Application of several advanced oxidation processes for the destruction of terephthalic acid (TPA)

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Abstract

Terephthalic acid (TPA) is widely applied as a raw material in making polyester fiber, polyethylene terephthalate (PET) bottles, polyester films, etc. TPA is toxic and is known to act as endocrine disruptor. TPA wastewater is traditionally treated by biological process and this study aims to evaluate the effectiveness of several advanced oxidation processes on TPA removal. The oxidation processes studied were: $UV–TiO_2$, $UV–H_2O_2$, $UV–H_2O_2–Fe$, O_3, O_3/Fe, O_3/TiO_2, $UV–O_3–H_2O_2–Fe$ and $UV–O_3–H_2O_2–Fe–TiO_2$. The results indicate that the time required for the complete destruction of 50 ppm of TPA can be minimized from 10 h using $UV–TiO_2$ system, to less than 10 min by $UV–H_2O_2–Fe–O_3$ system. Some of the likely organic intermediates identified during TPA destruction include, benzoquinone, benzene, maleic acid and oxalic acid. Possible destruction pathway of TPA has been proposed. TPA degradation by various systems was also analyzed based on the reaction kinetics and operating costs.
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Keywords: Terephthalic acid; Advanced oxidation process; Photofenton oxidation; Catalytic ozonation; Titanium dioxide (TiO_2)

1. Introduction

The *para* form of phthalic acid, known as terephthalic acid (1,4-benzenecarboxylic acid) (TPA) has been used mainly as a raw material of polyester fiber, but lately it has been applied for various uses such as non-fiber field, PET-bottle, PET-film and engineering plastics and as poultry feed additives. Phthalic acid derivatives are also widely used to make dyes, medicines, synthetic perfumes, pesticides, and other chemical compounds.

On the other hand, due to its extensive applications, large scale production and its chemical characteristics, this refractory organic material and its associated class of organics have become ubiquitous environmental pollutants; they have been found in sediments, natural waters, soils, and aquatic organisms [1,2]. Some of them are suspected mutagens and carcinogens [3,4] and have been added to the list of priority pollutants by the US Environmental Protection Agency [5]. Known as endocrine-disrupting chemicals, selective phthalates may also interfere with the reproductive system and normal embryonic development of animals and humans [6–8].

So far, studies on the destruction of TPA have been by biological means, using microorganisms [8–17]. It has been noted in these studies that the biodegradation of TPA and associated phthalate materials were not very effective. It is slow, activity of the biomass is lost during biodegradation, strongly rate limiting and inhibition of microorganisms by TPA and in the presence of compounds like acetate and benzoate.

Recently, advanced oxidation processes such as photocatalytic oxidation ($UV–TiO_2$), ozonation, fenton oxidation ($H_2O_2–Fe$) have gained popularity for effective organic destruction from wastewater [18–21]. These processes work on the principle of generation of highly reactive oxidizing free radicals, which oxidizes the organic contaminants, either completely thereby mineralizing the contaminants or converting it into less harmful or short chain compounds, which can then be treated biologically. Unlike other conventional treatment methods like coagulation, where the waste is merely converted from one form to another, advanced oxidation process allows these hazardous organic materials to be effectively degraded. Also, it is operated at ambient temperature. There have been some studies on biological degradation of TPA, as mentioned above, but very limited studies have been carried out on TPA removal by oxidation process [22]. Park et al. [22] applied

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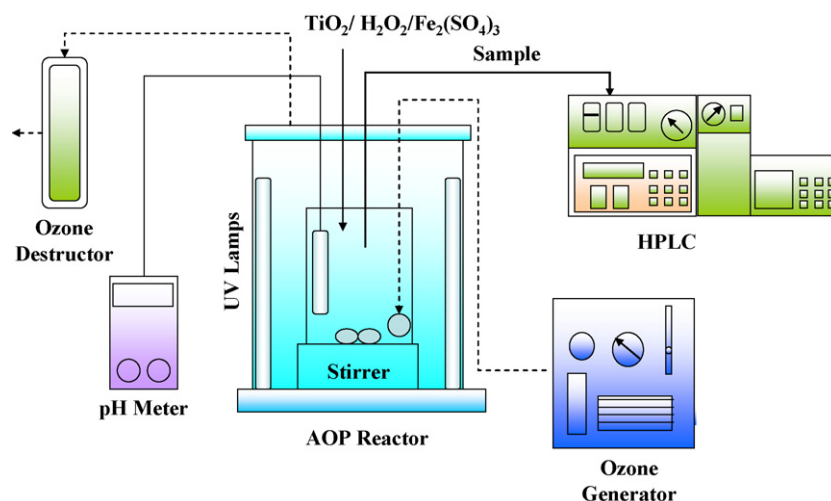*E-mail address:* ismoon@sunchon.ac.kr (I.S. Moon).

Fig. 1. Schematic of advanced oxidation system.

supercritical water oxidation process for TPA wastewater treatment.

The similarity between the mechanisms of destruction in the case of different advanced oxidation techniques indicates that appropriate combination of these oxidation systems could give better performance, as compared to individual processes. Moreover, some of the drawbacks of the individual techniques can be eliminated by some characteristics of other techniques. The efficacy of these processes depends strongly on the rate of generation of the free radicals and their utilization by organic molecules.

The objective of this study was to evaluate TPA removal performance by various advanced oxidation processes such as photocatalytic oxidation (UV–TiO$_2$), photochemical oxidation (UV–H$_2$O$_2$), photofenton oxidation (UV–H$_2$O$_2$–Fe), ozone oxidation (O$_3$), catalytic ozonation (O$_3$–TiO$_2$/Fe) and appropriate combination of these individual techniques.

2. Experimental

The TPA (98% purity) used in this study was purchased from Sigma Aldrich Co., Ltd. (Korea). TPA aqueous solutions were prepared with ultra pure water from reverse osmosis treatment, under alkaline condition. The pH of the prepared solution with 250 mg/L of TPA was 10. Hydrogen peroxide (H$_2$O$_2$, 30–35%) was purchased from Daejung Chemicals & Metals Co. Ltd., Korea and ferric sulfate (Fe$_2$(SO$_4$)$_3$) was from Shinyo Pure Chemicals Co. Ltd., Japan. P-25 TiO$_2$ particles (Degussa, Germany) were used as photocatalyst. Average diameter, BET surface area, and density of TiO$_2$ particles were 20 ± 5 nm, 50 ± 15 m^2/g, and 3.89 g/cm^3 at 20 °C, respectively.

The TiO$_2$ suspension (1 L) containing TPA was irradiated in the photocatalytic reactor using six quartz tube mercury vapor lamps (TUV 36 SP T5, Philips, USA) with a power input of 40 W each. The irradiation intensity was 144 μW/cm^2 and the wavelength was 253.7 nm. Constant amount of ozone (2.4 mg/h) was introduced, when required.

The amount of TPA in the aqueous solution was measured by high-performance liquid chromatography HPLC (Shimadzu LC-10 VP, Japan) equipped with a UV detector (Shimadzu SPD-10A VP) and a Shim-pack CLC-ODS column. The elution was monitored at 240 nm. The elutant used was a solvent mixture of 1% acetic acid and acetonitrile (85:15, v/v). The flow rate of the mobile phase was 1 mL/min. The TiO$_2$ photocatalyst was removed from the solution by filtration, and the resulting solution was analyzed with HPLC. For detailed analysis of intermediate products, a GC/MS (Shimadzu QP2010, Japan) equipped with HP-5 capillary column (60 m × 0.25 mm i.d) was used. Each peak obtained from GC–MS chromatogram, was identified by comparing with GC–MS WILEY7 library data. Some of the possible intermediate compounds were also tested for its presence using HPLC analysis. All samples were analyzed as per the standard procedures [23]. The schematic diagram of the overall treatment process is shown in Fig. 1.

3. Results and discussion

3.1. Photocatalytic oxidation (UV–TiO$_2$)

Fig. 2 shows the performance of photocatalytic oxidation in TPA removal, at different operating conditions. Initially, by keeping the parameters such as the TiO$_2$ and organic concentrations same, initial solution pH was varied. It was found that near neutral pH was favorable and high alkaline condition decreased the efficiency of organic removal (Fig. 2a). With the initial solution pH of 8 and TiO$_2$ concentration of 1000 mg/L, complete degradation of target material (TPA) for 10, 30 and 50 mg/L was achieved at 4, 7 and 10 h, respectively (Fig. 2c). More time was needed (>10 h) for complete degradation, when the initial organic concentration was further increased. Assuming 50 mg/L as the middle value, initial concentration of TPA was varied five times lower and five times higher (10–250 mg/L), in order to test the effect of organic concentration. The effect of TiO$_2$ amount was evaluated as shown in Fig. 2b. At a specific
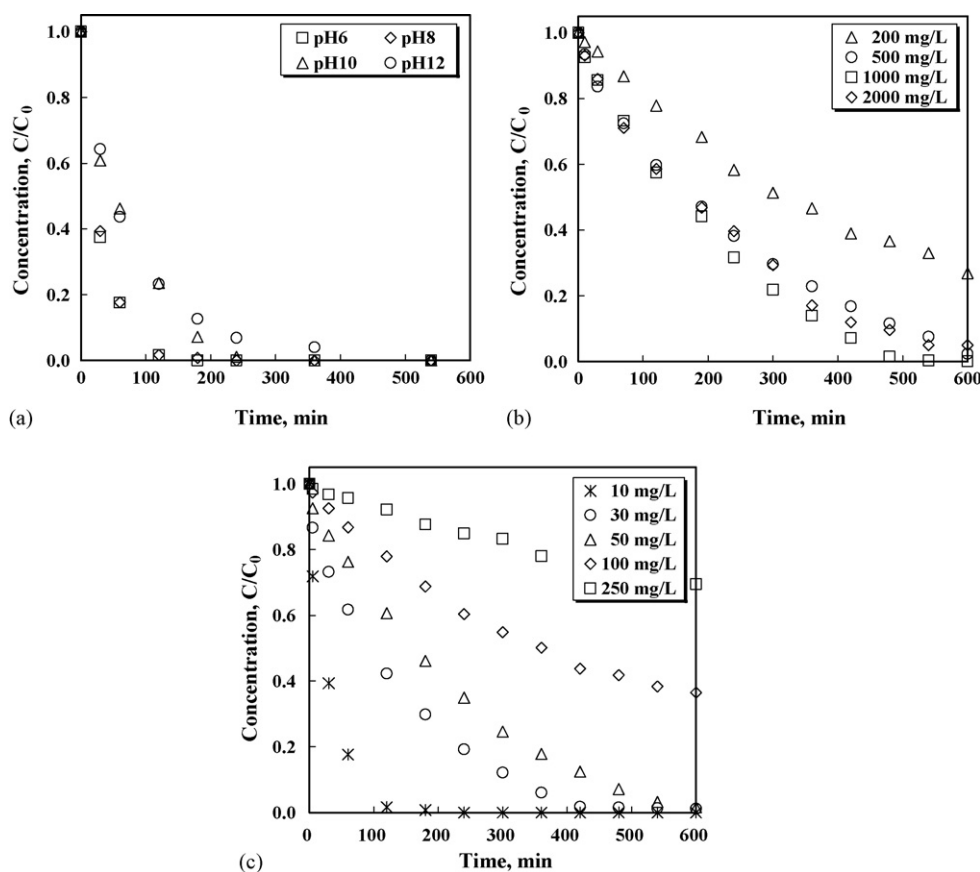
Fig. 2. TPA degradation performance by photocatalytic oxidation (UV–TiO$_2$) process (a) at different solution pH (TPA concentration 10 mg/L), (b) with different TiO$_2$ concentration (TPA concentration 50 mg/L, pH 8) and (c) at different TPA concentration (pH 8, TiO$_2$ concentration 1000 mg/L).

light intensity, increase in TiO$_2$ concentration beyond a certain amount (1000 mg/L) was found to decrease the photocatalytic efficiency. After 10 h of reaction, TPA removal was lower at 2000 mg/L TiO$_2$ compared to the 1000 mg/L. TiO$_2$ is a fine white powder which forms a milky white solution when dispersed in water (1000 mg/L = 5000 NTU turbidity). So, when the catalyst TiO$_2$ powders are suspended in a stirred solution, the amount of TiO$_2$ would affect the passage of light through the solution and hence will affect the degree of absorption of light by the catalyst surface.

3.2. Photochemical oxidation and photofenton oxidation (UV–H$_2$O$_2$ and UV–H$_2$O$_2$–Fe)

UV–H$_2$O$_2$ and UV–H$_2$O$_2$–Fe systems have known to be very effective in decolorization and mineralization of textile dye wastewater [24–26]. UV/H$_2$O$_2$ systems generate hydroxyl radicals (OH$^\bullet$) which are highly powerful oxidizing species. The OH$^\bullet$ yield can be further increased by addition of Fe(II) species, which acts as a catalyst. Fig. 3 shows the TPA removal performance by UV–H$_2$O$_2$ and UV–H$_2$O$_2$–Fe systems. In the range of pH 6–8, no significant difference in TPA removal efficiency was observed in UV–H$_2$O$_2$ system (Fig. 3a). It is generally agreed that the performance is more efficient at strongly acidic medium (<pH 4). However, in the present study using TPA, operation at very low pH would not be possible as TPA becomes insolu-

ble at strong acidic pH. Operation at very high pH is also not recommended as at high pH range, H$_2$O$_2$ undergoes photodecomposition to water and oxygen rather than forming hydroxyl radical [27–29]. H$_2$O$_2$ concentration had a positive effect on the organic destruction; yet, increase in H$_2$O$_2$ concentration above a certain amount was not beneficial, as there was no improvement in the TPA destruction efficiency (Fig. 3b). The results indicate that the optimum amount of H$_2$O$_2$ appears to be 3 mM, for the destruction of 50 mg/L TPA. At higher H$_2$O$_2$ concentrations, H$_2$O$_2$ acts as a hydroxyl radical quencher, consequently lowering hydroxyl radical concentration [27–29].

The degradation performance of TPA rapidly increased with the addition of Fe salt (Fe$_2$(SO$_4$)$_3$) to UV–H$_2$O$_2$ system. It was evident that photofenton oxidation reaction (hydrogen peroxide in the presence of ferrous salt and UV irradiation) was strongly affected by solution pH (Fig. 3c). The reaction mechanism involved in the organic degradation is believed to be due to the formation of reactive oxidative species such as hydroxyl radicals and aquo or organocomplexes of the high valence iron, the ferryl ion [30]. At very low pH (pH < 3), scavenging effect of hydroxyl radicals by hydrogen ions becomes very important and at very high pH the efficiency of organic degradation is reduced because of the decrease of the free iron species in the solution due to the formation of Fe(II) complexes and due to the precipitation of insoluble iron hydroxides, which inhibits the regeneration of ferrous ions [30,31]. Also, the oxidation potential of the OH$^\bullet$
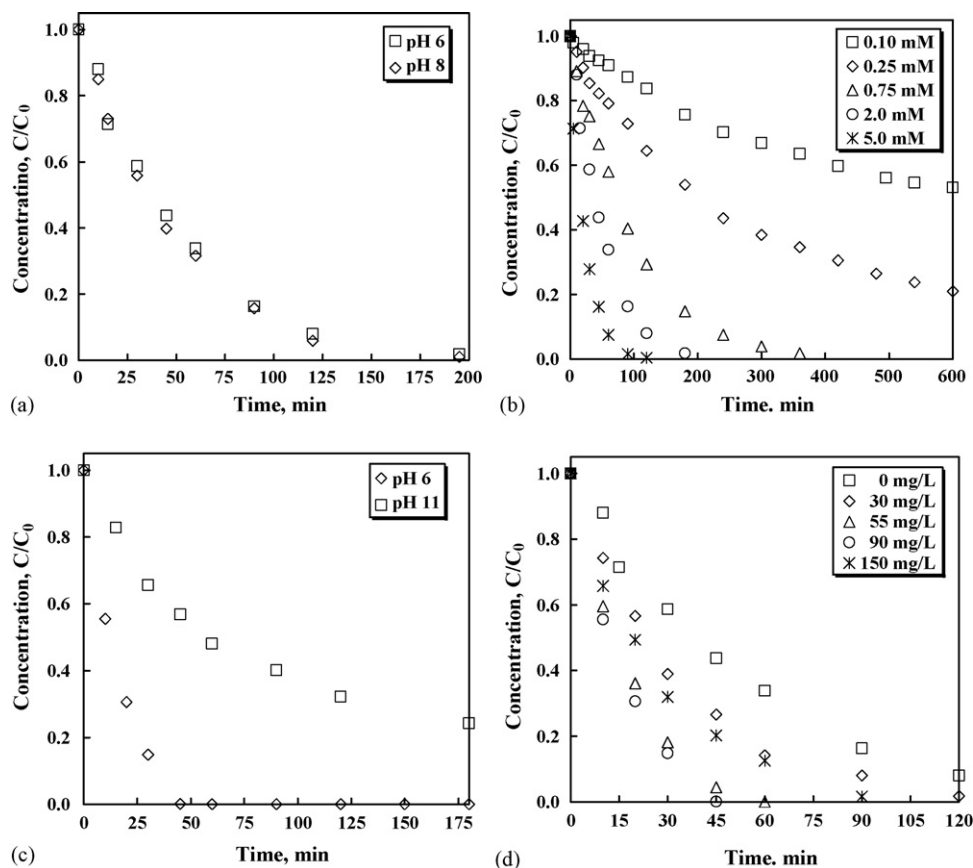
Fig. 3. TPA degradation performance by photochemical oxidation (UV–H_2O_2) (a, b) and photofenton oxidation (UV–H_2O_2–$Fe_2(SO_4)_3$) (c, d) processes: (a) performance of UV–H_2O_2 system at different solution pH (TPA concentration 50 mg/L, H_2O_2 concentration 3 mM), (b) at different H_2O_2 concentration (TPA concentration 50 mg/L, pH 6), (c) performance of UV–H_2O_2–$Fe_2(SO_4)_3$ system at different solution pH (TPA concentration 50 mg/L, H_2O_2 concentration 3 mM, $Fe_2(SO_4)_3$ concentration 90 mg/L) and (d) at different $Fe_2(SO_4)_3$ concentration (TPA concentration 50 mg/L, H_2O_2 concentration 3 mM, pH 6).

radical is known to decrease with the increase in pH [32]. Generally, the optimum pH is around 3 [33], but nature of our target material (TPA) would not favor very low pH conditions.

As it can be seen from Fig. 3d, the degradation rate of TPA increased with increasing initial Fe concentration. Complete degradation of 50 mg/L TPA, under these operating conditions, was reached within 45 min with 90 mg/L of $Fe_2(SO_4)_3$ concentration. However, further increase in $Fe_2(SO_4)_3$ concentration to 150 mg/L resulted in the reduction of TPA removal efficiency. According to Neyens and Baeyens [34], the organic materials compete with Fe ions for $OH^\bullet$ radicals. Hence, by increasing Fe concentration in solution, the availability of $OH^\bullet$ for the organics would be decreased.

3.3. Catalytic ozonation (O_3–TiO_2/Fe)

Application of this technique for TPA destruction, proved to be very effective, compared to previously described advanced oxidation processes. Fig. 4 shows the TPA removal performance by ozonation and ozone in the presence of two different catalysts, TiO_2 and $Fe_2(SO_4)_3$, tested individually. The presence of catalyst showed appreciable improvement in performance compared to the process with ozone alone. Earlier studies have reported on the destruction of several organic materials other than TPA

by catalytic ozonation and have demonstrated similar increase in performance compared to ozonation, due to the presence of even small amounts inorganic metal ions [35–39].

It was evident that 50 mg/L of TPA could be almost completely degraded in 10 min of reaction time by catalytic ozonation with 55 mg/L of $Fe_2(SO_4)_3$ or 90 mg/L of TiO_2.
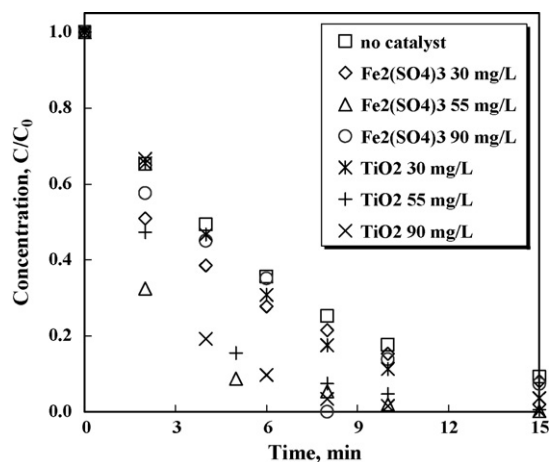

Fig. 4. Performance of ozone oxidation and in the presence of catalysts on TPA destruction (initial TPA concentration 50 mg/L).
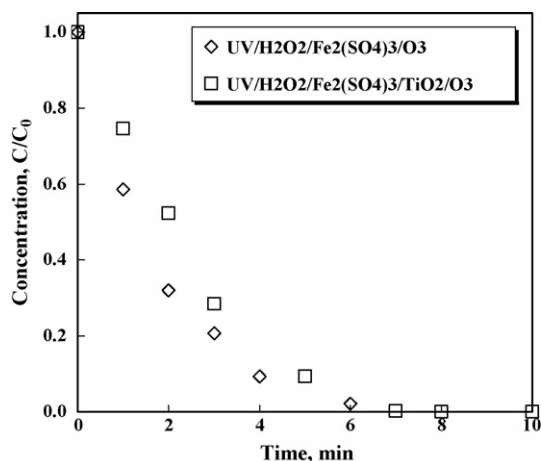
Fig. 5. TPA degradation by photofenton combined ozone oxidation (UV–H$_2$O$_2$–Fe–O$_3$) and photofenton hetro catalytic ozonation (UV–H$_2$O$_2$–Fe–TiO$_2$–O$_3$) (TPA concentration 50 mg/L, H$_2$O$_2$ 3 mM, TiO$_2$ 55 mg/L, Fe$_2$(SO$_4$)$_3$ 55 mg/L).

Increase in TiO$_2$ catalyst concentration from 55 to 90 mg/L had no significant improvement in removal efficiency, whereas, increase in iron ion concentration to 90 mg/L decreased the removal performance. Similar pattern of decrease in oxidation performance beyond a certain amount of Fe concentration in the presence of ozone was observed by Contreras et al. [40].

Recently, it is believed that the mechanism of oxidation of organic materials in the presence of Fe and other transition metal catalysts is different from that reported for non-catalyzed ozonation [41–43].

3.4. Photofenton combined ozone oxidation (UV–H$_2$O$_2$–Fe–O$_3$) and photofenton hetro catalytic ozonation (UV–H$_2$O$_2$–Fe–TiO$_2$–O$_3$)

Combining several advanced oxidation process improved the organic destruction efficiency, appreciably. UV–H$_2$O$_2$–Fe–O$_3$ was found to completely destruct 50 mg/L of TPA within 6 min, under the study conditions adopted (Fig. 5). A slight

synergic effect in TPA removal was observed with the combined system. Heredia et al. [44] reported greatest free radical component generation for UV–H$_2$O$_2$–Fe–O$_3$ system. However, UV–H$_2$O$_2$–Fe–TiO$_2$–O$_3$ system needed slightly more time for complete mineralization (Fig. 5). It is to be noted that, merely combining and increasing the number of oxidizing agents in the system, need not always result in the greater synergic effect in overall performance. It is evident that while combining oxidation processes, optimizing the amount of oxidizing reagents are very essential. Similar observation was reported by Chen et al. [45], while adopting the oxidation system in the presence of H$_2$O$_2$ and TiO$_2$.

3.5. Organic intermediates

There has been no complete analysis on the degradation by-products of terephthalic acid reported in the literature so far, with the exception of small discussion on the intermediate formed during the degradation of phthalate compounds in the biological treatment methods [16]. In the present study, some of the likely intermediate compounds, such as benzoquinone, benzene, maleic acid, oxalic acid were identified from GC–MS and HPLC analyses and a possible mechanistic approach for the breakdown of TPA is shown in Fig. 6.

3.6. Degradation kinetics and cost evaluation

The removal of TPA by different AOP systems were analyzed, based on pseudo-first-order kinetics [46,47]. The overall pseudo-first-order kinetic rate constants and half-life (time for 50% organic degradation) were calculated for each system and tabulated in Table 1. Cost analysis for a full-scale treatment system should take into consideration various aspects such as capital costs, operating costs and maintenance costs and would also depend on the factors, such as operating conditions, treatment system adopted, reactor configuration and the type of effluent to be treated. A rough estimate of the cost based on the operating parameters for various batch systems are given in Table 1. Cost
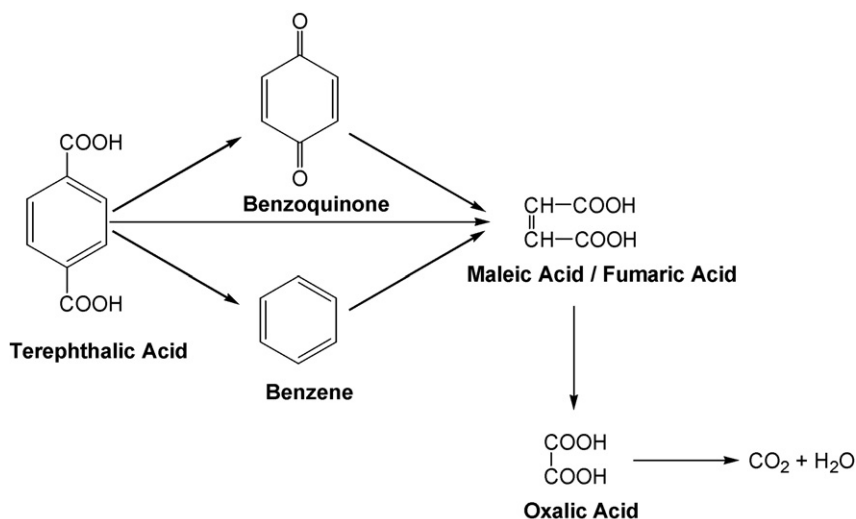

Fig. 6. Possible degradation pathway for TPA by advanced oxidation process.

Table 1
The overall pseudo-first-order kinetic rate constants ($k_{overall}$), half-life ($t_{1/2}$) and operating cost evaluation for TPA destruction (TPA 50 mg/L, pH 6)

System	$k_{overall}$ (1 min^{-1})	Time for 50% organic degradation, $t_{1/2}$ (min)	$ (m^3)
UV/H_2O_2/Fe/O_3	0.6075	1.1409	2.8
UV/H_2O_2/Fe/O_3/TiO_2	0.4419	1.5685	3.01
O_3/Fe	0.4062	1.7050	1.02
O_3/TiO_2	0.3323	2.0858	1.04
UV/H_2O_2/Fe	0.0548	12.6478	2.12
UV/H_2O_2	0.0334	20.7826	2.9
UV/TiO_2	0.0044	157.5537	1.7

analysis based on the electrical energy requirement in kWh was carried out using the formula given below [48]:

$$E = \frac{P \times 1000}{V_0} \times \frac{\ln 10}{60} \times k \tag{1}$$

where P is the lamp power (kW), k the pseudo-first-order constant (1/min), V_0 the volume of the solution and E is the energy in kWh required for achieving 90% destruction of pollutants in 10^3 L of waste water. Values of E not higher than 2.5 are considered suitable for practical applications [48]. Cost of reagents include H_2O_2 (35%): $1.0 kg^{-1}, $Fe_2(SO_4)_3$: $18 kg^{-1}, TiO_2: $75 kg^{-1}, O_3: $2.3 kg^{-1} and electricity: $0.07 kW^{-1}. Although UV/H_2O_2/Fe/O_3 system was found to have the best organic degradation performance (with minimum degradation time), catalytic ozonation (O_3/Fe) seems to show a satisfactory organic degradation performance and to be economically more viable choice for the degradation of terephthalic acid.

4. Conclusions

Several advanced oxidation processes were successfully applied for the complete degradation of toxic organic material, terephthalic acid. Under the study conditions, as a first approximation, following order of efficiency of the systems for TPA removal can be suggested: UV–TiO_2 < UV–H_2O_2 < UV–H_2O_2–Fe(III) < O_3 < O_3–Fe(III) < O_3–TiO_2 < UV–H_2O_2–Fe(III)–TiO_2–O_3 ≤ UV–H_2O_2–Fe–O_3. There appears to be a slight synergistic effect when two or more oxidation systems were combined. This may not hold true always and also increases the complexity of the oxidation system, which calls for careful combination of systems and optimization of parameters including each of the oxidants concentrations. In the present study, the time required for the complete destruction of 50 mg/L of TPA was decreased from 10 h using UV–TiO_2 system to less than 10 min using UV–H_2O_2–Fe–O_3 system. However, catalytic ozonation (O_3/Fe) seems to show a satisfactory organic degradation performance and to be economically more viable choice for the degradation of terephthalic acid. Some of the likely intermediate compounds identified during the destruction of TPA by advanced oxidation process include benzoquinone, benzene, maleic acid and oxalic acid. Even though, the optimal conditions obtained in this work for TPA degradation cannot be generalized for treating other organic pollutants, it gives an indication of the performance of the systems that could be applied to the oxidation of other organic pollutants dissolved in water.

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