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**Photoreductive defluorination of trifluoroacetic acid (TFA)
in the aqueous phase by hydrated electrons**

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Abstract

Due to its extremely high stability and continuous accumulation in the environment, which lead to a widespread environmental distribution, trifluoroacetic acid (TFA) is a global concern in ecosystems. In this study, TFA was decomposed through photoreduction by hydrated electrons (e_{aq}^-) with potassium iodide (KI) as a mediator in the aqueous phase. The reaction proceeded under irradiation at 254 nm in a solution with the following parameters: pH 11.0, anoxic conditions and room temperature (25°C). In 48 h, $91.4\% \pm 1.1\%$ of the fluoride ions (F^-) on all the TFA molecules in the UV/KI system were released, indicating the effective defluorination of TFA. Kinetic analysis indicated that TFA decomposition fit the first-order model with a rate constant of $0.147 \pm 0.014 \text{ h}^{-1}$. The optimal reaction conditions were 0.2 mM KI, 0.05 mM TFA and pH 11.0. In addition to fluoride ions (F^-) and CO_2 , other intermediates, including formic acid ($HCOO^-$) and acetic acid (CH_3COO^-), were identified and quantified in the aqueous phase by ion chromatography (IC), and small amounts of gas-phase CF_3H and CF_4 were detected by gas chromatography-mass spectrometry (GC/MS). Finally, possible TFA degradation pathways were proposed. This method may be effective for the treatment of TFA in aquatic environments.

Keywords:

Trifluoroacetic acid

Hydrated electron

Photoreductive degradation

Potassium iodide

1. Introduction

Per- and polyfluoroalkyl substances (PFASs), especially perfluorocarboxylic acids ($C_nF_{2n+1}COO^-$, PFCAs) and perfluorosulfonic acids ($C_nF_{2n+1}SO_3^-$, PFSAAs), have attracted global attention due to their widespread application, environmental persistence and bioaccumulation [1]. Trifluoroacetic acid (CF_3COOH , TFA), an ultrashort-chain PFCA, is of great concern because it has been widely detected in the global aquatic environment at concentrations ranging from 0.5 to 40,900 ng/L [2, 3], and continuously accumulates [4–6] due to its high aqueous solubility ($>1.0 \times 10^4$ g/L) and persistence in rain and natural waters [7, 8]. Additionally, TFA is also one of the main decomposition products of fluorocarbon substitutes that have been used for over 30 years (e.g., chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs)) [9]. With the replacement of traditional PFASs by short-chain PFASs (carboxylic acid $\leq C_6$, sulfonic acid $\leq C_5$) [10], environmental exposure to short-chain PFASs has increased. The TFA concentrations detected in water connected to potential PFAS point sources such as firefighting training and landfill sites, accounted for more than 20% of the total concentration of 29 PFASs. In water collected from rock shelters equipped with sprinkler systems for fire protection at firefighting training sites (FFTSs), the concentration of TFA was up to 14,000 ng/L; thus, such water bodies have become one of the main sources of TFA [11]. In addition, in the production of fluorochemicals, fluoropolymers decompose at high temperature to produce TFA precursors (e.g., polytetrafluoroethylene), leading to the further generation of TFA [3, 8]. The extensive sources of TFA indicate that it has become one of the main PFASs

1 present in aquatic environments. High TFA accumulation in water will undoubtedly
2 cause more adverse long-term effects on the ecosystem than long-chain PFASs. The
3 toxicity of TFA to humans has also attracted attention because the analogous
4 chlorinated compound trichloroacetic acid (CCl_3COOH) is a known liver carcinogen
5 [12]. The toxic effect threshold for humans [13] is approximately 0.25 mg/L TFA, and
6 TFA exhibits developmental toxicity to zebrafish embryos [14]. Studies have shown
7 that the concentration of TFA in drinking water ranges from 11 ng/L to 16 $\mu\text{g/L}$; since
8 TFA is highly polar and therefore has a low bioaccumulation potential, the low
9 concentration in drinking water does not pose a threat to humans [15]. However,
10 because TFA is persistent, its concentration in the aquatic environment will continue
11 to increase with the continuous use of TFA as an intermediate or final product in
12 chemical synthesis. For example, the TFA concentration observed in the river
13 downstream of a fluorinated inorganic and organic chemicals producer was 140 $\mu\text{g/L}$,
14 which exceeds the safe concentration of 100 $\mu\text{g/L}$ for aquatic environments [16, 17].
15 In addition to the production of TFA as a final product, the compound of this producer
16 is also used for the production of CF_3 - containing building blocks like ETFBO
17 (4-ethoxy-1,1,1-trifluoro-3-buten-2-one) for the organic syntheses of plant protecting
18 agents, and when appropriate CF_3 -containing precursors are present, WWTP influents
19 can potentially form TFA [16]. In addition, current drinking water purification
20 methods cannot remove PFASs, resulting in continuous human exposure to elevated
21 TFA concentrations. Therefore, the potential impact of TFA on human health should
22 be considered. Current research has mostly focused on the environmental

1 characteristics and concentrations of TFA [18, 19], but there have been a few studies
2 on technology for high-efficiency TFA treatment. Due to its increasing environmental
3 accumulation and biological toxicity, it is necessary to develop a method for effective
4 TFA decomposition.

5 Due to the high bond dissociation energies (BDEs) of $-\text{CF}_3$ bonds (116.8 kcal/mol)
6 [20, 21], TFA is difficult to decompose by general biological and chemical methods.
7 Studies have shown that TFA cannot be decomposed effectively by methods such as
8 anaerobic or aerobic biodegradation [22], conventional advanced oxidation (e.g.,
9 ozone oxidation or $\cdot\text{OH}$ oxidation) [23], or high-temperature pyrolysis (e.g., 165°C)
10 [24]. Some researchers have demonstrated that TFA can be decomposed by
11 photocatalytic oxidation. A total of 19.3% of TFA decomposed after 48 h of reaction
12 in a $\text{UV}/\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ system with an oxygen partial pressure of 0.55 MPa [25].
13 After the reactor was pressurized to 0.48 MPa with oxygen gas, 86.6% of the TFA
14 decomposed in a $\text{UV}/\text{K}_2\text{S}_2\text{O}_8$ system [26]. Other methods, such as electrocatalytic
15 oxidation [27] and microwave radiation [28], can achieve nearly 100% TFA
16 decomposition within 2 h. However, the cost of electrode materials and the energy
17 requirement of the above systems are not low. Thus, it is of great significance to
18 develop a mild method to effectively decompose TFA into harmless species.

19 Quantitative structure-activity relationship (QSAR) analysis shows that TFA is
20 more suitable for reductive degradation than oxidative degradation due to the
21 electron-withdrawing groups (EWGs) in its molecular structure ($-\text{COOH}$ and F atoms)
22 [29, 30]. Hydrated electrons (e_{aq}^-) are an extremely strong reducing agent with a

1 standard reduction potential of -2.9 V and can be produced by UV irradiation
 2 mediated by various inducers (e.g., iodide [31, 32], sulfite [33] and indole [34]).
 3 Research showed that 96.0% of initial perfluorooctanoic acid (PFOA) was
 4 decomposed after 12 h, with 98.0% defluorination in a UV/KI system [33]. However,
 5 in the PFCA family, TFA is the most difficult to decompose. This is because the
 6 structure of TFA contains -CF₃, and the C-F bonds on -CF₃ have an extremely high
 7 BDE of 116.8 kcal/mol; thus, in contrast to that of other PFCAs, the degradation of
 8 TFA does not begin with the decomposition of -CF₂- (BDE=106.8–107.3 kcal/mol)
 9 [20]. All PFCAs (C3-C12) except TFA can be decomposed through polychromatic
 10 irradiation (λ =200 – 1,000 nm) [35]. In a UV/SO₃²⁻ system, the complete
 11 decomposition of all PFCAs except TFA was achieved within 8 to 12 h [20].
 12 Long-chain PFCAs could cause TFA accumulation through the
 13 decarboxylation-hydroxylation-elimination-hydrolysis (DHEH) pathway [36] during
 14 photodegradation, which also indicates that TFA is much more recalcitrant than C_≥3
 15 PFCAs. Thus, it is feasible but challenging to use e_{aq}⁻ for the effective decomposition
 16 of TFA. To eliminate the influence of other PFASs, a system with only TFA is needed
 17 to explore whether TFA can be efficiently decomposed. Based on the above
 18 considerations, the UV/KI system has great potential, as it requires an extremely low
 19 amount of catalyst (4-fold the pollutant concentration) and a 254 nm low-pressure
 20 mercury lamp (33.1 μW/cm²). We estimated the electrical energy per order (E_{EO}) for
 21 degrading TFA with different methods, which is defined as the number of
 22 kilowatt-hours (kWh) of electrical energy required to reduce the pollutant

1 concentration by 1 order of magnitude per m^3 of water [37]. The E_{EO} in the UV/KI
2 system is $326.3 \text{ kWh/m}^3/\text{order}$, which is lower than those in many other photocatalytic
3 systems ($457\text{--}1.3\times 10^7 \text{ kWh/m}^3/\text{order}$) (Table S4, Supplementary Material).
4 Furthermore, the UV/KI system needs less catalyst than that of the UV/SO_3^{2-} system
5 and $\text{UV/K}_2\text{S}_2\text{O}_8$ system (10–400-fold the pollutant concentration). Therefore, the
6 above experimental conditions are relatively mild compared to other photocatalytic
7 systems.

8 This research develops an effective method that requires relatively mild conditions
9 for the decomposition of TFA with e_{aq}^- generated by a UV/KI reduction system. The
10 effects of different conditions (e.g., UV irradiation, KI concentration and initial pH)
11 on the decomposition process are studied, and the optimal reaction conditions are
12 proposed. In addition, the possible pathways of TFA decomposition are proposed
13 based on product analysis.

14 2. Materials and methods

15 2.1. Chemicals and materials

16 TFA (99.0%) and difluoroacetic acid (DFA, 99.0%) were purchased from
17 Sigma-Aldrich (St. Louis, MO). Ammonium hydroxide (25.0%), ammonium chloride,
18 formic acid (HCOOH , 96.0%), acetic acid (CH_3COOH , 99.7%), sodium fluoride and
19 potassium iodide were available from TEDIA Co. (USA). Sodium acetate ($\geq 99.0\%$)
20 was purchased from Fluka (Switzerland); methanol ($\geq 99.9\%$) was purchased from
21 Sigma-Aldrich. Chemical reagents such as sodium chloride, calcium chloride,
22 hydrochloric acid, sodium hydroxide, nitric acid, sulfuric acid, potassium hydroxide,

1 and potassium persulfate were purchased from Sinopharm Chemical Reagents
2 (China). Milli-Q water (Millipore, USA) was used throughout the experiment.
3 Standard gases, CF₃H, CF₄, C₂F₆, and CO₂, were produced by Weichuang Company
4 (Shanghai).

5 **2.2. Photoreductive decomposition**

6 The photoreductive decomposition reaction was carried out in a stainless steel
7 cylindrical reactor (740 mL volume, 60 mm) equipped with a low-pressure mercury
8 lamp (15 W, $\lambda = 254$ nm, Bright Star Light & Electricity Industry Co., Guangdong,
9 China) with a quartz tube protection device (for details, see **Fig. S1**). The intensity of
10 the UV light was 2.17×10^{-6} Einstein $\cdot$ L⁻¹s⁻¹. The reactor was filled with 720 mL of a
11 solution containing TFA (0.05 mM) and KI (0.2 mM), purged with N₂ for 30 min,
12 stirred with a magnetic stirrer at a speed of 120 rpm, and irradiated with a tube lamp
13 to initiate TFA decomposition by e_{aq}⁻ under anaerobic conditions. Ammonium
14 hydroxide-ammonium chloride buffer was used to adjust the initial pH to 11.0. A
15 circulating water bath was passed through the outer layer of the reactor to maintain
16 the reaction temperature at room temperature (25°C). Photoreductive decomposition
17 under this condition served as the experimental control group.

18 To study the influence of different reaction conditions, 4 sets of control
19 experiments were carried out under the same conditions of the experimental group but
20 with the following modifications: without UV irradiation, without KI, with air
21 prebubbling and without nitrogen prebubbling. To study the treatment effects of
22 different processes, two control experiments were conducted under the same

conditions: $K_2S_2O_8$ was added after oxygen prebubbling when the solution pH was 3.0, and $H_3PW_{12}O_{40} \cdot 6H_2O$ was added after oxygen prebubbling when the solution pH was 1.0. In addition, to explore the effects of the elicitor concentration and initial pH on the reaction system, we established different experimental groups with different dosages of KI (0.025 mM, 0.05 mM, 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM and 0.5 mM) and initial pH values (pH=4.0, 6.0, 9.0, 10.0, 11.0, 12.0 and 13.0). The buffer concentrations in the variable-pH experiments are listed in **Table S1**.

Samples were taken from the sampling port at different reaction times. The liquid-phase samples were analyzed by ion chromatography (IC) to detect F^- , TFA and the other short-chain products, before which the samples were filtered through a 0.22 μm nylon filter (Millipore) membrane. The gas-phase samples were temporarily stored in a sealed syringe, and then detected by gas chromatography-mass spectrometry (GC/MS).

2.3. Analytical methods

Concentrations of TFA, fluoride and possible aqueous-phase intermediate products were determined by ion chromatography (Dionex, ICS-3000, Sunnyvale, CA, USA) with a conductivity detector and a self-regenerating suppressor, utilizing standard solutions of TFA, F^- , DFA, $HCOOH$ and CH_3COOH . The ion chromatogram showed a good resolution with no obvious interference of peaks (**Fig. S2**). Potassium hydroxide eluent with a flow rate of 1.5 mL/min was fed by an eluent generator (EG with CR-ATC). A sample (1.0 mL) was injected into a Dionex IonPac AG11 guard column (50 mm $\times$ 4 mm inner diameter) and separated on a Dionex IonPac AS11-HC

1 separation column (250 mm × 4 mm inner diameter). Then the separated sample was
2 quantified by a conductivity detector. For more detailed information, please see the
3 **Supplementary Material**.

4 The products in the gas phase were determined by a GC/MS system consisting of
5 a gas chromatograph (GC 2000, Thermo Fisher Scientific, Inc., Waltham, MA, USA)
6 fitted with an HP5 MS capillary column (30 m length, 0.25 mm diameter, 0.25 µm
7 film thickness) and a single-quadrupole mass spectrometer (Trace DSQ, Thermo
8 Fisher Scientific). Helium was used as the carrier gas at a constant flow of 1.0
9 mL/min. The injection temperature was maintained at 120°C. Effluents from the GC
10 column were transferred to a 70 eV electron ionization source maintained at 250°C.
11 Identification was based on probability-based matching to mass spectra in a NIST
12 library and matching with the mass spectra of the standard reference compounds.
13 Standard gases of CF₃H, CF₄, C₂F₆ and CO₂ were used for quantitative analysis. For
14 more detailed information, please see the **Supplementary Material**.

15 **2.4. Laser flash photolysis experiments**

16 Nanosecond laser flash photolysis for the detection of e_{aq}⁻ was performed using an
17 LP980 Edinburgh instrument (UK) with laser excitation at 266 nm from a Surelite
18 I-10 Q-Switched Nd:YAG laser (35 mJ). Detailed information about the instrument
19 and experiment is available in the **Supplementary Material**.

20 **2.5. UV-Vis characterization**

21 UV-Vis spectra were recorded at room temperature (25°C) with a Shimadzu
22 spectrophotometer (UV-1900i, Shimadzu, Japan). N₂-saturated TFA solutions (0.05

1 mM) with different KI concentrations (0.025 mM, 0.05 mM, 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM and 0.5 mM) were prepared with Milli-Q water. Ammonium hydroxide-ammonium chloride buffer was used to adjust the initial pH to 11.0.

4 3. Results and discussion

5 3.1. Decomposition and defluorination of TFA

6 As in the experimental group, the photoreduction of TFA in the aqueous phase
7 proceeded with KI as a mediator under 254 nm UV irradiation and anoxic conditions.
8 The initial concentrations of TFA and KI were 0.05 mM and 0.2 mM, respectively.
9 The initial pH of the solution was adjusted to 11.0 by $\text{NH}_3\text{OH}/\text{NH}_4\text{Cl}$. Four control
10 experiments were conducted without UV irradiation, without KI, with air prebubbling
11 or without N_2 prebubbling, while keeping the other conditions the same as those for
12 the experimental group. The decomposition (**Eq. 1**) and defluorination (**Eq. 2**) of TFA
13 were calculated as follows:

$$14 \quad \text{Decomposition} = \left(1 - \frac{c_t}{c_0}\right) \times 100\% \quad (1)$$

$$15 \quad \text{Defluorination} = \frac{c_F}{c_0 \times 3} \times 100\% \quad (2)$$

16 where c_t is the concentration of TFA (mM) at t h; c_0 is the initial concentration of
17 TFA (mM), c_F is the concentration of fluoride ions (mM), and the factor of 3
18 corresponds to the number of fluorine atoms in one TFA molecule.

19 The efficiencies of TFA decomposition and defluorination under different
20 conditions are summarized in **Fig. 1**. TFA barely decomposed without UV irradiation
21 (first control group). Only $32.8\% \pm 2.1\%$ of TFA decomposed after 9 h of pure UV
22 irradiation (second control group), and TFA defluorination became very slow after 6 h

1 and reached $24.9\% \pm 0.7\%$ at 24 h. The decomposition ($72.3\% \pm 1.2\%$) and
 2 defluorination ($58.6\% \pm 1.2\%$) of TFA in the UV/KI system at 9 h (experimental
 3 group) were 2-fold and 3-fold higher than those with pure UV irradiation,
 4 respectively. Up to $95.7\% \pm 2.1\%$ of TFA was decomposed after 48 h, and the
 5 concentration of F^- released into solution was 0.137 mM with $91.4\% \pm 1.3\%$
 6 defluorination. In the pure UV irradiation system, the quantum yield was low (0.23
 7 mmol/Einstein). However, there was still $45.3\% \pm 1.3\%$ decomposition and even
 8 $24.9\% \pm 0.7\%$ defluorination of TFA at 24 h. Due to the lack of KI, the direct
 9 photolysis system does not have favorable conditions for the generation of e_{aq}^- . The
 10 decomposition of TFA is mainly due to the cleavage of the C-C bond by UV
 11 irradiation [38]. According to research by Qu et al. [31], the hydrolysis during direct
 12 photolysis cannot be ignored, so the TFA may be further defluorinated by hydrolysis
 13 (Eq. 3). In addition, the mercury lamp that is used exhibits a little UV excitation at
 14 230–239 nm (corresponding to the photon energy of 5.2–5.4 eV) in addition to the
 15 dominant wavelength of 254 nm (Fig. S3). Thus, a fraction of e_{aq}^- could be generated
 16 from water splitting (dissociation energy of H_2O is about 5.2 eV) (Eq. 4) [39] and the
 17 charge-transfer-to-solvent (CTTS) reaction of hydroxide ions (OH^-) in a strong
 18 alkaline solution ($pH > 10.0$) (Eq. 5) [40]. Although e_{aq}^- may be immediately
 19 scavenged via the recombination with $\cdot OH$ (Eq. 6), a fraction of e_{aq}^- is involved in
 20 TFA defluorination and decomposition [39]. However, the TFA aqueous solution
 21 demonstrates low absorbance of the dominant wavelength at 254 nm (Fig. S4), which
 22 limits the generation of e_{aq}^- , and results the low efficiency of the pure UV irradiation

1 system. Additionally, in the UV/KI system, KI can produce e_{aq}^- under UV irradiation
 2 [41], which effectively promotes the decomposition and defluorination of TFA. Thus,
 3 e_{aq}^- plays a major role for the decomposition and defluorination of TFA in the
 4 photoreduction system .

5 The decomposition and defluorination efficiencies in O_2 -saturated aqueous
 6 solution (third control group) and oxygen-containing aqueous solution (fourth control
 7 group) were much lower than those in the N_2 -saturated solution (experimental group)
 8 as a result of the scavenging of e_{aq}^- via their rapid reaction with O_2 ($k_2=1.9\times 10^{10}$
 9 $M^{-1}\cdot s^{-1}$) (Eq. 7) [42]. Moreover, the generation of e_{aq}^- could be reduced by the easy
 10 oxidation of I^- to I_2 in the O_2 -saturated solution. Thus, the presence of O_2 will severely
 11 reduce the TFA reaction efficiency, which further shows that e_{aq}^- is the key free
 12 radical for the decomposition and defluorination of TFA.

Fig. 1. Temporal profiles of TFA decomposition (a) and defluorination (b) during photolysis under different conditions. Experimental group: TFA (0.05 mM), KI (0.2 mM), UV irradiation, pH (11.0), N₂ saturation. First control group: TFA (0.05 mM), KI (0.2 mM), pH (11.0), N₂ saturation. Second control group: TFA (0.05 mM), UV irradiation, pH (11.0), N₂ saturation. Third control group: TFA (0.05 mM), KI (0.2 mM), UV irradiation, pH (11.0), O₂ saturation. Fourth control group: TFA (0.05 mM), KI (0.2 mM), UV irradiation, pH (11.0), without N₂ prebubbling. All experiments were repeated 3 times, and error bars indicate the standard deviation.

The efficiencies of this developed method and other methods for decomposing TFA were compared by conducting the reaction in the same reactor with different mediators (**Fig. 2**). The conditions for the first treatment group were the same as those for the experimental group in **Fig. 1**. The second treatment was conducted in solutions of TFA (0.05 mM) and $K_2S_2O_8$ (0.5 mM) at pH 3.0 and triggered after bubbling with O_2 . The third treatment group was subjected to the same conditions as the second treatment group, except the mediator $H_3PW_{12}O_{40} \cdot 6H_2O$ (0.06 mM) and pH (1.0) were different. The last two treatments referred to the reports of **Hori et al.** [25,43] except for the power of UV light.

Fig. 2. Temporal profiles of TFA decomposition (a) and defluorination (b) during photolysis with different mediators. First treatment group: TFA (0.05 mM), KI (0.2 mM), N₂ saturation, pH (11.0). Second treatment group: TFA (0.05 mM), K₂S₂O₈ (0.5 mM), O₂ saturation, pH (3.0). Third treatment group: TFA (0.05 mM), H₃PW₁₂O₄₀·6H₂O (0.06 mM), O₂ saturation, pH (1.0). All experiments were repeated 3 times, and error bars indicate the standard deviation.

As shown in **Fig. 2**, TFA decomposition and defluorination under anoxic conditions with KI were significantly higher than those under oxidative conditions with K₂S₂O₈ or H₃PW₁₂O₄₀·6H₂O, especially defluorination. The defluorination of TFA was 88.2% ± 1.1% in the UV/KI system but only 32.9% ± 2.1% and 37.1% ± 0.9% in the UV/K₂S₂O₈ and UV/H₃PW₁₂O₄₀·6H₂O systems, respectively. The apparent reaction rate coefficient (k_{app}^{TFA}) and half-life (t_{app}^{TFA}) of TFA for the first 6 h in the first treatment group were estimated to be $0.147 \pm 0.014 \text{ h}^{-1}$ and $5.0 \pm 0.5 \text{ h}$, respectively. The reaction rate for the UV/KI system was 2–4-fold faster, and the corresponding half-life was 2–4-fold shorter than those for the other two systems

- 1 $(k_{\text{app}}^{\text{K}_2\text{S}_2\text{O}_8} = 0.067 \pm 0.002 \text{ h}^{-1}, t_{\text{app}}^{\text{K}_2\text{S}_2\text{O}_8} = 10.3 \pm 0.3 \text{ h}; k_{\text{app}}^{\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}} = 0.040 \pm 0.004$
 2 $\text{h}^{-1}, t_{\text{app}}^{\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}} = 17.3 \pm 1.5 \text{ h}).$

3 From the above results, TFA was decomposed faster and more thoroughly in the
 4 UV/KI system than in the other two oxidative systems. The electronegativity of the F
 5 atom makes TFA resistant to AOPs (e.g., UV/H₂O₂ system) [44, 45]. However,
 6 thermodynamic investigations show that the reaction of TFA with e_{aq}⁻ is favorable
 7 because compounds with EWGs have lower Gibbs free energy (ΔG_{SET}) during
 8 reductive degradation [29, 30]. For example, the reaction rate of TFA and the
 9 effective free radical SO₄^{-•} generated by S₂O₈²⁻ ($k_2 = 1.6 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$) [46] is very
 10 slow under oxidative conditions. Furthermore, the reaction rate of SO₄^{-•} and initiator
 11 S₂O₈²⁻ ($k_2 = 6.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) [47] is an order of magnitude faster than that of SO₄^{-•}
 12 and TFA. Since S₂O₈²⁻ and SO₄^{-•} were consumed by each other as the reaction
 13 progressed, the decomposition and defluorination of TFA slowed. To increase the
 14 extent of decomposition, the UV/K₂S₂O₈ system may require more S₂O₈²⁻ exposure
 15 and energy to produce more SO₄^{-•} (716 kWh/m³/order). The key to TFA
 16 decomposition with H₃PW₁₂O₄₀·6H₂O is the precomplexation of TFA and
 17 [PW₁₂O₄₀]³⁻, so extensive decomposition may occur only when a large amount of
 18 [PW₁₂O₄₀]³⁻ is added to the high-concentration aqueous TFA solution and requires
 19 more energy (1199.2 kWh/m³/order). The E_{EO} for TFA in the UV/KI system was
 20 326,3 kWh/m³/order, which was lower than those of two oxidative system (**Table S4,**
 21 **Supplementary Material**).

22 The analysis showed that UV irradiation was indispensable for effective TFA

decomposition. The UV/KI system was the most efficient among all the photocatalytic systems mentioned: this system did not need a high concentration of initiators or pollutants and consumed the least energy. All the results indicated that reduction was more suitable than oxidation for TFA decomposition.

3.2. Products of TFA photochemical decomposition

The products were detected and analyzed to further study the reaction mechanism and pathway of TFA degradation in the UV/KI system. The temporal profiles of the main decomposition products of TFA in the UV/KI system are shown in **Fig. 3**. The main liquid-phase products detected by IC were F^- , HCOO^- , CH_3COO^- and undecomposed TFA (**Fig. 3a**). GC/MS measurements showed that the main gas-phase product was CO_2 , and a small amount of CF_3H and CF_4 was also detected in the gas phase (**Fig. 3b**). The possible liquid- and gas-phase products DFA (CF_2HCOOH) and C_2F_6 were below the detection limit (see **Table S2** and **Table S3** for details), which are not listed in **Fig. 3**.

Fig. 3. Temporal profiles of liquid- (a) and gas- (b) phase products in the UV/KI system.

Reaction conditions: TFA (0.05 mM), KI (0.2 mM), N₂ saturation, pH (11.0). All experiments were repeated 3 times, and error bars indicate the standard deviation.

In **Fig. 3a**, the concentration of the liquid-phase product F⁻ increased with the reaction time, and F⁻ accumulated rapidly during the first 6 h of reaction, after which the accumulation rate decreased. However, the F⁻ accumulation rate returned to the initial reaction rate during hours 9–12 of the reaction, which indicated that some fluorine-containing intermediate products were decomposed during this period to generate F⁻, in addition to the F⁻ produced by TFA decomposition. The remaining liquid products HCOO⁻ and CH₃COO⁻ increased in only the early stage of the reaction and then started to decompose at 9 h and 12 h, respectively. **Fig. 3b** shows that the gas-phase product CO₂ accumulated continuously as the reaction progressed. A small amount of gas-phase CF₃H was produced, reaching a peak value (128.8 ± 24.9 ppm) after 9 h of reaction and decomposing to F⁻ from 9–12 h, which contributed to the

1 rapid F^- accumulation from 9–12 h. CF_4 was also detected in the reaction, but its
 2 concentration remained extremely low. After 48 h of reaction in the UV/KI system,
 3 the concentrations of CO_2 , CF_3H and CF_4 were 1436.9 ± 118.5 ppm, 21.5 ± 20.5 ppm
 4 and 0.3 ± 0.1 ppm, respectively.

5 To further confirm the photolysis products of TFA (including the products of pure
 6 UV irradiation), we also detected the products of the photocatalytic reduction systems
 7 with non-ideal conditions (the same conditions shown in **Fig. 1**). The liquid-phase
 8 products under different photolysis conditions were also F^- , $HCOO^-$ and CH_3COO^- ,
 9 and the yield of $HCOO^-$ and CH_3COO^- was directly proportional to the decomposition
 10 efficiency in **Fig. 1** (**Fig. S5**). DFA was also below the detection limit.

$$11 \quad N_c = [TFA]_0 \times 2 - ([TFA] \times 2 + [HCOO^-] + [CH_3COO^-] \times 2) \quad (8)$$

$$12 \quad N_F = [TFA]_0 \times 3 - ([TFA] \times 3 + [F^-]) \quad (9)$$

13 The environmental impact of the products should not be ignored. Studies have
 14 shown that F^- in water can be rendered harmless via reaction with or adsorption to
 15 particles containing SiO_2 [48], but the recovery and disposal of gaseous products are
 16 difficult. To investigate the environmental impact of the gas-phase products in the
 17 different systems, the carbon (N_c , **Eq. 8**) and fluorine (N_F , **Eq. 9**) contents of the
 18 gas-phase products were calculated from the corresponding contents of the
 19 liquid-phase products. As shown in **Fig. S6**, the main liquid phase products in the
 20 UV/ $K_2S_2O_8$ system and UV/ $H_3PW_{12}O_{40} \cdot 6H_2O$ system were F^- , $HCOO^-$ and
 21 CH_3COO^- . Therefore, F^- , $HCOO^-$, CH_3COO^- and undecomposed TFA were regarded
 22 as the liquid-phase product contents of the two oxidative systems and reductive

1 systems under different photolysis conditions for the calculations. The calculation
2 results of systems with different catalysts are shown in **Fig. 4**. The gas-phase carbon
3 and fluorine contents in the two photocatalytic oxidation systems showed increasing
4 trends with the reaction time. The gas-phase carbon content in the UV/KI system
5 increased as the reaction time increased, while the fluorine content rose first and then
6 declined. These results indicated that the fluorine-containing gaseous products in the
7 UV/K₂S₂O₈ system and the UV/H₃PW₁₂O₄₀·6H₂O system accumulated continuously,
8 but those in the UV/KI system (e.g., CF₃H) were ultimately decomposed. Comparing
9 the ratio of the fluorine content to the carbon content in the gas phase (fluorocarbon
10 ratio) for the three systems at 24 h (**Table 1**) revealed that the proportion of fluorine
11 in the gaseous products of the UV/KI system was extremely low (fluorocarbon ratio
12 of 0.07 ± 0.04) because CF₃H and CF₄ were minor gaseous products, with the major
13 product being CO₂. The fluorocarbon ratios of the UV/K₂S₂O₈ and
14 UV/H₃PW₁₂O₄₀·6H₂O systems were both close to 1, much higher than that of the
15 UV/KI system. Therefore, the two oxidation systems produced a large amount of
16 fluorine-containing products. Moreover, the fluorine content in the gas phase
17 increased during direct photolysis, indicating that other undetected
18 fluorine-containing gases may be produced in the process (**Fig. S7**). The fluorocarbon
19 ratios under the non-ideal conditions of the reductive systems were all close to 1
20 (**Table 1**), which was the same as the two oxidative systems, so the production of
21 fluorocarbons was high under these conditions. In summary, only under the
22 conditions where e_{aq}⁻ played a leading role was the defluorination high and the main

1 gas-phase product CO_2 instead of being fluorocarbons. The greenhouse effect of
 2 fluorocarbon gases is much higher than that of CO_2 ; for example, the global warming
 3 potential (GWP) of CF_3H is 11,700-fold that of CO_2 [49], so the fluorine-containing
 4 gas produced by the degradation of TFA deserves attention, especially for the two
 5 oxidation systems without e_{aq}^- .

6 The above experiments show that the UV/ $\text{K}_2\text{S}_2\text{O}_8$ system, UV/ $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$
 7 system and non-ideal systems with a few e_{aq}^- could produce a large amount of
 8 fluorine-containing gases with extremely high greenhouse effects, and these
 9 fluorine-containing gases cannot be further degraded. In comparison, the UV/KI
 10 system in which e_{aq}^- plays a leading role can not only decompose TFA efficiently but
 11 also further decompose fluorine-containing intermediate products into more
 12 environmentally friendly products.

13

Fig. 4. Temporal profiles of theoretical gas-phase carbon (a) and fluorine (b) contents during photolysis with different mediators. Reaction conditions were the same as those in **Fig. 2**. All experiments were repeated 3 times, and error bars indicate the standard deviation.

Table 1. Theoretical gas-phase carbon (N_c) and fluorine (N_F) contents for photolysis with different mediators and conditions at 24 h

Reaction conditions	N_c /mM	N_F /mM	Fluorocarbon ratio
UV+N ₂ +KI	0.042 ± 0.002	0.003 ± 0.002	0.07 ± 0.04
UV+O ₂ +K ₂ S ₂ O ₈	0.021 ± 0.001	0.022 ± 0.001	1.05 ± 0.1
UV+O ₂ +H ₃ PW ₁₂ O ₄₀ ·6H ₂ O	0.026 ± 0.003	0.028 ± 0.003	1.08 ± 0.04
UV+N ₂	0.021 ± 0.002	0.022 ± 0.001	1.05 ± 0.07
UV+O ₂ +KI	0.018 ± 0.002	0.019 ± 0.001	1.06 ± 0.17
UV+ KI	0.018 ± 0.002	0.02 ± 0.003	1.11 ± 0.11

N₂+KI

0

0

-

3.3. Decomposition mechanism

Our study demonstrated that e_{aq}^- played a key role in the photoreductive decomposition of TFA in the UV/KI system. Therefore, we conducted a laser flash photolysis study to characterize e_{aq}^- , showing the capability of e_{aq}^- generation by KI and H₂O (Fig. S8). To explore the pathway of TFA decomposition by e_{aq}^- , the changes in the mass balance of carbon and fluorine over time were calculated and were shown in Fig. 5. The mass balance of carbon and fluorine was expressed as the recovery of carbon (R_C , Eq. 10) and fluorine (R_F , Eq. 11) after the reaction, respectively. R_C is the ratio of the total carbon in the undecomposed TFA, CH₃COO⁻, HCOO⁻, CF₃H, CF₄ and CO₂ to that in the initial TFA. R_F is the ratio of the total fluorine in the undecomposed TFA, F⁻, CF₃H and CF₄ to that in the initial TFA.

$$R_C = 100 \times \left(\frac{[TFA] \times 2 + [HCOO^-] + [CH_3COO^-] \times 2 + [CO_2] + [CF_4] + [CF_3H]}{[TFA]_0 \times 2} \right) \quad (10)$$

$$R_F = 100 \times \left(\frac{[TFA] \times 3 + [F^-] + [CF_4] \times 4 + [CF_3H] \times 3}{[TFA]_0 \times 3} \right) \quad (11)$$

Fig. 5. Temporal profiles of mass balances in the UV/KI system: (a) carbon mass balance and (b) fluorine mass balance. Reaction conditions were the same as those in **Fig. 3**.

As shown in from **Fig. 5**, the recovery of carbon reached 91.7% and that of fluorine was almost 100% after 24 h of chemical reaction. These results indicated that the main products had been detected and listed, and some fluorine- or carbon-based compounds might have remained undetected (e.g., CO). The carbon and fluorine recoveries from each product were used to observe the changes in products. In **Fig. 5a**, the carbon recovery as HCOO^- increased from 0 to 11.7% from 0–9 h, and then the proportion of HCOO^- began to decrease. The carbon recovery as HCOO^- decreased to 5.0% after 48 h. The carbon recovery as CH_3COO^- increased from 0 to the peak value (36.7%) at 12 h, and decreased to 13.3% after 48 h. In **Fig. 5b**, it can be seen that the system produced intermediates with a high fluorine content, mainly CF_3H , during the reaction. The recovery of CF_3H increased from 0 to 10.0% over the first 12 h and then finally decreased and finally decreased to 3.3% after 48 h.

1 However, the proportions of CO_2 and F^- increased continuously, and the carbon
 2 recovery as CO_2 reached 63.3% after 48 h, accounting for approximately
 3 three-quarters of the R_C . Fluorine recovery as F^- ultimately accounted for 93.2% of
 4 the R_F . Therefore, the intermediates HCOO^- , CH_3COO^- and CF_3H were gradually
 5 decomposed in the UV/KI system, and the final products of TFA decomposition were
 6 mainly CO_2 and F^- .

7 $-\text{CF}_3$ in the TFA structure contains three C-F bonds with high bond energy (BDE
 8 = 116.8 kcal/mol) [20], which makes it difficult to break the C-F bonds of TFA first
 9 in direct defluorination and hydrogenation reactions [50, 51]. The absence of DFA
 10 (CF_2HCOOH) in the experiment confirmed this point. The C-C bonds could be
 11 broken by e_{aq}^- or UV irradiation first due to their low bond energy (BDE = 82.7
 12 kcal/mol) [38]. **Qu et al.** proved through experiments that in the UV/KI system, when
 13 the pH value is higher than 7.0, e_{aq}^- is the main reducing agent, causing the cleavage
 14 of the C-F and C-C bonds of PFOA with a similar phenomenon also being observed
 15 for TFA [52]. **Bentel et al.** [51] also found that in the UV/ SO_3^{2-} system at pH=9.5, the
 16 C-C bond of TFA is broken by e_{aq}^- to generate CF_3OH and then hydrolyzed for
 17 defluorination. So e_{aq}^- has a tendency to break the C-C bond of TFA preferentially.
 18 The products after C-C cleavage contained C-F bonds, which could not be effectively
 19 destroyed by UV irradiation due to their high bond energy. The extent of TFA
 20 defluorination ($24.9\% \pm 0.7\%$) under pure UV irradiation being much lower than the
 21 extent of TFA decomposition ($45.3\% \pm 1.3\%$) also supports this mechanism. The
 22 electronegativity of fluorine (4.0) in TFA makes the molecule highly electron

1 absorbing, so fluorine serves as a chemical reaction center when nucleophiles
 2 approach [53]. Therefore, e_{aq}^- could act as the nucleophile for the cleavage of C-F
 3 bonds. On the basis of the above discussion, the following TFA decomposition
 4 pathway in the UV/KI system could be proposed: first, e_{aq}^- and UV irradiation break
 5 the C-C bonds of TFA, and then the C-F bonds are further dissociated by e_{aq}^- .

6 In detail, e_{aq}^- plays a leading role in the UV/KI system to break the C-C bond and
 7 C-F bond of TFA, while UV irradiation can break only the C-C bonds of some TFA
 8 to decompose it into $\cdot CF_3$ and $\cdot COO^-$ (Eq. 12). Under the action of e_{aq}^- and
 9 hydrolysis, the C-C bond and C-F bond of TFA are broken, and TFA is defluorinated
 10 and hydrogenated to produce the main product F^- and the liquid-phase intermediate
 11 products $HCOO^-$ and $\cdot CH_2$ (Eq. 13). $\cdot CH_2$ is a reactive species, which can be further
 12 hydrolyzed to produce $\cdot CH_3$ (Eq. 14) [31], and $\cdot CH_3$ can recombine with $\cdot COO^-$ to
 13 produce the main intermediate product CH_3COO^- (Eq. 15). Reaction 12 is the key
 14 reaction in the UV/KI system. Furthermore, e_{aq}^- can also act on the carbonyl group of
 15 TFA, further breaking the C-C bonds of a small amount of TFA to produce $\cdot CF_3$ and
 16 CO (Eq. 16) [44]. The e_{aq}^- further breaks the C-F bond of $\cdot CF_3$ and removes one $\cdot F$
 17 from $\cdot CF_3$ to produce CF_2^- [54] (Eq. 17). $\cdot F$ reacts with $\cdot COO^-$ in the system to
 18 produce another main product, CO_2 (Eq. 18). $\cdot CF_3$ can also be hydrolyzed to generate
 19 CO_2 and HF (Eq. 19). In a strong alkaline solution, HF is quickly converted to F^- (Eq.
 20 20), resulting in the pure UV irradiation system achieving $24.9\% \pm 0.7\%$
 21 defluorination. The gas-phase intermediate products CF_3H and CF_4 are formed by the
 22 hydrolysis or the further combination of $\cdot CF_3$ and $\cdot F$ (Eqs. 21–22).

In the proposed mechanism for TFA degradation via UV irradiation or reaction with e_{aq}^- , the C-C bonds break first to produce $\cdot CF_3$ and other free radicals, which promote further rapid degradation of the C-F bonds by e_{aq}^- . The proposed mechanism could also explain how CF_3H , $HCOO^-$ and CH_3COO^- were decomposed. $\cdot H$ could be removed from CF_3H to generate $\cdot CF_3$, so the decomposition of $\cdot CF_3$ is the key to the degradation of intermediate fluorocarbons. As mentioned above, as the chemical reaction proceeded, the level of e_{aq}^- increased, causing the decomposition of $\cdot CF_3$ to $\cdot F$ to promote the complete decomposition of CF_3H (Eq. 17). Complete fluorocarbon decomposition occurred only when e_{aq}^- was in sufficient quantities, causing fluorocarbons to accumulate in the two oxidation systems when e_{aq}^- levels were too low. At the same time, under continuous UV irradiation and the action of e_{aq}^- , $HCOO^-$ and CH_3COO^- were easily decomposed to generate $\cdot COO^-$. The above mechanism shows that an increase in the $\cdot F$ concentration could promote the decomposition of $\cdot COO^-$ into CO_2 (Eq. 18), and the equilibrium calculation showed that the proportions of $HCOO^-$ and CH_3COO^- began to decrease at 9 h and 12 h, respectively.

We compared the mechanisms of the UV/KI system proposed in this study and the UV/ SO_3^{2-} system [51]. Bentel et al. found that H/F exchange and DHEH were both present in the UV/ SO_3^{2-} system (pH=12.0). The main intermediate products generated by H/F exchange were DFA (CF_2HCOOH) and MFA (CFH_2COOH), which were then degraded into the final product CH_3COO^- . DHEH was another major pathway for TFA degradation, in which TFA was first decarboxylated to generate unstable

perfluoroalcohol (CF₃OH), and then CF₃OH was defluorinated to generate the final product CO₃²⁻ and F⁻. DHEH is the only way to degrade TFA at pH 9.5 in the UV/SO₃²⁻ system. However, the intermediate products formed before generating the final products CO₂ and F⁻ in the UV/KI system in this study were mainly HCOO⁻, CH₃COO⁻ and CF₃H (**Fig. 5**). Since DFA was not detected, no H/F exchange reaction occurred in the UV/KI system. The CH₃COO⁻ in the UV/KI system was generated by the recombination of ·COO⁻ and ·CH₃ (generated by TFA defluorination) instead of H/F exchange. The intermediate products in the UV/KI system (e.g., HCOO⁻) would not be generated during DHEH because the intermediate product of DHEH was CF₃OH, which was extremely unstable and could not be detected. The final product, CO₂, in the UV/KI system was also different from the final product, CO₃²⁻, of DHEH. Thus, the mechanisms of the two systems are different. The pathway of TFA degradation in the UV/KI system is described by the following equations.

From the discussion of the above mechanism, it can be seen that e_{aq}^- , the core of the UV/KI system, plays a key role in the decomposition of TFA and intermediates. There are two main steps in the decomposition pathways in the UV/KI system: the C-C bonds are first broken by e_{aq}^- or UV irradiation, and then the C-F bonds are attacked by the nucleophile e_{aq}^- and finally broken in the hydrolysis or photoreduction reaction. Based on the above hypothetical mechanism, the possible TFA decomposition pathways in the UV/KI system are summarized in **Fig. 6**.

Fig. 6. Possible TFA decomposition and defluorination pathways in the UV/KI system.

3.4. Effect of the iodide concentration

As discussed in section 3.1, iodide played a critical role in producing e_{aq}^- in the UV/KI system, so the iodide concentration has an important effect on the reaction. The decomposition and defluorination of TFA in the UV/KI system under different KI concentrations were studied as shown in **Fig. S9**. When the concentration of KI

1 increased from 0.025 mM to 0.2 mM, the decomposition of TFA increased from
 2 $55.9\% \pm 3.2\%$ to $90.6\% \pm 2.0\%$, and the defluorination increased from $50.5\% \pm 2.8\%$
 3 to $88.2\% \pm 1.1\%$ over 24 h. However, the decomposition of TFA began to decline
 4 when the KI concentration exceeded 0.2 mM. When the concentration of KI reached
 5 0.5 mM, the decomposition and defluorination of TFA in 24 h dropped to $34.4\% \pm$
 6 1.5% and $19.9\% \pm 1.7\%$, respectively. To clarify the effect of the KI concentration on
 7 TFA decomposition and determine a pattern, the reaction rate constants for the first 6
 8 h of TFA decomposition were associated with the KI concentration (**Fig. 7**). As the
 9 concentration of KI increased, the rates of the TFA reaction first increased and then
 10 declined. The reaction rate increased as the KI concentration increased when the KI
 11 concentration was 0.025–0.2 mM and reached a peak when the concentration of KI
 12 was 0.2 mM, which was approximately 2-fold higher than the peak at $[KI]=0.025$
 13 mM.

15
 16 **Fig. 7.** Relationship between the initial KI concentration and the apparent rate of the TFA

reaction. Reaction conditions: TFA (0.05 mM), N₂ saturation, pH (11.0), and KI concentrations of 0.025 mM, 0.05 mM, 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM and 0.5 mM.

The experiment was repeated 3 times, and the error bars indicate the standard deviation.

The aqueous iodide under UV irradiation produced a caged complex of an iodide atom and an electron (I[•], e⁻) through charge transfer (**Eqs. 23–24**), which may dissociate into e_{aq}⁻ and I[•] (**Eq. 25**). I[•] species could combine with each other to generate iodine (I₂) (**Eq. 26**), and I₂ could undergo disproportionation to generate iodide ions (I⁻), realizing the self-circulation of I[•] [55] (**Eq. 27**). A higher concentration of I[•] in the system would promote the generation of e_{aq}⁻, which is the main species that can break the C-F bonds in TFA. Therefore, TFA decomposition increased with increasing KI concentration when the KI concentration was less than 0.2 mM.

TFA decomposition declined with further increases in the KI concentration (>0.2 mM) because excess I[•] generated e_{aq}⁻ scavengers (e.g., diiodide (I₂⁻) [56] and triiodide (I₃⁻) [32, 57]) (**Eqs. 28–30**). I₂⁻ and I₃⁻ acted as oxidants to react with e_{aq}⁻ (**Eqs. 31–32**), reducing the concentration of e_{aq}⁻ in the system. In summary, more e_{aq}⁻ was produced in the reaction due to the increase in I[•] and its self-circulation when the

1 [KI] < 0.2 mM; however, the increasing contents of I_2^- and I_3^- scavenged e_{aq}^-
 2 when the [KI] > 0.2 mM.

3 The reductive decomposition of PFOA in the UV/KI system with different KI
 4 concentrations was reported by **Qu et al. [31]**, and they found that the photochemical
 5 reactivity increased with the KI concentration in the range of 0.1-0.3 mM. The peak
 6 rate was observed at a KI concentration of 0.3 mM; however, a further increase in the
 7 KI concentration resulted in a decrease in the initial decomposition rate of PFOA,
 8 which is similar to the phenomenon observed in this article.

14 As the KI concentration increased, the absorbance (A) increased, causing a
 15 decrease in the transmittance (T) in the solution (**Eq. 33**). Due to the internal filter
 16 effect, transmittance that is too low reduces the photocatalytic rate. To study the
 17 influence of this internal filtering effect, the initial absorbance at 254 nm of reaction
 18 solutions with different KI concentrations was detected (**Fig. 8**). The absorbance
 19 values of the solutions with different KI concentrations were low (<0.14 Abs).
 20 Consequently, the absorbance had a limited effect on the degradation of TFA in our
 21 system (T>70%). Therefore, the tendency depicted in **Fig. 7** was not caused by the
 22 internal filter effect, and the relevant reactions of KI at different concentrations were

the key to affecting the degradation of TFA.

$$A = \log_{10} \frac{1}{T} \quad (33)$$

The experimental results showed that the concentration of KI within a certain range played an important role in the UV/KI system. A KI concentration that was too high reduced the reaction efficiency. The optimal KI concentration in the UV/KI system was 0.2 mM for 0.05 mM TFA.

Fig. 8. UV absorption (254 nm) of TFA solutions with different initial KI concentrations.

Reaction conditions: TFA (0.05 mM), N₂ saturation, pH (11.0), and KI concentrations of 0.025 mM, 0.05 mM, 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM and 0.5 mM.

3.5. Effect of pH

The pH of the solution is also an important condition affecting the production of e_{aq}^- in the UV/KI system. The decomposition (**Fig. S10a**) and defluorination (**Fig. S10b**) of TFA in the UV/KI system under different initial pH values were examined. TFA could hardly be decomposed at pH 4.0. In addition, TFA decomposition and

defluorination were less than 11.0% and 5.0% from pH 4.0–9.0, respectively. Decomposition ($26.4\% \pm 1.6\%$) and defluorination ($16.4\% \pm 2.5\%$) were significantly increased at pH 9.0. The efficiency of TFA decomposition further increased from pH 9.0–11.0. The decomposition ($90.6\% \pm 2.0\%$) and defluorination ($88.2\% \pm 1.1\%$) of TFA in 24 h reached their peak values at pH 11.0, which were approximately 8-fold and 22-fold higher than those at pH 6.0 ($10.9\% \pm 1.6\%$ and $4.0\% \pm 0.4\%$), respectively. Then, the decomposition and defluorination efficiency of TFA began to decline as the pH further increased. The decomposition ($11.3\% \pm 0.9\%$) and defluorination ($4.6\% \pm 0.5\%$) at pH 13.0 were extremely low and were equivalent to those at pH 6.0.

Fig. 9. Rate constant of the TFA reaction at different initial pH values after 6 h. Reaction conditions: TFA (0.05 mM), KI (0.2 mM), N_2 saturation, and initial pH (4.0, 6.0, 9.0, 10.0, 11.0, 12.0 and 13.0) adjusted with $\text{NH}_4\text{Cl-NH}_3\cdot\text{H}_2\text{O}$ buffer solution. The experiment was repeated 3 times, and the error bars indicate the standard deviation.

1

2 To clarify the effect of the initial pH of the solution on TFA decomposition, the
 3 first-order kinetics simulation of TFA decomposition at different pH values for the
 4 first 6 h is shown in **Fig. 9**. Clearly, the reaction rate first increased and then
 5 decreased as the initial pH increased, reaching a peak value at pH 11.0, which was
 6 consistent with the result in **Fig. S10**. The reaction rates were very low under acidic
 7 conditions. For example, the rate constant at pH 11.0 ($k_1=0.147 \pm 0.014 \text{ h}^{-1}$) was
 8 approximately 17-fold higher than that at pH 6.0 ($k_1=0.009 \pm 0.001 \text{ h}^{-1}$). The reaction
 9 rate under strong alkali conditions (pH=13.0) was also very low ($k_1=0.014 \pm 0.002$
 10 h^{-1}).

11 As the above analysis shows, the decomposition efficiency of the UV/KI system
 12 strongly depended on pH. This phenomenon was mainly based on several reactions
 13 under acidic and alkaline conditions. First, the concentration of hydrogen ions (H^+)
 14 under acidic conditions was high, and e_{aq}^- could be scavenged rapidly via reaction
 15 with H^+ ($k_2=2.3 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$) (**Eq. 34**) [58]. Hydrogen radicals ($\text{H}\cdot$), the product of
 16 this reaction, could react with I^- to produce I_2^- under acidic conditions (**Eq. 35**). As
 17 shown in section 3.4, e_{aq}^- could be scavenged by I_2^- (**Eq. 32**). Thus, the decrease in
 18 the I^- and e_{aq}^- scavenging reactions led to a decline in the e_{aq}^- concentration.
 19 Therefore, at pH=4.0, there were almost no e_{aq}^- in the UV/KI system. Both the
 20 photolysis and reduction of TFA weakly occurred under acidic conditions, resulting in
 21 the low decomposition and defluorination of TFA (**Fig. S10**), and this phenomenon
 22 was consistent with the experimental phenomenon studied by Qu et al. [52]. Second,

1 alkaline conditions ($\text{pH} > 8.5$) [31] could promote the disproportionation of I_2 to I^- and
 2 IO_3^- (Eq. 27) for more I^- recycling and less generation of I_3^- (Eq. 30). This makes it
 3 possible to increase the yield of e_{aq}^- and reduce its scavenging reaction with I_3^- (Eq.
 4 31). This principle is consistent with the experimental results in Fig. S10a: TFA
 5 decomposition was significantly improved at pH 9.0–11.0.

6 The clearly increased decomposition of monochloroacetic acid by e_{aq}^- with
 7 increasing pH was reported by Li et al. [59]. The reductive decomposition of PFOA
 8 in the UV/KI system at different initial pH values was reported by Qu et al. [52], and
 9 they found that from pH 5.0 to 10.0, the decomposition and defluorination of PFOA
 10 by e_{aq}^- increased with increasing pH , and the rate constant at pH 10.0 was 49-fold
 11 higher than that under acidic conditions. These results were similar to the results we
 12 observed in this article from pH 4.0 to 11.0, that is, e_{aq}^- were scavenged under acidic
 13 conditions, but under alkaline conditions the concentration of e_{aq}^- increased due to the
 14 disproportionation reaction.

15 However, the efficiency of TFA decomposition began to decrease at $\text{pH} > 11.0$ and
 16 was extremely low at pH 13.0. On the basis of the mechanisms of e_{aq}^- production and
 17 TFA degradation, more OH^- would promote the generation of more I^- from I_2 during
 18 the disproportionation reaction (Eq. 27), and the analysis in section 3.4 showed that
 19 too much I^- would scavenge e_{aq}^- and reduce the decomposition efficiency. A highly
 20 alkaline environment ($\text{pH} > 12.0$) may provide excess OH^- and is therefore not the
 21 preferred pH range for the UV/KI system. The experimental results show that the
 22 initial pH of the solution is a key parameter of the UV/KI system, with strict

requirements for the initial pH range. A pH that is too low or high will affect the decomposition and defluorination of TFA. Therefore, the optimal pH is 11.0 for the UV/KI system.

4. Conclusion

(1) A novel method for the photoreductive decomposition of TFA by e_{aq}^- with KI as the mediator was developed. The results reported in this paper suggested that TFA was readily degraded by the developed process. Compared with other oxidation systems, the discussed UV/KI system consumed less energy ($E_{EO}=326.3$ kWh/m³/order) and did not need high concentrations of initiators or pollutants to achieve complete defluorination of TFA. This showed that TFA was more suitable for reduction than oxidation. The products of the UV/KI system have less environmental impact than the products of other oxidation systems.

(2) The initial TFA decomposition reaction in this study fit first-order kinetics with a 0.147 ± 0.014 h⁻¹ rate coefficient (k_{app}^{TFA}), and the half-life ($t_{0.5}$) of TFA was estimated to be 5.0 ± 0.5 h.

(3) e_{aq}^- , the critical agent degrading TFA, can be produced by the photolysis of KI through a series of reactions, so the role of UV irradiation is important. The yield of e_{aq}^- was greatly affected by the concentration of KI and the initial pH. The optimal concentration of KI for 0.05 mM TFA was 0.2 mM. The optimal initial pH of the system was 11.0.

1 (4) TFA degradation pathways to degrade TFA were proposed. In the UV/KI
2 system, two major reactions occurred with the present method: e_{aq}^- or UV irradiation
3 broke the C-C bonds first, and then e_{aq}^- enhanced the decomposition of TFA by
4 breaking the C-F bonds.

5 This study has demonstrated that e_{aq}^- attaches to and dissociates TFA via the
6 cleavage of C-F and C-C bonds, which may be a suitable method for the treatment of
7 low-concentration TFA in aquatic environments.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: