2.7:

$$C_{6}F_{5}COOH + 5O_{2}(air) + 2H_{2}O \xrightarrow[h_{\nu}]{\text{TiO}_{2}}7CO_{2} + 5HF$$
(1)

This mineralisation is caused mainly by hydroxy radical, a strong oxidizing species produced by TiO_2 on irradiation with 254 nm light (Eqs. (2)–(7)) [19,20]:

$$\mathrm{TiO}_2 + h\nu \to \mathrm{e_{CB}}^- + \mathrm{h_{VB}}^+ \tag{2}$$

$$h_{VB}^{+} + OH_{(ads)}^{-} \to {}^{\bullet}OH$$
(3)

$$h_{VB}^{+} + H_2 O_{(ads)} \rightarrow {}^{\bullet}OH + H^+$$
(4)

$$\mathbf{e_{CB}}^- + \mathbf{O}_2 \to \mathbf{O}_2^{\bullet -} \tag{5}$$

$$2O_2^{\bullet-} + 2H_2O \rightarrow 2^{\bullet}OH + 2OH^- + O_2 \tag{6}$$

Since the defluoridation was effective with 254 nm light, the effects of pH and oxidants on this process had been carried out using 254 nm light to find out the optimum conditions.



Fig. 2. Effect of pH on adsorption of pentafluorobenzoic acid: [PFBA] = 100 ppm; catalyst suspended = 100 mg; airflow rate = 8.1 mL s^{-1} .

2.2. Effect of pH on adsorption and deflouridation

The effect of pH on the adsorption of PFBA is shown in Fig. 2. The adsorption of PFBA on TiO₂ surface increases from pH 1 to 3 and then decreases. The point of zero charge (PZC) of TiO₂-P25 is 6.8 [21]. When the solution pH is lower than PZC, the TiO₂ surface is positively charged. The ionization of PFBA in water is also influenced by pH as it contains the COOH group. The pK_a value of PFBA is 1.75. When pH is higher than the p K_a of PFBA, it ionizes to give solvated H⁺ and pentafluorobenzoate anion. At pH 3 the electrostatic attraction between positively charged TiO₂ and negatively charged pentafluorobenzoate ion leads to strong adsorption of PFBA on the TiO₂ surface. The effect of pH on the photocatalytic defluoridation of PFBA was investigated for pH range of 1-10. The results are presented in Fig. 3. After 60 min of irradiation 93.6, 140, 126.6, 126.4 and 128.4 mg of fluoride ions were released at pH 1, 3, 5, 7 and 10, respectively in presence of TiO₂. pH 3 is found to be more favorable for defluoridation. The



Fig. 3. Effect of pH on photodefluoridation of pentafluorobenzoic acid: [PFBA] = 400 ppm; catalyst suspended = 175 mg; airflow rate = 8.1 mL s⁻¹; $I_{254 \text{ nm}} = 2.54 \times 10^{-5}$ einstein L⁻¹ s⁻¹.

effect of pH on the photocatalytic reaction is generally attributed to change in the surface charge property of TiO_2 , which depends on pH of the solution.

Since the adsorption is maximum at pH 3 more defluoridation occurs at this pH. This reveals that photocatalytic reaction is more facilitated at the catalyst surface. At pH above 3, the change in adsorption is not much and also the defluoridation decreases slightly. But at pH 1 the defluoridation is less. At high acidic conditions TiO₂ particle agglomeration may take place and this may reduce the photo adsorption [12].

2.3. Effect of substrate concentration

The effect of initial PFBA concentration on the defluoridation rate was investigated by varying the initial concentration from 100 mg to 600 mg L^{-1} at constant pH and catalyst loading. The results are shown in Fig. 4. From the results, it is clear that on increase of the initial concentration increases the time required to defluoridate the PFBA. After 60 min irradiation, 100% fluoride ion was released when the concentration was 100 mg L^{-1} whereas only 52.8% fluoride ion was released at the concentration of 600 mg L^{-1} . The increase of PFBA concentration decreases the defluoridation rate. The rate of defluoridation relates the amount of [•]OH radical formation on catalyst surface and the probability of [•]OH radical reacting with PFBA molecules. For all initial PFBA concentrations, the catalyst concentration (175 mg) and UV power $(2.54 \times 10^{-5} \text{ einstein } \text{L}^{-1} \text{ s}^{-1})$ are same. Since the generation of hydroxyl radical remains constant the probability of PFBA molecule to react with hydroxyl radical decreases.

2.4. Effect of inorganic oxidants

Usually molecular oxygen is used as a electron acceptor in an heterogeneous photocatalytic reaction for the prevention of



Fig. 4. Effect of various substrate concentration of pentafluorobenzoic acid: catalyst suspended = 175 mg; airflow rate = 8.1 mL s⁻¹; pH 7; $I_{254 \text{ nm}} = 2.54 \times 10^{-5}$ einstein L⁻¹ s⁻¹.

Table 1	
Effect of oxidants on photodefluoridation of PFBA	

Oxidants	$[F^{-}]$ mg L^{-1}		
	Without TiO ₂	With TiO ₂	
KIO ₄	119.6	180.0	
H_2O_2	90.1	158.3	
KBrO ₃	80.2	144.0	
$(NH_4)_2S_2O_8$	86.0	146.4	
KClO ₃	18.6	112.5	

[PFBA] = 400 ppm; catalyst suspended = 175 mg; oxidants = 125 mg; H₂O₂ = 0.01 M; irradiation time = 30 min; airflow rate = 8.1 mL s⁻¹; $I_{254 \text{ nm}} = 2.54 \times 10^{-5}$ einstein L⁻¹ s⁻¹.

electron hole recombination. Inorganic oxidants such as KIO_4 , $(NH_4)_2S_2O_8$, $KCIO_3$, $KBrO_3$ and H_2O_2 can compensate for the lack of oxygen caused either by oxygen consumption or slow oxygen mass transfer. These oxidants on irradiation generate other oxidizing species to accelerate the defluoridation and hence they play a dual role in this process. This dual role is also confirmed by the significant defluoridation caused by oxidants alone on irradiation. The Table 1 shows the release of fluorides ions (mg L⁻¹) by both oxidants and the oxidants with TiO₂.

In the dark IO_4^- , BrO_3^- , H_2O_2 , $S_2O_8^{2-}$ and CIO_3^- exhibit negligible activity. Irradiation of UV light ($\lambda_{max} = 254$ nm) with PFBA and oxidants alone enhances the defluoridation rate. After 30 min of irradiation time with $S_2O_8^{2-}(125 \text{ mg})$, BrO_3^- (125 mg), $IO_4^-(125 \text{ mg})$, H_2O_2 (0.01 M) and CIO_3^- (125 mg) released 86, 80.2, 119.6, 90.1 and 18.60 mg of fluoride ion respectively. The defluoridation efficiencies of $UV/S_2O_8^{2-}$, UV/BrO_3^- processes are nearly equal to the efficiency of UV/ TiO_2 process (88.2 mg). But UV/IO_4^- process is more efficient than UV/TiO_2 process whereas UV/CIO_3^- is least efficient one.

The higher degree of defluoridation in UV/IO₄⁻ process is due to formation of highly reactive intermediates, such as IO₃[•], •OH, IO₄[•], O[•] (Eqs. (9)–(11)) [22]. Therefore defluoridation occurs by free radical pathways and is more efficient at high intensity of light:

$$\mathrm{IO}_4^{\bullet-} + h\nu \to \mathrm{IO}_3^{\bullet} + \mathrm{O}^{\bullet-} \tag{9}$$

$$\mathbf{O}^{\bullet-} + \mathbf{H}^+ \to {}^{\bullet}\mathbf{O}\mathbf{H} \tag{10}$$

$$^{\bullet}\mathrm{OH} + \mathrm{IO_4}^{-} \to ^{-}\mathrm{OH} + \mathrm{IO_4}^{\bullet} \tag{11}$$

H₂O₂ on irradiation with 254 nm light produces [•]OH radicals:

$$H_2O_2 \xrightarrow{n\nu} OH$$
 (12)

 $S_2O_8^{2-}$ can generate sulfate radical anion (SO₄^{•-}) photolytically in aqueous solution. SO₄^{•-} then reacts with H₂O to produce [•]OH radicals:

$$S_2 O_8^{2-} \xrightarrow{h\nu} 2S O_4^{\bullet-}$$
(13)

$$\mathrm{SO_4}^{\bullet-} + \mathrm{H_2O} \to {}^{\bullet}\mathrm{OH} + \mathrm{SO_4}^{2-} + \mathrm{H^+}$$
(14)

 $SO_4^{\bullet-}$ itself is a strong oxidant ($E_0 = 2.6 \text{ eV}$) and can directly react with PFBA. Addition of these oxidants to UV/TiO₂

process enhances the defluoridation rate strongly when compared with UV/oxidant system as seen in Table 1. 146.4, 144, 180, 160.3 and 71.2 mg of fluoride ions were released in UV/ $TiO_2/S_2O_8^{2-}$, UV/ TiO_2/BrO_3^{-} , UV/ TiO_2/IO_4^{-} , UV/ $TiO_2/$ H₂O₂ and UV/ TiO_2/CIO_3^{-} after 30 min of irradiation with 254 nm light.

The enhancement in UV/TiO₂ process by the addition of oxidant is due to increased charge separation. This is done by accepting the conduction band electron (Eqs. (15)-(17)).

$$S_2 O_8^{2-} + e_{CB}^- \to SO_4^{\bullet-} + SO_4^{2-}$$
 (15)

 $BrO_{3}^{-} + 6e_{CB}^{-} + 6H^{+} \rightarrow Br^{-} + 3H_{2}O$ (16)

$$ClO_3^- + 6e_{CB}^- + 6H^+ \rightarrow ClO_2^- + H_2O_2$$
 (17)

The order of reactivity is:UV/TiO₂/IO₄⁻ > UV/TiO₂/H₂O₂ > UV/TiO₂/S₂O₈²⁻ \approx UV/TiO₂/BrO₃⁻ > UV/TiO₂/ClO₃⁻.

 $UV/TiO_2/oxidant$ processes are more efficient than the UV/TiO_2 process. The lower efficiency at $UV/TiO_2/CIO_3^-$ process is due to poor light absorption capacity of CIO_3^- ion.

2.5. Effect of inorganic ions

Wastewater contains not only organic contaminants but also considerable amounts of inorganic anions such as nitrate, sulfate, phosphate and carbonate, etc. Hence it is useful to study the influence of these ions on this photocatalytic process. Two possible ways of the inorganic ions influencing the photocatalytic reaction are (i) changing the ionic strength of reaction medium and (ii) inhibition of catalytic activity of the photocatalyst. The effects of added inorganic ions on the defluoridation of PFBA are shown in Table 2.

The results clearly show that the addition of inorganic anions on the photocatalytic process decreases the defluoridation rate. After 30 min of irradiation time 86.2, 74.6, 73.4, 71.2 and 72.0 mg of fluoride ions were released by the addition of 100 mg of NaNO₃, Na₂SO₄, NaHCO₃, Na₂CO₃ and K₂HPO₄, respectively. The order of inhibition of these ions is $HPO_4^{2-} > CO_3^{2-} > HCO_3^{-} > SO_4^{-} \approx NO_3$. It has been reported that HPO_4^{2-} has higher inhibiting capacity than HCO_3^{-} in photocatalytic degradation of organic compounds with TiO₂ [23]. Addition of NO₃⁻ did not affect of the defluoridation rate appreciably. The inhibition effect of these

 Table 2

 Effect of anions on photodefluoridation of PFBA

Anions	% of defluoridation
TiO ₂	88.2
NaNO ₃	84.2
Na ₂ SO ₄	75.8
NaHCO ₃	46.0
Na ₂ CO ₃	52.4
K ₂ HPO ₄	63.4

[PFBA] = 400 ppm; catalyst suspended = 175 mg; anions = 125 mg; irradiation time = 30 min; airflow rate = 8.1 mL s⁻¹; $I_{254 \text{ nm}} = 2.54 \times 10^{-5}$ einstein L⁻¹ s⁻¹.

ions is due to the reaction of these ions with holes and $^{\circ}$ OH (Eqs. (18)–(22)).

$$SO_4{}^{2-} + h_{VB}{}^+ \to SO_4{}^{2-}$$
 (18)

$$\mathrm{SO_4}^{2+} + {}^{\bullet}\mathrm{OH} \to \mathrm{SO_4}^{\bullet-} + \mathrm{OH}^- \tag{19}$$

$$\mathrm{HCO}_{3}^{-} + {}^{\bullet}\mathrm{OH} \to \mathrm{CO}_{3}^{\bullet-} + \mathrm{H}_{2}\mathrm{O}$$

$$\tag{20}$$

$$\mathrm{CO}_3^{2-} + {}^{\bullet}\mathrm{OH} \to \mathrm{OH} + \mathrm{CO}_3^{\bullet-}$$
 (21)

$$\mathrm{HPO}_{4}^{2-} + {}^{\bullet}\mathrm{OH} \to \mathrm{HPO}_{4}^{\bullet-} + \mathrm{OH}^{-}$$
(22)

2.6. Effect of metal ions

The presence of dissolved metal ions is common in industrial wastewater and they can sensibly affect the rate and efficiency of photocatalytic reactions. The effect of added metal ions on photocatalytic defluoridation is shown in Fig. 5. Except Cu²⁺, other metal ions have not influenced the defluoridation rate initially for 30 min. For 90 min of irradiation, 180, 177.8, 170, 156.2 and 114 mg of fluoride ions were released by the addition of Cu²⁺, Mg²⁺, Fe²⁺, Fe³⁺ and Ag⁺ ions respectively. The order of reactivity of these ions is Cu²⁺ > Mg²⁺ > Fe²⁺ > Fe³⁺ > Ag⁺. The enhancement of defluoridation by addition of these ions is due to their acceptance of conduction band electron, which promote the charge separation.

$$\begin{split} M^{n+} + e_{CB}{}^- &\to M^{(n-1)}, \\ M \, = \, Cu^{2+}, \, Fe^{2+}, \, Fe^{3+}, \, Mg^{2+}, \, Ag^+ \end{split}$$

The process with Fe^{2+} , Fe^{3+} and Mg^{2+} showed a steady effect in the defluoridation of PFBA and at the end of 120 min, 100% defluoridation was achieved. For Cu^{2+} ion 100% defluoridation was obtained in 90 min. Ag⁺ addition had retardation effect on the defluoridation due to deposition of



Fig. 5. Effect of addition of metal ions of pentafluorobenzoic acid: [PFBA] = 400 ppm; catalyst suspended = 175 mg; airflow rate = 8.1 mL s⁻¹; metal ions = 10 mg; $I_{254 \text{ nm}} = 2.54 \times 10^{-5}$ einstein L⁻¹ s⁻¹.



Scheme 1.

silver on the TiO₂ surface. The deposited silver blocks the active sites of TiO₂ and consequently decreases the defluoridation rate. Similar inhibition effect was observed in the photocatalytic and photoelectrolytic degradation of HCOOH on Ag deposited TiO₂ film [24]. The maximum enhancement by Cu^{2+} may be due to its regeneration from Cu⁺ by holes (Eq. (24)) [25].

$$Cu^+ \xrightarrow{h^+} Cu^{2+}$$
(24)

2.7. Photodefluoridation pathway

Irradiation of air equilibrated aqueous suspension containing photocatalyst TiO_2 -P25 and pentafluorobenzoic acid being examined under UV 254 nm light leads to conversion of fluorinated derivatives into detectable intermediate aromatic products and eventually to the evolution of stoichiometry quantities of fluoride and carbon dioxide.

An attempt was made to identify the intermediate products formed in the photocatalytic defluoridation of the pentafluorobenzoic acid through GC–MS analysis of the solution obtained after 30 and 60 min irradiation. We get three predominant peaks for retention times of 2.185, 19.45 and 20.294. These three products were identified as pentafluorobenzene (1), pentafluorophenol (2) and tetrafluoroquinone (3) based on their molecular ion and mass spectrometric fragmentation peaks and are given below.

Compound	Mass spectrum (m/z)
1	168, 149, 137, 118, 99, 84, 75, 61, 51, 47, 31
2	181, 163, 149, 135, 121, 112, 104, 92, 77, 56, 41, 29
3	184, 168, 156, 142, 128, 112, 100, 84, 70, 58, 44, 41

From Scheme 1, first band cleaved in the one electron oxidised PFBA is the C–C bond between C_6F_5 and COOH. This cleavage produces $C_6F_5^{\bullet}$ and CO₂. The photo-kolbe mechanism was proposed for a similar cleavage reported in

pentafluoropropionic acid [10] and trifluoroacetic acid [26]. The attack of OH radical may produce pentafluorophenol (2), which produce tetrafluoroquinone (3). In general, the attack of PFBA by OH radical replaces fluorine atoms producing more hydroxyl functional groups and the intermediates are ultimately mineralised to carbon dioxide and fluoride ions [27].

3. Conclusions

The results of this study show that the strong C–F bond can be cleaved by photolysis with the oxidants such as IO_4^- , BrO_3^- , $S_2O_8^{2-}$, H_2O_2 and CIO_3^- and TiO_2 -P25 using 254 nm light. Except for KClO₃, the addition of other oxidants significantly enhance the UV/TiO₂ process. Inorganic anions inhibits the defluoridation and the order of their inhibition is $HPO_4^{2-} > CO_3^{2-} > HCO_3^- > SO_4^- \approx NO_3^-$. Addition of Cu^{2+} increases the defluoridation rate, whereas Ag⁺ has a retardation effect. The maximum enhancement by Cu^{2+} is assumed to be due to its regeneration by holes. Based on GC– MS analysis pentafluorobenzene, pentafluorophenol and tetrafluoroquinone have been identified as intermediates of photocatalytic defluoridation by TiO₂-P25.

4. Experimental

4.1. Materials

Pentafluorobenzoic acid (99% purity) was obtained from Aldrich Chemical Co. and was used without further purification. TiO₂-P25 (80% anatase, 20% rutile) BET surface area 50 m² g⁻¹, mean particle size 30 nm was supplied by Degussa. AnalaR grade reagents (NH₄)₂S₂O₈, KIO₄, KBrO₃, KCIO₃, H₂O₂ (30% w/w), NaCl, NaNO₃, Na₂SO₄, NaHCO₃ and K₂HPO₄ were used as received. All experiments were carried out using deionised and double distilled water. The pH of the solution was adjusted with H₂SO₄ or NaOH as required.



Fig. 6. Photoreactor.

4.2. Photoreactor

The photocatalytic defluoridation has been carried out with a Heber immersion type photoreactor model HIPR-LP 6/8/116 whose schematic diagram is shown in Fig. 6. This model consisted of a double walled immersion well made of a quartz reactor of 175 cm³ capacity. A small diameter inlet tube extended down the annular space to ensure flow of the coolant from bottom of well upwards to outlet. In the center of cylindrical reactor, the lamps used for light source was placed inside the quartz tube. For the experiments, lamps with different wavelength emission were used. One was 16 W low pressure mercury with emission mainly on the mercury resonance line at 253.7 nm. The other lamp was 8 W medium pressure mercury lamp with broadband emission predominantly emitting at 365 nm. For both the lamps photon flux of the light source was determined by ferrioxalate actinometry and the values of 16 W low pressure Hg lamp and 8 W medium pressure Hg lamp were $I_{254 \text{ nm}} = 2.54 \times 10^{-5}$ Einstein $L^{-1} s^{-1}$ and $I_{365 nm} = 2.08 \times 10^{-6}$ Einstein $L^{-1} s^{-1}$ respectively. The reaction vessel had an arm at the top for gas purging. The temperature of the experimental solution was maintained at 25 ± 1 °C by circulating water during the experiments. The above set-up was placed in the magnetic stirrer for complete mixing of the catalyst.

4.3. Defluoridation analysis

Fluoride ion concentration was determined using Orion expandable ion analyzer model (EA940). The analysis was done using fluoride ion selective electrode in conjugation with Ag/AgCl reference electrode. The instrument was calibrated using standard sodium fluoride solution of various concentrations between 10 and 250 ppm of fluoride ion. The sample from photochemical reactor was taken into 50 mL polyethylene beaker at a regular interval of 30 min. Five

milliliters of water and 20 mL of ionic strength adjustable buffer (TISAB) were added to the solution. This solution was stirred for 5 min and fluoride ion concentration was measured. The pH of the solutions were measured using Metrohm 744 pH meter.

4.4. GC-MS analysis

For identification of intermediate products of PFBA photocatalytic defluoridation, the sample taken after 30, 60 and 90 min was analysed. The sample for analysis was prepared by the following method. The centrifuge obtained after irradiation was extracted five times with HPLC grade dichloromethane. The extract was dried over anhydrous sodium sulfate to remove the water present in the solution. The solvent was removed by evaporation under reduced pressure. The final residual mass was taken for GC–MS analysis.

The GC (Perkin-Elmer Auto System) is equipped with an MSHP 5 capillary column (30 μ m × 250 μ m) and 1micron film thickness (Perkin-Elmer elite series) and interfaced directly to the MS (Perkin-Elmer turbo mass spectrophotometer). The GC column was operated at a temperature of 50 °C for 2 min then increased to 280 °C at the rate of 10 °C min⁻¹. The other experimental conditions are: EI impact ionization 70 eV, helium as carrier gas, injection temperature 260 °C, source temperature 180 °C.

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