

## **Role of sonication in decomposition of Perfluorooctanoic acid (PFOA) by Sonophotocatalysis**

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**Abstract:-** The omnipresence of perfluoroalkyl acids (PFAAs) in the environment and subsequent health and environmental effects has raised a significant interest in the scientific community challenging their elimination from the environmental matrices. Accordingly, in the quest of suitable and efficient treatment processes for the decomposition of recalcitrant PFAAs the present research focused on exploring the capabilities of a combinatorial process of sonophotocatalysis, involving the synergistic effect offered by ultrasonication and photocatalysis, in degrading Perfluorooctanoic acid (PFOA), a widespread contaminant candidate of PFAAs. A decomposition efficiency of about 80% has been achieved. PFOA has been decomposed into shorter carbon chain length compounds. The combination of sonication with photocatalysis has exhibited a synergy of 75%. The role of sonication in the decomposition of PFOA has been construed as an aid in enhancing the mass transfer of the reactants and rejuvenation of the TiO<sub>2</sub> photocatalyst surface while the photocatalytic process has initiated the decomposition of PFOA by electron transfer from the perfluoroalkyl radical to the excited photocatalyst. The performance of the sonophotocatalytic treatment has been evaluated on the basis of energy requirements. Accordingly the process has demonstrated less energy requirement when compared to individual processes. The present research shows that the process of sonophotocatalytic treatment seems to offer an exciting option for the decomposition of perfluorocarboxylic acids under ambient conditions.

**Keywords:-** PFOA, decomposition, sonophotocatalysis, sonication, photocatalysis.

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### **I. INTRODUCTION**

Perfluoroalkyl acids (PFAAs) are ubiquitous in the environment due to their extensive applications as industrial surfactants, surface coating agents, firefighting foams, additives, and several other products. Because of the prevalence, bioaccumulation and toxicity concern; certain agencies and governments has been considering regulating the PFAAs. For example European Commission has prohibited the use of perfluorooctane sulfonate (PFOS) as a constituent chemical in most consumer products [1] while U.S. has banned the manufacture of PFOS [2]. The Stockholm convention has labeled PFOS as a persistent organic pollutant (POP). Recently, perfluorooctanoic acid (PFOA) has been enlisted in Contaminant Candidate List-3 by US EPA [3].

PFAAs find their way into the environment either by direct emissions or are formed indirectly due to the degradation of their precursors [4-6]. Perfluorocarboxylic acids (PFCAs) form an important class of PFAAs bearing a general chemical formula C<sub>n</sub>F<sub>2n+1</sub>COOH, the most prominent being PFOA. The major commercial applications of PFCAs is in the fluoropolymer manufacturing process as processing aid, and a plethora of industrial and consumer applications [5,6]. In addition, PFCAs are terminal degradation products from abiotic and biotic degradation of certain precursor perfluoroalkyl sulfonates. Other shorter and longer chain PFCAs are also of significant importance in the environmental pollution [7,8]. PFCAs resist various conventional treatment processes in both drinking and wastewater treatment plants [7,9,10]. The higher resistance to treatment is offered by the extremely strong carbon-fluorine bond in the molecules. Biological methods are unsuccessful to degrade PFAAs as evident by their occurrence in wastewater treatment plant effluents [11-13]. Particularly PFCAs responded to treatment by unit operations such as photochemical, sonochemical or a combination however with a wide variation in effectiveness [14-18]. The degradation pathways suggested in photochemical treatment involved electron-transfer while in sonochemical treatment degradation was achieved by pyrolytic decomposition.

Heterogeneous photocatalysis with TiO<sub>2</sub> has been shown to be effective in treating scores of organic contaminants including PFCAs. Photocatalysis is influenced by different parameters like irradiation, TiO<sub>2</sub>

loading, pH, and surface chemistry. Despite several photochemical studies on decomposition of PFAAs, sonochemical treatment methods are the only one that has been reported to achieve complete mineralization to date [17]. Nevertheless the energy requirements by different treatment methods as compared by Lin et al [18] shows that photolysis and photocatalysis requires more energy when compared to sonication or photolysis with persulfate. Sonication-assisted photocatalysis requires less energy along with alkaline ozonation treatment especially in the presence of H<sub>2</sub>O<sub>2</sub>. This is because combinatorial processes exhibit synergy [19-21]. Due to this reason, combination of treatment techniques has been successfully applied for the treatment of various pollutants including PFOA [15, 19-21].

The previous report on sonication-assisted photocatalytic treatment of PFOA reports 64% decomposition efficiency where sonication with a frequency of 40 kHz was applied along with photocatalysis with TiO<sub>2</sub> for first half an hour of the treatment beyond which only photocatalytic treatment was continued [15]. The role of sonication in the sonication-assisted photocatalysis was understood as an aid for the physical dispersion of TiO<sub>2</sub> and ease mass transfer by rejuvenating the surface of TiO<sub>2</sub>. A detailed decomposition mechanism of PFOA by photocatalysis with TiO<sub>2</sub> under acidic medium was elaborated which shows that the decomposition is a cyclic process involving ionization, electron transfer, decarboxylation and oxidation into shorter chain compounds [16].

Combination of different advanced oxidation processes (AOPs) has exhibited efficiency in environmental detoxification. The present study explores the potential of sonophotocatalysis in the decomposition of PFOA. Sonophotocatalysis engross simultaneous use of ultrasound (US) and heterogeneous photocatalysis. The decomposition kinetics of PFOA in water under low frequency sonolysis or photocatalysis with TiO<sub>2</sub> (UV+TiO<sub>2</sub>), employed either separately or in combination (US+UV+TiO<sub>2</sub>) was compared. The main reaction intermediates were also identified and monitored during the decomposition of target PFOA, in order to identify reaction pathway eventually prevailing under different experimental conditions. The synergistic effects of the combination of US and photocatalysis were observed in terms of energy consumption also. These aspects might assist in detailed understanding of the advanced processes towards decomposition of PFOA.

## II. MATERIALS AND METHODS

### Chemicals

Perfluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), and perfluoropropanoic acid (PFPA) were purchased from Sigma Aldrich (USA) and the purity of all the chemicals was > 96%. LC-MS grade methanol was obtained from J. T. Baker. Fluoride standard (99.99%) was from High Purity Standards (USA) and acetic acid from Acros, USA. Ethanol (95%) was obtained from You-He in Taiwan. All chemicals were used without any further purification. Powdered titanium dioxide was purchased from Riedel-de Haën (Germany) with measured Brunauer-Emmett-Teller (BET) surface area of 10.30 m<sup>2</sup> g<sup>-1</sup>, particle diameter of 100-200 nm, and energy band gap of 3.14 eV. Milli-Q (deionized, DI) water was prepared by Millipore with conductance of 18.2 MΩ cm at 25 °C was used in all the experiments.

### Experimental Procedure

Experimental setup of sonophotocatalysis used in the present study is similar to the one described in our previous publication [15]. The reaction solutions contained 50 mg L<sup>-1</sup> (120 μM) (unless otherwise indicated) initial concentration of the PFOA in the DI water. A 50 mg L<sup>-1</sup> (120 μM) initial concentration was used in the experiments in order to clearly quantify the intermediates and study the decomposition mechanism although this amount is not readily seen in the environmental matrices [7-8, 11- 13]. The solution was poured into a 3-L glass reactor into which 0.66 g L<sup>-1</sup> of TiO<sub>2</sub> was added, and oxygen gas (purity 99.99%) was bubbled at a flow rate of 140 mL min<sup>-1</sup>. TiO<sub>2</sub> loading of 0.66 g L<sup>-1</sup> was used in our study because a higher efficiency was achieved during photocatalysis in comparison to TiO<sub>2</sub> loading of 0.33 and 2 g L<sup>-1</sup> [15]. The whole mixture was stirred in the dark condition for 30 min before UV-irradiation to attain adsorption-desorption equilibrium for PFOA, TiO<sub>2</sub>, and oxygen. The solutions were then irradiated with a 16W (254 nm) low-pressure mercury UV-lamp (Phillips) housed in a single walled quartz tube. The light intensity was 0.45mWcm<sup>-2</sup> at the outer surface of the quartz sleeve measured with a UVP Multi-Sense MS-100 optical radiometer. Simultaneously ultrasonication was employed with the help of a sonication probe. The reactor vessel has provision for inserting the sonication probe with frequency of 40 kHz and 500 W power. The temperature was controlled at 25 ± 1 °C through circulating water bath and all the experiments were carried out at atmospheric pressure. The reaction solution was constantly stirred with magnetic stirrer while experimentation and hence was placed on a magnetic stirrer. The gaseous products were not monitored in the present study. Aliquots of sample were taken at the desired time intervals and filtered through 0.22 μm nylon filters to remove the TiO<sub>2</sub> and stored at 4 °C until analysis.

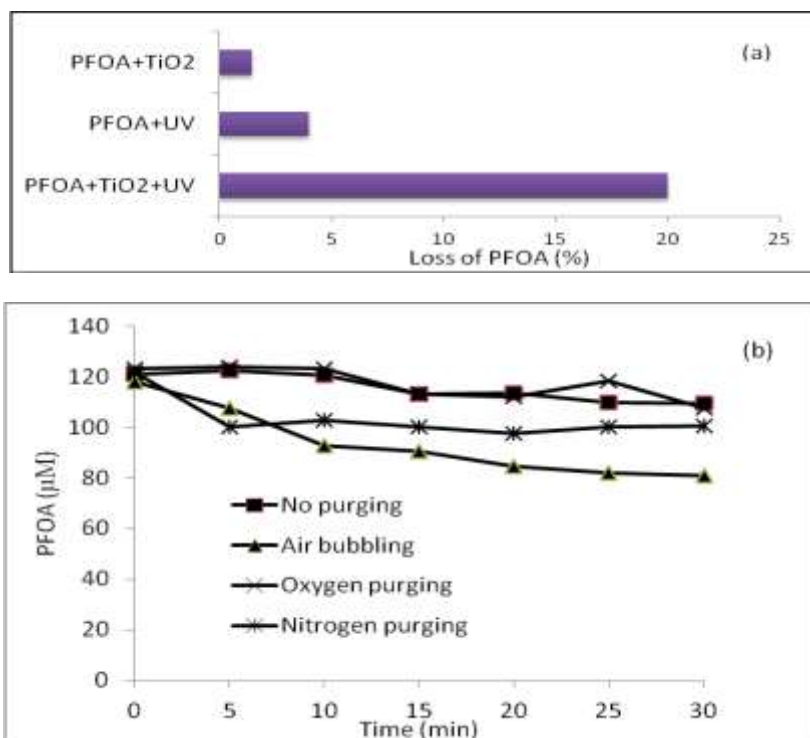
### Analytical Procedures

Sample aliquots were filtered with 0.22  $\mu\text{m}$  Chrom Tech nylon syringe filters, and the concentrations were measured using LCMS/MS procedures (detailed in our previous papers [9, 16]). In brief, 20  $\mu\text{L}$  of sample was injected into an Agilent 1200 module (Agilent, Palo Alto, CA, USA) equipped with a ZORBAX Eclipse XDB-C18 column (150 $\times$ 4.6 mm, 5  $\mu\text{m}$  pore size). A binary gradient with a flow rate of 1.0  $\text{mL min}^{-1}$  was maintained. The elution program was started with 63% of water containing 1 mM of ammonium acetate, increased to 95% of methanol containing 1 mM of ammonium acetate by 4.8 min, and finally decreased to 37%. The total elution time was 7 min, after which all compounds had been separated and eluted. Mass spectrometric measurements were accomplished on the Applied Biosystems Sciex API 4000 (Foster City, CA, USA) equipped with an electrospray ionization interface and placed in negative ion mode. The ions were acquired in multiple reaction monitoring mode with a dwell time of  $\pm 30$  ms of retention time and with a unit mass resolution on both mass analyzers. Mass spectrometric parameters were set at the following levels: ion spray voltage  $-4.5$  kV; curtain gas, nebulizer gas, turbo gas at 10  $\text{L h}^{-1}$ , 50  $\text{L h}^{-1}$  and 40  $\text{L h}^{-1}$  respectively; heated capillary temperature 500  $^{\circ}\text{C}$ ; collisionally activated dissociation 5. Quantification was based on an external calibration curve in a linear range spanning from 0.1 to 100  $\mu\text{g L}^{-1}$ .

### III. RESULTS AND DISCUSSION

#### Sonolysis, photocatalysis and sonophotocatalysis of PFOA

Control experiments on PFOA in DI water were performed (Fig 1) in the dark and under UV-irradiation either with or without  $\text{TiO}_2$ . Almost no PFOA was lost ( $<1\%$ ) during control experiments under dark condition after a period of 8h. Also adsorption of PFOA onto  $\text{TiO}_2$  was insignificant suggesting that the stereochemical configuration of PFOA is unsuitable for chelating with  $\text{TiO}_2$ . The loss of PFOA was only 4% under UV-irradiation and 20% during photocatalysis. Sonication control experiments were also performed on 50  $\text{mg/L}$  initial concentration of PFOA and the results for a period of 30 min are shown in Fig 1b. Sonication without any air bubbling, with air bubbling, oxygen and nitrogen purging were observed. More or less the results are not much varied due to purging the difference in removal efficiency being not more than 10%. Comparative to no purging, air bubbling in to the reactor seems to give better results. The present study was aimed to observe the combinatorial effect of sonication and photocatalysis together on decomposition of PFOA and hence oxygen purging was used in further studies.



**Fig. 1.** Decomposition of 120  $\mu\text{M}$  of PFOA during control experiments (a) for photocatalysis (b) sonication

PFOA was decomposed by sonolysis, photocatalysis and combined use of sonication and photocatalysis (called as sonophotocatalysis) and the results for a period of 4h experimentation are shown in Fig. 2. Sonication could decompose 21% of initial PFOA. It can be seen from Fig 1b that the decomposition of PFOA with nitrogen purging is slightly higher than that of air or oxygen bubbling. In fact bubbling of oxygen

gas during sonication should have enhanced the production of hydroxyl radicals. If hydroxyl radicals were instrumental in the decomposition PFOA the results should indicate higher removal percentage when oxygen gas was purged compared to nitrogen. The present result complements the findings that the decomposition of PFOA by sonication seems to be achieved by the cleaving of the C-C bonds or C-F bonds rather than by hydroxyl radical attack [14, 17].

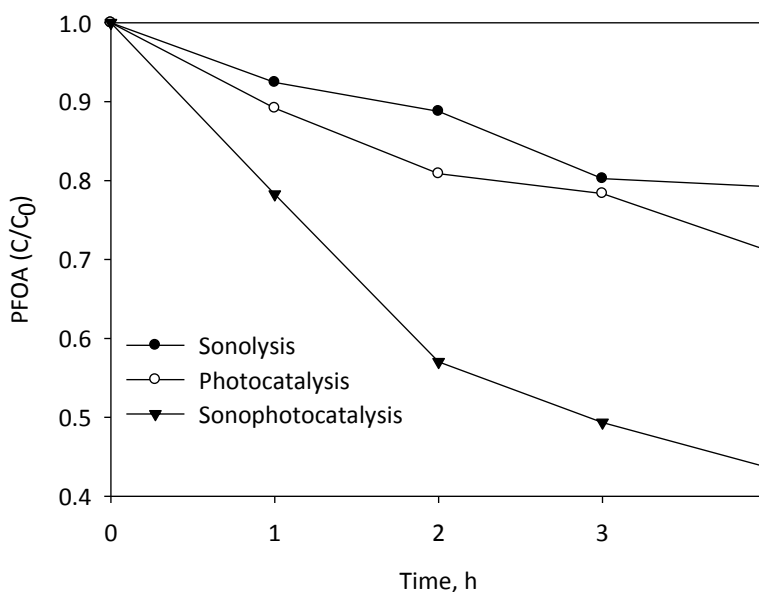


Fig. 2. Decomposition of 120 µM of PFOA by sonolysis, photocatalysis and sonophotocatalysis

Photocatalysis could decompose PFOA with slightly better efficiency of 29% within 4 h. It was noted that the decomposition of PFOA proceeds with electron transfer from perfluoroalkyl radical to the excited TiO<sub>2</sub> upon irradiation [16]. However when sonolysis and photocatalysis were combined, the decomposition efficiency of PFOA has been doubled (57%). Therefore, combined usage of sonolysis with photocatalysis seems to be advantageous. Previously when sonication was used only for 30 min in conjunction with photocatalysis after which sonication was stopped continuing photocatalysis, 65% of PFOA was decomposed after 7 h [15]. The improved decomposition efficiencies by the combinatorial processes for the treatment of various compounds have been reported [19-21]. Here, sonolysis coupled with photocatalysis for the whole experimental period has been demonstrated to be beneficial.

#### Kinetics and synergistic effect of sonophotocatalysis

The kinetics of the three different kinds of processes was fitted to pseudo-first order kinetic equation (Eq. 1).

$$\ln \frac{C}{C_0} = k_a t \quad (1)$$

Where  $k_a$  is apparent reaction rate constant ( $k_{US}$  is apparent rate constant of sonolysis,  $k_{UV+TiO_2}$  is apparent rate constant of photocatalysis, and  $k_{US+UV+TiO_2}$  is apparent rate constant of sonophotocatalysis),  $C_0$  and  $C$  are initial and final concentrations of PFOA respectively. If the data of Fig. 2 are plotted in the form of Eq. (1), straight lines passing through the origin fit the experimental data reasonably well, thus suggesting pseudo-first order kinetics. The kinetic rate constants and the corresponding regression constants are shown in Table 1. The apparent reaction rate constant values are in the order of  $k_{UV+TiO_2} < k_{US} < k_{US+UV+TiO_2}$ .

It is also interesting to note that a synergistic effect appears to exist between ultrasound and ultraviolet irradiation in the presence of TiO<sub>2</sub> since rate constants of the combined process is approximately 2.4 times greater than the sum of rate constants of individual processes ( $k_{US+UV+TiO_2} > (k_{US} + k_{UV+TiO_2})$ ). The synergy was quantified as the normalized difference between the rate constants obtained under sonophotocatalysis and the sum of the individual processes (Eq. (2)).

$$\text{Synergy} = 100 \times \frac{k_{US+UV+TiO_2} - (k_{US} + k_{UV+TiO_2})}{k_{US+UV+TiO_2}} \quad (2)$$

Synergy of the sonophotocatalysis is referred in % (Table 1).

**Table 1.** Pseudo first order rate constants of PFOA decomposition and synergy of sonophotocatalysis

Compound	Process	Decomposition (%)	Apparent rate constant ( $k_a$ )	R <sup>2</sup>	Synergy <sup>a</sup>
PFOA	Sonolysis	21	0.0621	0.9388	-
PFOA	Photocatalysis	29	0.0684	0.9589	-
PFOA <sup>b</sup>	sonophotocatalysis	79	0.3845	0.9839	75
PFOA	sonophotocatalysis	57	0.2266	0.9591	58

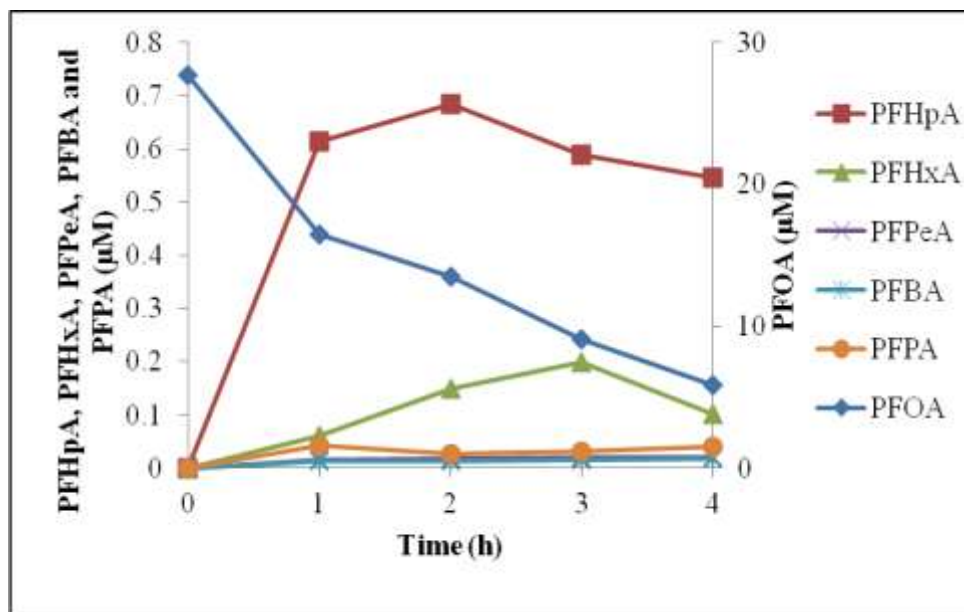
<sup>a</sup>synergy calculated based on Eq. 2

<sup>b</sup>Initial concentration of PFOA is 24  $\mu$ M, in all other cases it is 120  $\mu$ M

The synergy of the combined process was 58% that is considerably high. Therefore the combination of the individual sonolysis and photocatalysis seems to have beneficial effect. The synergistic effect of sonophotocatalysis may be attributed to several reasons in general such as: (1) increased production of hydroxyl radicals, (2) enhanced mass transfer of organics between the liquid bulk phase and the catalyst surface [20], (3) excitation of catalyst by ultrasound-induced luminescence, (4) increased catalytic activity due to ultrasound-facilitated de-aggregation of TiO<sub>2</sub> particles, (5) increased surface area of TiO<sub>2</sub> due to their de-aggregation, and (6) replenishment of fluid film near the catalyst surface [15, 22-23]. All the mentioned possibilities are the probable beneficial actions of ultrasound on photocatalysis in sonophotocatalysis. Photocatalysis also might have some action on sonolysis by improving the organic degradation due to TiO<sub>2</sub> particles, providing extra nuclei for bubble formation [24].

The results of the present study lead us to construe an anticipated PFOA degradative mechanism (Fig. 5). The mechanism of decomposition of PFOA by sonophotocatalysis seems to be similar to that of sonication-assisted photocatalysis. In the case of sonophotocatalytic decomposition of PFOA, although both the individual sonication and photocatalysis processes would have decomposed the target contaminant, based on the better decomposition efficiency achieved due to photocatalysis than sonolysis alone, and synergistic effect of combinatorial process, the mechanism of PFOA decomposition through sonophotocatalytic treatment was interpreted as follows. The PFOA decomposition mechanism was initiated with the excitation of TiO<sub>2</sub> by photons supplied by 254 nm UV lamp [12, 15]. The excited TiO<sub>2</sub> takes away electron from the ionized PFOA generating peroxy perfluoroalkyl radical. The peroxy perfluoroalkyl radical is very unstable and thus loses carbon dioxide through Kolbe-electrolysis process generating peralkyl radicals [16]. The generated perfluoroalkyl radicals are then oxidized to shorter carbon chain length compound with one less carbon and two less fluorine atoms generating PFHpA [16]. Since the pH of the solutions was acidic to neutral and at that pH range superoxide radicals are predominant, the oxidation of peralkyl radical was presumed to be achieved by superoxide radicals during sonophotocatalysis [15] or even by the hydroxyl radicals generated due to the sonication [14-15]. This time along with PFOA, even the shorter carbon chain length compounds also undergo similar process until mineralization to final products. Therefore it can be summarized that the decomposition of PFOA occurs by following four dominant steps viz. ionization, electron transfer, decarboxylation, and oxidation of perfluoroalkyl radicals [16]. The decomposition pathway of PFOA by sonophotocatalysis has been depicted in Fig. 5, wherein blue arrows indicate the dominant decomposition path followed by the target contaminant undergoing photocatalytic decomposition. The red arrows in the background represent the augmentation of PFOA decomposition by sonication in the combinatorial process. The role of the sonication at each step has been identified and presented in the dialog boxes at the corresponding locations. Albeit role of sonication throughout the sonophotocatalysis process cannot be differentiated with any particular individual steps, an attempt has been made of what might be helpful at the particular decomposition step. In view of that, sonication might have enhanced the excitation of TiO<sub>2</sub> due to ultrasound-induced luminescence along with UV rays at the first step. Due to the charge specific behavior, it is possible for the TiO<sub>2</sub> particles to agglomerate thereby limiting the available surface active sites for the decomposition [15]. Sonication will facilitate proper dispersion of the TiO<sub>2</sub> particles during the treatment process and accelerate the decomposition reaction at the electron transfer stage. Further sonication will enhance the available surface area of TiO<sub>2</sub> due to de-agglomeration consequently the catalyst action will be improved. Throughout the sonophotocatalytic treatment process, sonication facilitates mass transfer of reactants and refreshes the fluid film on the TiO<sub>2</sub> surface. Sonication produces hydroxyl radicals due to pyrolysis of water molecules [14, 22-23] and the then produced hydroxyl radicals may also contribute to the oxidation of the perfluoroalkyl radicals to their successive by products [15, 18]. Meanwhile sonication could have also achieved decomposition of PFOA by pyrolytic decomposition

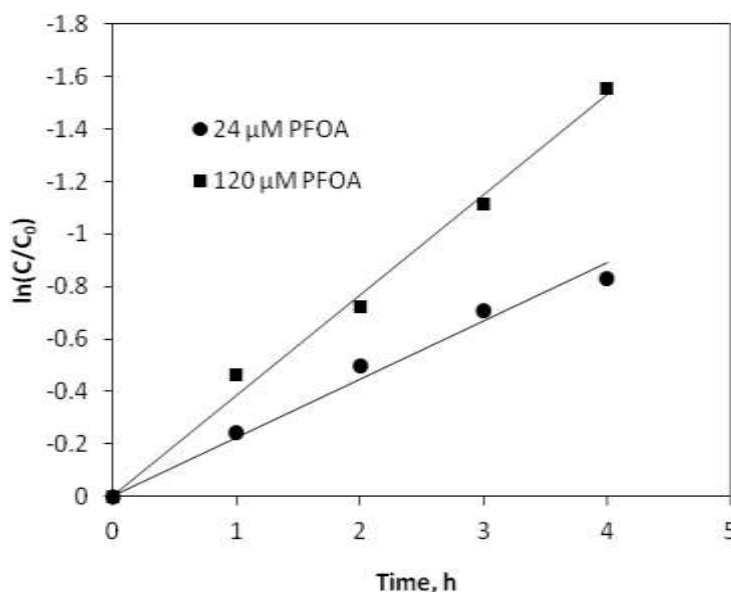
however this could be a meager process. Based on the synergistic effect, the function of sonication is to enhance the mass transfer of the reactants and also replenishment of the  $\text{TiO}_2$  surface thereby enhancing the decomposition. Since combination of sonication and photocatalysis with  $\text{TiO}_2$  as photocatalyst is beneficial in terms of both decomposition and synergistic effect, sonophotocatalysis seems to be a viable alternative technology to treat PFOA.



**Fig. 4.** Sonophotocatalytic decomposition products of 40 μM PFOA

**Effect of initial concentration of PFOA on sonophotocatalytic treatment**

Two different initial concentrations of PFOA (24 μM and 120 μM) are compared to see the effect of initial PFOA concentration on sonophotocatalysis. The reaction kinetics of both initial concentrations follow pseudo-first order rate (Fig. 3). With five times increase in the initial concentration, the rate constant decreased 1.7 times from 0.384 to 0.226 with corresponding decomposition efficiencies of 79% and 57% respectively. There is difference in synergistic effect (Table 1) that decreased from 75% to 58% with increase in initial PFOA concentration from 24 μM to 120 μM. Since the concentration of PFOA in real samples would be less than the concentration used in this study, we anticipate that sonophotocatalysis will be a challenging treatment technique to decompose PFOA.



**Fig. 3.** Pseudo-first order Kinetics of sonophotocatalytic decomposition of PFOA

### Anticipated PFOA Decomposition mechanism

Decomposition products of PFOA during sonophotocatalytic treatment were observed. The monitored byproducts are shorter length carbon chain compounds than PFOA including PFHpA, PFHxA, PFPeA, PFBA, and PFPA. With the disappearance of PFOA, the concentrations of byproducts started appearing with decreasing concentrations of decreasing carbon chain lengths in our study. By the end of 4 h treatment of 40  $\mu\text{M}$  of initial PFOA, 80% decomposition was achieved. It can be observed from Fig 4 that the concentration of PFHpA rose until 2 h and then started disappearing, after which the concentration of PFHxA reached maximum by 3 h and then started reducing. The concentrations of other intermediate products are however less.

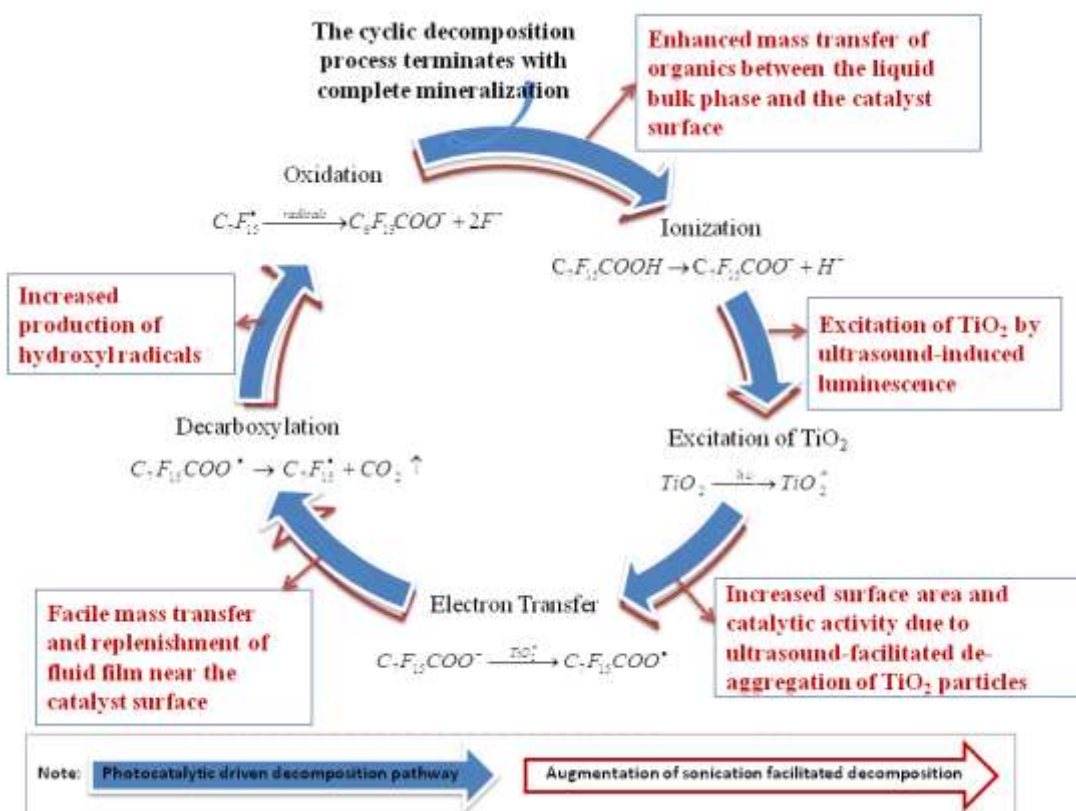


Fig. 5. Schematic of sonophotocatalytic decomposition mechanism of PFOA (blue arrows indicate photocatalytic driven decomposition pathway and the red background arrows indicate the augmentation of sonication facilitated decomposition of PFOA)

### Energy efficiency of sonophotocatalytic treatment

The sonophotocatalytic treatment was evaluated on the basis of energy requirements. The energy requirements were calculated on the basis of equation 2 and the results along with half-lives were presented in Table 2. Comparison of energy requirements with other studies of sonication and photocatalysis was performed.

$$\frac{E \times 0.06 \times t_{1/2}}{[PFOA_0] / 2 \times V} \quad (2)$$

Where E is input energy in W, 0.06 is the W-to-kJ/min conversion factor, and  $t_{1/2}$  is the half-life in min,  $[PFOA_0]$  is the initial PFOA concentration in  $\mu\text{M}$ , and V is the volume of the reactor in liters.

Table 2. Energy requirements for sonophotocatalytic and other treatment processes for the decomposition of PFOA.

It can be observed from the Table 2 that sonophotocatalysis of PFOA requires less energy (31 kJ/ $\mu\text{M}$ ) when compared to any other energy requirements mentioned in the table. Any direct comparison would not be possible because of different experimental conditions. However, a preliminary idea can be had from the above comparisons. The energy consumption decreased from 3720 kJ to 2234 kJ with decrease in initial concentration of PFOA from 120  $\mu\text{M}$  to 24  $\mu\text{M}$  while the energy required raised from 31 to 93 kJ/ $\mu\text{M}$  as in case of sonolysis studies by vecitis et al [17]. Since occurrence of these contaminants will be in trace quantities than the studied concentrations in this study, it can be observed that only less energy is possibly required to treat such wastewaters. The energy requirement by direct photolysis is much higher followed by sonolysis (in this study).

If we have to compare sonolysis of this study and that of Vecitis et al [17], obviously the other study shows superior results. This could be due to difference in experimental conditions such as volume of the treatment solution, initial concentration of the solution, energy applied, etc. Sonication-assisted photocatalysis has indeed consumed and requires less energy compared to sonophotocatalysis but the half-life time is longer. Comprehensively it can be seen that sonophotocatalysis offers a better option for the treatment of PFOA in terms of removal efficiency, energy requirement and ambient experimental conditions.

**Table 2.** Energy requirements for sonophotocatalytic and other treatment processes for the decomposition of PFOA

Technology [reference]	[PFOA <sub>0</sub> ] μM	Power (W)	Vol (L)	K <sub>a</sub>	t <sub>1/2</sub> (min)	Energy (kJ/μM)
Sonophotocatalysis [Present study]	120	16 & 500	3	0.2266h <sup>-1</sup>	180	31(3720kJ)
Sonophotocatalysis [Present study]	24	16 & 500	3	0.3845h <sup>-1</sup>	108	93(2234kJ)
Sonolysis [Present study]	120	500	3	0.0621	660	110(13200kJ)
Photocatalysis [Present study]	120	16	3	0.0684	607	3.24(388.8kJ)
Sonication-assisted photocatalysis [15]	120	16 & 500	3	0.1309	288	9.8(588kJ)
Direct Photolysis [12]	1350	200	0.022	0.69 d <sup>-1</sup>	1440	1163(1570050kJ)
Sonolysis [17]	20	150	0.6	0.018min <sup>-1</sup>	39	67(1340kJ)
Sonolysis [17]	200nM	150	0.6	0.047min <sup>-1</sup>	15	1300(260kJ)

#### IV. CONCLUSIONS

The decomposition of PFOA has been achieved by sonophotocatalysis with TiO<sub>2</sub> as photocatalyst. The decomposition efficiency was as high as 80% within a period of 4 h of treatment. The combination of ultrasonication with photocatalysis has demonstrated an improved efficiency without need to alter the pH of the solutions. The synergy of the sonophotocatalytic process was found to range from 58-75% when the initial PFOA concentration varied from 24-120 μM. The sonophotocatalytic treatment has demonstrated less energy requirement than individual sonolytic and photocatalytic treatment processes. The sonophotocatalytic process was found to decompose the PFOA into shorter chain length carbon compounds. The mechanism of PFOA decomposition started from the electron transfer to the excited photocatalyst after which photo-kolbe like process continued resulting in the decomposition of PFOA into shorter carbon chain length compounds. Sonolysis augmented the photocatalytic decomposition of PFOA by predominantly enhancing the mass transfer of the reactants and also replenishment of the TiO<sub>2</sub> surface. The process of sonophotocatalytic treatment seems to offer an exciting option for the decomposition of perfluorocarboxylic acids under ambient conditions and with less energy requirements.

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