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### **Paper:**

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## Accepted Manuscript

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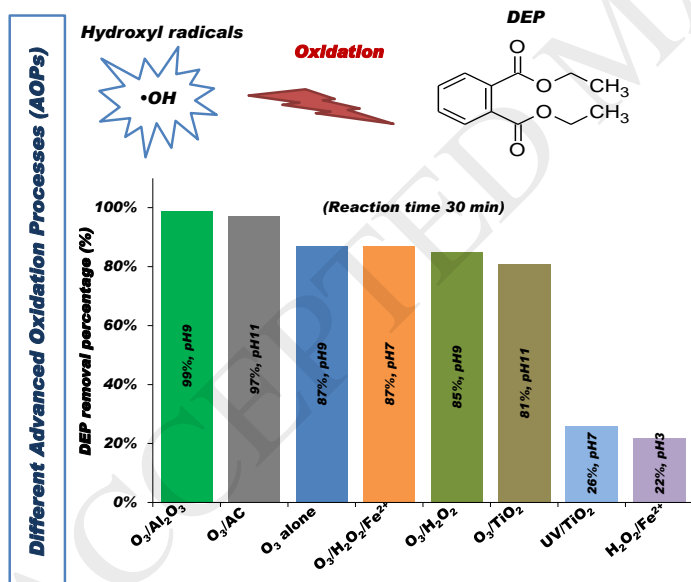
## A comparative study on ozone, hydrogen peroxide and UV based advanced oxidation processes for efficient removal of diethyl phthalate in water

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### Graphical abstract



### Highlights

- Several AOPs were compared for DEP removal in water

- Oxidation by  $\bullet\text{OH}$  was the prevailing pathway for DEP degradation
- Ozone-based AOPs were the most effective for DEP removal
- $\text{O}_3/\text{Al}_2\text{O}_3$  gave the highest DEP removal
- Reaction products and their kinetics were identified by LC/MS/MS

## Abstract

Several Advanced Oxidation Processes (AOPs) including  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{TiO}_2$ ,  $\text{O}_3/\text{activated carbon (AC)}$ ,  $\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{O}_3/\text{Fe}^{2+}/\text{H}_2\text{O}_2$  and  $\text{UV}/\text{TiO}_2$  have been investigated and compared for the removal of diethyl phthalate (DEP), an endocrine disrupting compound, in aqueous solutions. Hydroxyl radicals were the main species responsible for DEP degradation and this was supported by computational chemistry calculation, scavenger experiments, and LC/MS/MS analysis. The change of the abundance of reaction products over time was determined. Organic acids as well as anhydride and hydroxylated products were found to accumulate in solution even after long reaction time (2h). Careful choice of the operating parameters (pH, ozone concentration and catalyst dosage) was crucial to achieve enhanced performance of the combined processes above what each oxidant and catalyst can achieve alone.  $\text{O}_3/\text{AC}$  process was found to reduce the oxidation efficiency of  $\text{O}_3$  at high ozone concentrations. Heterogeneous catalytic ozonation with  $\text{Al}_2\text{O}_3$  was the most effective process for DEP removal (~100% removal in about 15 min) and based on pseudo-first-order kinetics at pH7, the studied oxidation processes followed the order:  $\text{O}_3/\text{Al}_2\text{O}_3(0.093\text{min}^{-1}) > \text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}(0.076\text{min}^{-1}) > \text{O}_3/\text{AC}(0.069\text{min}^{-1}) > \text{O}_3/\text{H}_2\text{O}_2(0.053\text{min}^{-1}) > \text{O}_3/\text{TiO}_2(0.050\text{min}^{-1}) > \text{O}_3 \text{ alone } (0.039\text{min}^{-1}) > \text{UV}/\text{TiO}_2(0.009\text{min}^{-1})$ .

**Keywords:** Diethyl phthalate; ozone; advanced oxidation processes; photocatalysis; hydroxyl radical.

## 1. Introduction

The occurrence of substances in the aquatic environment that cause disruption of the endocrine system is becoming a major environmental and human health concern [1]. Phthalic acid esters (PAEs) belong to this category of substances [1, 2] with several PAEs (e.g. diethyl phthalate, butyl benzyl phthalate, diethylhexyl phthalate) being classified as priority pollutants by the US EPA [3]. Out of the PAEs family, diethyl phthalate (DEP) is often detected at high concentrations in the environment due to its extensive use in numerous industrial plastic products, insecticides, and many cosmetic and personal care products [4-6]. DEP is not covalently bounded to the plastics in which it was added, hence it has potential to leach out easily from these products and reach wastewater, surface water, groundwater, and even drinking water [7, 8]. Despite being widely used, DEP exhibits an announced character of an endocrine disruptor and is linked to several diseases [9-12]. It has, for example, been found to interfere with the neuroendocrine and the male reproductive systems [13, 14], alters lipid metabolism and reduces fecundity [15] and has also been correlated to obesity in children [16]. Due to its high solubility in water ( $1,080 \text{ mg L}^{-1}$  at 293 K), DEP is highly mobile, making it one of the most distributed contaminants in the aquatic environment. Besides, DEP resists biological and photochemical degradations [17, 18] making its removal in conventional wastewater treatment plants difficult. Recourse to other wastewater treatment technologies such as advanced oxidation processes (AOPs) is hence required to limit its spread in the aquatic environment.

AOPs are promising alternative treatment technologies since they convert recalcitrant organic pollutants to less harmful compounds or even completely mineralise them into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and salts [19, 20]. AOPs rely on the in-situ generation of potent oxidising chemical entities, primarily hydroxyl radicals ( $\bullet\text{OH}$ ), and are achieved using a range of combinations of oxidants and catalysts. Ozone-, UV- and  $\text{H}_2\text{O}_2$ - based AOPs are common as they have proven to be effective in oxidising and mineralising a wide range of wastewater pollutants [21-25]. AOPs can be combined with biological processes as a pre-treatment step so to render the wastewater biodegradable or as a tertiary treatment to oxidise refractory organic pollutants [20, 26]. Studies on DEP removal have demonstrated that owing to  $\bullet\text{OH}$  reactions, AOPs were more powerful than common oxidants acting alone. Xu et al. [27] have used UV/ $\text{H}_2\text{O}_2$  to degrade DEP solutions at  $1 \text{ mg L}^{-1}$  and have found that neither UV nor  $\text{H}_2\text{O}_2$  alone

degraded DEP but when combined, 98.6% of DEP were removed, though after a long time. Long reaction times were also reported for DEP removal (>75%) by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> [28] and photocatalysis [29, 30]. In their study using O<sub>3</sub>/UV, Oh et al. [17] have shown that ozone alone was more effective than UV to degrade DEP but not to the extent that DEP is significantly removed. However, when ozone was combined with UV, the degradation of DEP was increased significantly and only about 0.5 h was sufficient to almost fully remove the substance [17]. Ozone combined with catalysts (e.g. activated carbon and metallic oxides) was also effective to remove DEP in about 0.5 h [22, 31-33]. Elmolla and Chaudhuri [34] have made a technico-economic comparison between Fenton, photo-Fenton, UV/TiO<sub>2</sub>, and UV/ZnO processes and have concluded that all processes were able to degrade the antibiotics they used and improve, with the exception of UV/ZnO, the solution biodegradability. They also concluded that photo-Fenton was the most cost-effective process. In a recent study, Asaithambi et al. [35] have compared Fenton and ozone combined with UV and H<sub>2</sub>O<sub>2</sub> AOPs and have concluded that ozone-photo-Fenton was able to fully remove colour and chemical oxygen demand of the distillery effluent they studied. They also reported that ozone-photo-Fenton had the lowest electrical energy per order (0.01 kWh/m<sup>3</sup>). Other comparative studies on various AOPs have also reported varying results between the types of AOPs studied [36-38].

According to the studies made so far, it is clear that the type of AOP and the experimental conditions used affect significantly the performance of the treatment process. However, there are no studies in the literature that systematically compared the performance of common AOPs to degrade DEP. Besides, the mechanism of DEP degradation is still unclear and the type and kinetics of accumulation of key reaction products are not explored before. This study provides new insights into these and evaluates how combinations of various oxidation treatments including ozone, UV, H<sub>2</sub>O<sub>2</sub>, Fenton, and metallic oxide catalysts enhance •OH generation for efficient DEP degradation. The findings are also useful to guide the selection of a suitable AOP for DEP degradation.

## 1. Materials and Methods

## 1.1. Reagents

Diethyl phthalate (99.5%) was purchased from Merck Chemical, Germany. DEP solutions at different initial concentrations (10 to 200 mgL<sup>-1</sup>) were prepared in MilliQ water. TiO<sub>2</sub> (Degussa P25; 75% anatase and 25% rutile; 50 m<sup>2</sup>g<sup>-1</sup>) was used as photocatalyst, and Al<sub>2</sub>O<sub>3</sub> (Sigma Aldrich, Germany; >40 m<sup>2</sup>g<sup>-1</sup>; p*H*<sub>zc</sub> = 9.4 to 10.1) and activated carbon (Chemviron, UK; 933 m<sup>2</sup>g<sup>-1</sup>; p*H*<sub>pzc</sub> = 10.68) were used as catalysts in ozonation. FeSO<sub>4</sub>·7H<sub>2</sub>O (99.5%) and H<sub>2</sub>O<sub>2</sub> (30% w/w) were purchased from Merck, Germany, and were used in the Fenton experiments. Tert-butanol (TBA) (Fisher Scientific, Germany; 99.5%) was used as a radical scavenger in ozone studies. Other chemicals were of reagent analytical grade or LC/MS grade and purchased from Sigma Aldrich or Fisher Scientific, UK.

## 1.2. Experimental set-up

### 1.2.1. Photocatalysis

A 1-L annular laboratory-scale Pyrex photoreactor equipped with a high pressure mercury lamp (Philips HPK 125 W;  $\lambda > 253$  nm) was used to carry out the photocatalytic experiments (Figure 1), as described by Mansouri et al. [30]. The photochemical reactor was made of glass with a plain quartz tube equipped with a magnetic stirring bar, a water-circulating jacket and openings for aeration and sample collection. Before switching-on the UV lamp, the solution containing the photocatalyst was stirred in dark (~30 min). Samples were collected at regular intervals and immediately filtered through 0.45  $\mu$ m Teflon syringe filters, to remove any particles of TiO<sub>2</sub> in the sample, before analysis. The filter was suitable for the analysis as its retention of DEP was less than 3%.

**Figure 1:** Experimental set-ups: (a) catalytic ozonation system; (b) Photocatalytic reactor with mercury UV lamp (HPK 125W)

### 1.2.2. Fenton reaction

Batch Fenton and O<sub>3</sub>/Fenton experiments were conducted at room temperature (20±1°C) in a well-mixed 1L Pyrex reactor. The required amount of iron (FeSO<sub>4</sub>·7H<sub>2</sub>O) was added to the aqueous

solution and the pH was adjusted by adding either H<sub>2</sub>SO<sub>4</sub> (0.1 M) or NaOH(1M) solutions. Thereafter, H<sub>2</sub>O<sub>2</sub> was added to the mixture signalling the start of the experiment. Collected samples were filtered through a 0.45- $\mu$ m filter before DEP analysis with HPLC.

### 1.2.3. Ozone oxidation

Ozone was produced from oxygen and supplied to a well-stirred 1L reactor via a sintered glass diffuser at constant flow rate 400 mL min<sup>-1</sup> and input ozone concentration (~45g m<sup>-3</sup> at Normal Temperature and Pressure (NTP) of 0 °C and 1 atm). 1-mL samples were collected and immediately quenched by adding 100  $\mu$ L of a sodium thiosulfate solution Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1 M) to remove any residual ozone. The samples were filtered through 0.45- $\mu$ m Teflon syringe filters before storage at 4°C for subsequent analysis by HPLC/UV. Those samples analysed by LC/MS/MS were quenched by bubbling air into the sample and were analysed immediately after sample collection. In some ozonation experiments, TBA was added to the solution as a radical scavenger. Ozone concentration in the liquid phase was determined using the indigo colorimetric method [39].

## 1.3. Analytical methods

### 1.3.1. DEP concentration and reaction products

An Agilent 1200 series high-performance liquid chromatograph HPLC/UV was used to measure DEP concentrations using a pre-determined calibration curve. Details of the chromatographic conditions can be found in Table S1 (Supplementary Information). The reaction products of DEP degradation using sole ozone process were identified using LC/MS/MS and GC/MS. Samples for GC/MS analysis were prepared using a liquid-liquid extraction method as in Jung et al. [40] while samples for LC/MS/MS analysis were directly injected. The LC/MS/MS analysis was performed on an Agilent 1200 series liquid chromatograph system coupled to a 6410 series triple quadrupole mass spectrometer. The chromatographic conditions were: mobile phase 80%v acetonitrile: 20%v aqueous 100mM ammonium formate; flow rate 0.4 mL min<sup>-1</sup>; injection volume 10 $\mu$ L; chromatographic column Acclaim Trinity P2 (3 $\mu$ m, 3mmx100 mm, Thermo Fisher Scientific, UK) fitted with a P2 guard. The



GC/MS analysis was made on an HP 6890 gas chromatograph (Hewlett Packard, USA). A 5973 mass selective detector (MS Detector Agilent, USA) was used, and the separation column was an HP-5 MS capillary column (film thickness, 0.25  $\mu\text{m}$ ; inner diameter, 0.32 mm; length, 30 m). Splitless injection mode was used and the carrier gas was helium at a flow rate of 0.9 mL  $\text{min}^{-1}$ . Further details regarding both methods can be found in Section A (Supplementary Information). A UV- visible spectrophotometer (Thermospectronic UV1, Thermo Spectronic-UK) was used to determine UV- visible spectra of DEP solutions. Total Organic Carbon (TOC) was measured using a Shimadzu-L TOC analyser and pH was measured with a WTW Multi 197i pH meter (WTW, Germany).

### 1.3.2. Computational Chemistry

To predict the position of oxidants attack on the DEP molecule and on the reaction intermediates, computational chemistry was used to optimise the geometry of the molecules and calculate the electron density and partial charge (PC) of each atom of the molecules. The calculation was made by the molecular orbital package MOPAC2016 using the accurate parametrization PM7 Hamiltonian model. The results of electron density and atomic partial charge obtained by MOPAC2016 along the experimental measurements made by the LC/MS/MS provided fundamental information on the reactions that took place during the oxidation of DEP molecule and supported the development of a plausible mechanism for DEP degradation by  $\cdot\text{OH}$ .

## Results and Discussion

### 2.1. DEP removal using single process

#### 2.1.1. Direct UV photolysis of DEP

After 3h irradiation, only 7% removal was observed indicating that photolysis of DEP was not effective (Figure 2(a)). This could be explained by the fact that emission maxima of the UV lamp are at wavelengths higher than the absorption wavelengths of DEP ( $<230$  nm). The UV lamp shows maximum energy at 365 nm, with additional substantial radiations at 435, 404, 313, and 253 nm, and a

small continuum from 200 nm to approximately 300 nm (data not shown). The latter part (i.e. 253, 300 to 200 nm) has <10% of maximum energy could be the only portion of the spectrum that is responsible for the slight DEP photolysis observed. This results in the low quantum yield of direct UV photolysis of DEP, which is in agreement with previous studies such as that by Xu et al. [27] who also found that DEP molecules cannot be eliminated by direct UV photolysis alone. Initial pH had no significant effect on the photolysis of DEP (Figure 2(b)). This could be explained by the non-dissociating structure of DEP molecule which results in its light absorption properties and photochemical excitation state being unaffected by pH changes.

**Figure 2:** UV/Vis absorption spectra of aqueous DEP solutions during photolysis: (a) as function of time (pH=7); (b) as function of pH (irradiation time=3h).

### 2.1.2. Hydrogen peroxide

Experiments of DEP oxidation by H<sub>2</sub>O<sub>2</sub> only were performed at different H<sub>2</sub>O<sub>2</sub> concentrations and at pH 3 and 7. The results showed that DEP degradation was not significant (<1% after 60 minutes). Xu et al. [27] and Mansouri et al. [41] have also found that DEP cannot be oxidised by H<sub>2</sub>O<sub>2</sub> alone and combination with other oxidants such as UV and ozone or catalysts is hence needed to produce a more potent oxidant <sup>•</sup>OH.

### 2.1.3. Ozonation

Figure 3 (a) shows the change of the ratio [DEP]/[DEP]<sub>0</sub> as function of the reaction time at different pHs and constant dissolved O<sub>3</sub> concentration (~0.98 × 10<sup>-4</sup> M); [DEP] and [DEP]<sub>0</sub> are DEP concentrations at time *t* and 0 respectively. As opposed to the other single processes discussed earlier, Figure 3(a) illustrates that ozone alone was effective to degrade DEP particularly at high pHs (7 to 11).

For example, at pH9, the DEP removal efficiency was almost 100% within 50 min of ozonation whilst at neutral pH, complete DEP elimination was obtained within 90 min of ozonation. However, in acidic conditions (pH3), the removal efficiency of DEP by ozone was poor (about 10% after 1h of reaction). The high efficiency of ozone at high pH is due to enhanced  $\cdot\text{OH}$  production at high pHs [42]. Besides, as the initial DEP concentration is lowered, the elimination of DEP by ozone becomes faster (Figure 3(b)). For example, the times required for 90% removal at  $[\text{DEP}]_0$  of  $200 \text{ mg L}^{-1}$  and  $10 \text{ mg L}^{-1}$  were 60 min and 8 min respectively. This obviously indicates that, the higher the initial DEP concentration, the longer it takes to fully degrade the molecule due to correspondingly increased amount of materials to oxidise (i.e. parent molecule and its reaction products) whilst the supplied ozone, by bubbling into solution, remained constant. The mineralisation of DEP by ozonation was also monitored through TOC analysis and the results are shown in Figure 3(c). According to the figure, even after extended reaction time of 120 min, only little TOC (about 21%) was removed from the solution whilst DEP was fully degraded. This indicates strong accumulation of reaction products in solution during the ozonation process.

**Figure 3:** Removal efficiency of DEP by ozone: (a) At different pH values ( $[\text{DEP}]_0 = 200 \text{ mg L}^{-1}$ ,  $C_{\text{O}_3\text{liquid}} = 0.98 \times 10^{-4} \text{ M}$ ); (b): At different initial DEP concentrations ( $\text{pH} = 7$ ,  $C_{\text{O}_3\text{liquid}} = 0.98 \times 10^{-4} \text{ M}$ ); (c) TOC removal ( $\text{pH} = 7$ ,  $[\text{DEP}]_0 = 200 \text{ mg L}^{-1}$ ).

## 2.2. Degradation pathways and oxidation reaction intermediates using ozone

The generation of intermediates during DEP ozonation results mainly from attacks by  $\cdot\text{OH}$  and to a lesser extent from reactions with molecular ozone [40, 43]. To illustrate and confirm the extent of radical contribution, experiments in the presence and absence of TBA at pH 7 were carried out. TBA is a radical scavenger that has negligible reaction rate with molecular ozone ( $k_{\text{O}_3} = 3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ) but reacts rapidly with  $\cdot\text{OH}$  ( $k_{\cdot\text{OH}} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) [32, 44] to generate inert intermediates that terminate the radical chain reaction of ozone decomposition to  $\cdot\text{OH}$ . In this study, TBA was found to

reduce the removal of DEP from 75% to 5%, which affirms that the elimination of DEP occurred predominantly via  $\bullet\text{OH}$ .

A mechanism for  $\bullet\text{OH}$  degradation of DEP is suggested and is presented in Figure 4. The figure also shows the changes over time of the relative abundance of each reaction product. The molecular structure of each reaction product was confirmed with collision-induced dissociation Product Ion MS/MS scans; Table S2 (Supplementary Information) shows examples of CID results. A proposed fragmentation pathway for DEP molecule is also shown in Figure S2 (Supplementary Information). The fragmentation patterns presented in Table S2 are consistent with the oxidation product structures and were not suggested in a random way since there is no violation of atom connectivity present in their corresponding precursor molecules.

Examination of the computational chemistry calculations (Table S3, Supplementary Information) shows that  $\bullet\text{OH}$  attack of the aromatic ring of the DEP molecule ( $m/z223$ ) can preferentially be made at carbon position C6 (charge -0.139) to form the hydroxylated compound A1 ( $[\text{A1}+\text{H}]^+$   $m/z239$ ) (Figure 4). Given the significant abundance of hydroxyl radicals in solution, since ozone was continuously supplied, further hydroxyl radical attacks take place on A1 at either carbon C4 or C5 to form a doubly hydroxylated product. Owing to steric effect, C5 is likely to be the site of  $\bullet\text{OH}$  attack leading to product A2 ( $[\text{A2}+\text{H}]^+$   $m/z255$ ). A2 is further attacked by  $\bullet\text{OH}$  at carbons C3 and C4 to produce A3 ( $[\text{A3}+\text{H}]^+$   $m/z271$ ) which is also attacked by  $\bullet\text{OH}$  to finally produce A4 ( $[\text{A4}+\text{H}]^+$   $m/z287$ ). Figure 4 (a) (relative abundance versus time) shows that these  $\bullet\text{OH}$  attacks proceed rapidly within the first 20 minutes possibly as a result of the initial high concentration of the parent molecule DEP.

According to Figure 4 (b), product A2 has the highest abundance by about 3 times higher than the other products while A4 reached a maximum after about 30 minutes. A1 also reached a maximum after 20 minutes while A2 reached a maximum after 80 minutes. The disappearance of A1 after 30 minutes reaction is more pronounced than the changes in abundance of A2-A4 indicates the continued oxidation of A1 to form other products in addition to A2. As the reaction time progresses towards 120

minutes, the relative abundances of products A1 to A4 decline, though at different rates, indicate their degradation to form other products.  $\bullet\text{OH}$  attacks on A1 to A4 at positions C1 or C2 are also possible, particularly for A3 and A4 given their high negative charges, leading to the opening of the aromatic rings to form new species.

Parallel to the attacks on the aromatic ring,  $\bullet\text{OH}$  also attacks the terminal carbons of the aliphatic chains via H-atom abstraction from  $-\text{CH}_3$  or  $-\text{CH}_2$  groups. The latter is most likely the site of attack [45, 46] and a proposed mechanism for this reaction is shown in Figure S3 (Supplementary Information). The attack of  $-\text{CH}_2$  takes place on the DEP molecule as well as on products A1 to A4 to produce products B1 to B5 which are also attacked by  $\bullet\text{OH}$  on the other  $-\text{CH}_2$  of the second aliphatic group to produce products C1 to C5. Hydrogen abstraction by  $\bullet\text{OH}$  from  $-\text{O}-\text{H}$  of the carboxylic groups in C1 to C5 leads to breakage of the bond between oxygen and hydrogen and the generation of water and the anhydride species (compounds D1 to D5). Parallel to these reactions presented horizontally,  $\bullet\text{OH}$  also attacks the benzene ring to form the hydroxylated intermediates as shown vertically in Figure 4(a) (e.g.  $\text{B1} + \bullet\text{OH} \rightarrow \text{B2}$ ). Comparing the absolute abundance values of each of the intermediates A1 to D5 (Figure 4(b-e)), intermediates C1 to C5 have the lowest abundances while at the end of the reaction time (i.e. 120 minutes), both A2 and D1 are found at the highest abundance.

Oxidation of products A1 to D5 proceed with further  $\bullet\text{OH}$  attacks leading to aromatic ring opening and the formation of open conjugated structures. The conjugated structures are further oxidised by  $\bullet\text{OH}$  via addition to unsaturated carbons and also via H-atom abstraction from C-H bonds in aliphatic compounds [47]. Given the abundance of double bonds in the conjugated structures formed following opening of the aromatic ring, oxidation with molecular ozone via  $\text{O}_3$  cyclo addition mechanism can also take place. These oxidation reactions continue to finally lead to smaller molecules of organic acids such as succinic acid ( $[\text{E1}-\text{H}]^-$  m/z117), malonic acid ( $[\text{E2}-\text{H}]^-$  m/z103), oxalic acid ( $[\text{E3}-\text{H}]^-$  m/z89), and propanoic acid ( $[\text{E4}-\text{H}]^-$  m/z73) identified in this study. The changes as function of time of the relative abundance of each of these acids are shown in Figure 4 (g). The figure shows a steady

progressive increase of the relative abundance of each of the acids as the reaction time increased, indicating that these acids are relatively stable within the 120 minutes reaction time and significantly accumulate in solution. This is in line with the TOC results shown in Figure 3(c) where the removal of TOC becomes harder from around 60 min reaction time. The full mineralisation to CO<sub>2</sub> of these acids will require either longer reaction times and/or more aggressive oxidation conditions. Besides, Figure 4(f) shows the changes of the absolute abundance values for each of the acids and according to the figure, succinic and oxalic acids were the most persistent acids. GC/MS was also used to identify the reaction products arising from DEP ozonation and products such as phthalic anhydride (D1), 4-hydroxy phthalic acid (C2), and succinic (E1) and malonic (E2) acids were also detected.

**Figure 4:** Proposed mechanism for •OH attack on DEP using ozone and the changes of relative and absolute abundance values of each product as function of time

## 2.2. Comparison of advanced oxidation processes for DEP removal

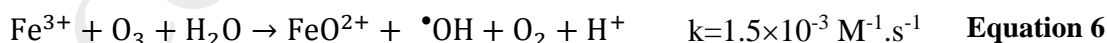
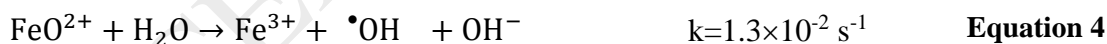
A comparison on the performance of the AOPs O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/TiO<sub>2</sub>, O<sub>3</sub>/AC, O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, Fenton (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>), and UV/TiO<sub>2</sub> is discussed in this section.

### 2.2.1. Effect of initial pH

The removal of DEP was significantly affected by pH in all studied oxidation systems (Table 1). A maximum DEP degradation of >80% was obtained with ozone-based AOPs operating in the pH range 7 to 9. Combination of ozone with OH<sup>-</sup> (i.e. high pH) results in a chain-reaction sequence that produces •OH in significant quantities and as a result O<sub>3</sub>/OH<sup>-</sup> is classified as an AOP [48]. The overall reaction for hydroxyl radical formation from ozone decomposition initiated by OH<sup>-</sup> is shown by Equation 1.



For pH values below 5, the DEP degradation by each AOP was lowest in comparison to higher pHs, except for the Fenton process which gave 22% removal at pH 3 and around 11% at higher pHs. This trend is expected for the Fenton process since it is normally effective in acidic solutions (pH~3) [49] but its highest performance in removing DEP is still low in comparison to the other AOPs. In the Fenton process, the generation of hydroxyl radical  $\cdot\text{OH}$ , besides  $\text{OH}^-$  ions, is related to the rate of decomposition of hydrogen peroxide and iron (II) salts in water, which is slow [50, 51]. Hence longer reaction times are required to achieve any substantial DEP removal by the Fenton process. However, the addition of ozone to the Fenton reagent (i.e.  $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ) has significantly improved the degradation of DEP to 87% at pH 7 and modestly to about 36% at pH 3. Thus, at neutral pH, the combination of ozone with Fenton reagents is more efficient for phthalate treatment than if each process was applied alone. The enhancement of DEP degradation in the  $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}$  may result from combined effects that lead to enhanced formation of  $\cdot\text{OH}$  through the reactions between ozone and  $\text{H}_2\text{O}_2$  (Equation 2), ozone and iron species (Equations 3-6), ozone and hydroxide ion (Equation 1), and the Fenton reaction itself (Equation 7) [42, 52, 53].



Under alkaline conditions, DEP removal by  $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}$  was significantly reduced to 64% at pH9 from 87% at pH7. This decrease could be attributed to a reduced concentration of ferrous ions due to precipitation (Equation 8) and also rapid precipitation of  $\text{Fe}^{3+}$  (Equation 9) once being produced by

oxidation of  $\text{Fe}^{2+}$  by ozone (Equations 3-5). Indeed, for a concentration of  $\text{Fe}^{2+}$  of  $5 \times 10^{-3} \text{ mol L}^{-1}$  used in this study, the precipitation of  $\text{Fe}(\text{OH})_2$  occurs at a pH 7.6 and the precipitation of  $\text{Fe}(\text{OH})_3$  occurs at a pH 3. Hence at pH 9, the concentrations of ferrous and ferric ions are significantly reduced to almost zero which leads to reduction of  $\cdot\text{OH}$  production from the reactions between ozone and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (Equations 3-6) and  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  (Equation 7). It can hence be concluded that the optimal pH for highest effectiveness of  $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}$  to remove DEP is a neutral pH.



The degradation and removal of DEP with  $\text{O}_3$  combined with heterogeneous catalysts ( $\text{TiO}_2$ , AC, and  $\text{Al}_2\text{O}_3$ ) was also affected by pH. At low pH (~2-3),  $\text{O}_3$  combined with  $\text{TiO}_2$  or  $\text{Al}_2\text{O}_3$  gave only a small removal of DEP (around 6%) which is comparable to that obtained with ozone alone at pH 3, whilst  $\text{O}_3$  combined with AC gave a much higher removal (~60%). Given the hydrophobic nature of DEP ( $\log(P)=2.42$ ), the increased removal obtained with the addition of AC at low pH could be explained by a significant adsorption of DEP on AC. However, as the pH was increased to 7, the removal of DEP was significantly increased for all the three catalysts used. At pH 7, the removal percentages of DEP were 78%, 95%, and 94% for  $\text{O}_3/\text{TiO}_2$ ,  $\text{O}_3/\text{Al}_2\text{O}_3$ , and  $\text{O}_3/\text{AC}$  respectively and a further increase to pH 9 resulted in further increases of the removal percentages to 79%, 99% and 96% for  $\text{O}_3/\text{TiO}_2$ ,  $\text{O}_3/\text{Al}_2\text{O}_3$ , and  $\text{O}_3/\text{AC}$  respectively (Figure 5). According to Figure 5, increasing the pH above 9 to 11 did not result in significant changes in the removal percentages; hence pH9 appears to be the most suitable operating pH for the heterogeneous catalytic ozonation processes. It should however be noted that at pH 9,  $\text{O}_3/\text{TiO}_2$  has a lower performance (79% removal) as compared to ozone alone (87%), which does not justify the use of this heterogeneous catalytic ozonation process. Remarkably, the  $\text{O}_3/\text{Al}_2\text{O}_3$  was capable to fully remove DEP, possibly due to a high production of hydroxyl radicals resulting from the significant decomposition of ozone by the strong Lewis-acid  $\text{Al}_2\text{O}_3$  [54].

The removal of DEP by photocatalysis (i.e. UV/ $\text{TiO}_2$ ) at the different studied pHs (2 to 9) showed lower removal percentages in comparison to the other AOPs; at best, 26% removal was obtained at



pH7 (200 mg DEP L<sup>-1</sup>; 1 g TiO<sub>2</sub> L<sup>-1</sup>; 30 minute) (Table 1). To obtain higher removal percentages of DEP with UV/TiO<sub>2</sub>, longer reaction times will be required. The pH of the highest DEP removal with UV/TiO<sub>2</sub> (i.e. pH7) is close to the zero point of charge of the photocatalyst (pH<sub>pzc</sub> range from 6.2 to 7.5) as also obtained by Muneer et al. [55].

Considering the AOPs studied here, it is clear that the removal of DEP is strongly affected by pH. Figure 6 provides the best pH values at which each AOP should be operated to give maximum DEP removal. Out of all AOPs studied, O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> appears the best AOP since it gave the highest DEP removal of 100% at pH 11 (Table 1) but could also be operated at pH 9, a pH that is more closer to real situations, to give a 99% removal. Using these optimum conditions and based on a 90% DEP removal, conservative operating costs of each AOP were calculated for illustration purposes using cost of the electrical energy and the main chemicals used in each AOP. Unit costs for bulk chemicals were obtained from www.alibaba.com and the unit electrical energy cost was estimated at £0.1/kWh. The results are displayed in Figure 6 inset table and indicate that, with the exception of Fenton which requires extremely long time, the O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> process is relatively the cheapest in comparison to the other AOPs. The reported cost figures obtained here are within the same magnitude to those reported elsewhere [34].

**Table 1:** Comparison of DEP removal with different AOPs (reaction time=30 min)

**Figure 5:** Effect of pH on the removal percentages of DEP by heterogeneous catalytic ozonation (reaction time is 30 min and the other operating conditions are as in Table 1)

**Figure 6:** Maximum DEP removal percentages at best pH for each AOP (operating conditions are as in Table 1). Inset table: cost estimation of each AOP based on a 90% DEP removal.

### 2.2.2. Effect of initial DEP concentration ( $[\text{DEP}]_0$ )

Table 2 illustrates that as  $[\text{DEP}]_0$  increased, removal percentages for all studied AOPs were reduced, which is in agreement with other studies [24, 37, 44]. At the lowest  $[\text{DEP}]_0$  of  $10 \text{ mgL}^{-1}$  and within only 15 minutes, all AOPs have achieved almost full removal of DEP, with the exception of UV/TiO<sub>2</sub> (44%) and ozone alone (84%). In the presence of H<sub>2</sub>O<sub>2</sub> or catalysts, ozone was more effective whereas UV/TiO<sub>2</sub> was a poor process at all concentrations used (Table 2). O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> has however outperformed all AOPs studied and showed greater ability to degrade DEP within a short time (15 minutes) even at high DEP concentrations (71% for  $200 \text{ mgL}^{-1}$  and 90% for  $100 \text{ mgL}^{-1}$ ) (Table 2). The enhanced degradation efficiency observed at low  $[\text{DEP}]_0$  could be attributed to high abundance of  $\cdot\text{OH}$  and catalyst active sites relative to the initial amount of DEP molecules [44, 56, 57].

The various oxidation processes used were also compared based on values of their pseudo-first-order rate constant ( $k_{\text{overall}}$ ) (Table 3). According to Table 3, catalytic ozonation gave the highest rate constants and UV/TiO<sub>2</sub> gave the lowest. Based on  $k_{\text{overall}}$  values, the processes followed the order: O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>>O<sub>3</sub>/AC>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>>O<sub>3</sub>/TiO<sub>2</sub>>O<sub>3</sub>>UV/TiO<sub>2</sub>.

**Table 2:** Effect of DEP initial concentration on removal percentages by each AOP (reaction time=15 min, pH=7, other operating conditions are as in Table 1)

**Table 3 :** Overall pseudo-first-order rate constants ( $k_{\text{overall}}$ ) ( $[\text{DEP}]_0=200 \text{ mg L}^{-1}$ ;  $[\text{O}_3]_{\text{in}}=45 \text{ g m}^{-3}\text{NTP}$ , pH=7)

### 2.2.3. Effect of ozone concentration

The overall DEP removal was increased by increasing the inlet ozone gas concentration  $[\text{O}_3]_{\text{in}}$  (Figure 7(a)). Notably, after reaction time of 10 minutes, the increase in DEP removal was highest for O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> from 8% to 55% as  $[\text{O}_3]_{\text{in}}$  increased from 0 to  $45 \text{ g/m}^3\text{NTP}$ . A significant improvement (~40%) was also observed for O<sub>3</sub>/TiO<sub>2</sub> and O<sub>3</sub>/Fenton systems but slightly lower (30%) for O<sub>3</sub>/AC as

$[O_3]_{in}$  increased from 0 to 45 g/m<sup>3</sup>NTP. Taking into account of the removals obtained with ozone alone ( $R_{O_3}$ ) and catalyst alone ( $R_{cat}$ ), an enhancement quantity (E) for the combined process was calculated ( $E=R-R_{O_3}-R_{cat}$ ); where R is the removal by the combined process. With the exception of Al<sub>2</sub>O<sub>3</sub>, the other catalysts showed significant enhancement at low  $[O_3]_{in}$  (9 to 16%) but as  $[O_3]_{in}$  increased to 45 g/m<sup>3</sup>NTP, the enhancement due to combined process was small (maximum 4% for O<sub>3</sub>/TiO<sub>2</sub>) (Figure 7(b)). Remarkably, combination of AC with ozone at high concentration (45 g/m<sup>3</sup>NTP) led to a negative E (-6%) indicating that the oxidation efficiency of O<sub>3</sub> was reduced by AC. This was possibly due to enhanced mass transfer of O<sub>3</sub> into the pores of AC (933 m<sup>2</sup>g<sup>-1</sup>), as a result of increased O<sub>3</sub> concentration, leading O<sub>3</sub> to reach the active sites faster than DEP where it decomposes to reactive species (e.g. •OH) that themselves quickly transform to less reactive species (e.g. •OH+•OH→H<sub>2</sub>O<sub>2</sub>) before DEP reaches them. In contrast, Al<sub>2</sub>O<sub>3</sub> provided insignificant enhancement at low  $[O_3]_{in}$  but as  $[O_3]_{in}$  increased to 45 g/m<sup>3</sup>NTP, E increased to about 11%. This is possibly due to a low interaction with O<sub>3</sub> since Al<sub>2</sub>O<sub>3</sub> has positive charge at the experimental pH ( $pH_{zc} = 9.4$  to 10.1) requiring higher ozone concentration to achieve any substantial diffusion of O<sub>3</sub> to the surface of Al<sub>2</sub>O<sub>3</sub>. It can hence be concluded that for a given catalyst, the ozone concentration should be chosen carefully otherwise the catalyst will not provide any additional benefit beyond what ozone alone or catalyst alone would provide and the use of a combined system O<sub>3</sub>/catalyst becomes unjustified.

**Figure 7:** Effect of inlet ozone gas concentration  $[O_3]_{in}$  on (a) DEP removal by catalytic ozonation; (b) enhancement due to combined O<sub>3</sub>/catalyst (pH = 7;  $[DEP]_0 = 200$  mg L<sup>-1</sup>; reaction time = 10 min).

### 2.2.3. Effect of catalyst dosage on DEP removal

#### 2.2.3.1. O<sub>3</sub>/TiO<sub>2</sub>, O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and O<sub>3</sub>/AC

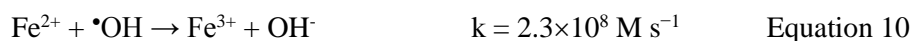
The effect of solid catalyst dosage on DEP removal was firstly evaluated by carrying out adsorption of DEP on the catalysts. Figure 8 indicates that DEP removal by adsorption on both metallic oxide catalysts was limited to only 16% (Al<sub>2</sub>O<sub>3</sub>) and 13% (TiO<sub>2</sub>). Removal by adsorption onto AC has almost doubled (23%) but still low. It is hence clear that adsorption alone was not effective to

significantly remove DEP. In contrast, when AC, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were combined with ozone, the removal of DEP increased to reach almost 79%, 63% and 80%, respectively (Figure 8). As catalyst dosages were increased from zero to 2 g L<sup>-1</sup>, the removal percentages after 25 min, for example, have also increased to reach 72%, 79% and 89% for TiO<sub>2</sub>, AC and Al<sub>2</sub>O<sub>3</sub> respectively (Figure 8). With almost 100% removal after 30 minutes reaction time, Al<sub>2</sub>O<sub>3</sub> gave the best removal result (data not shown). However, as the catalyst dosage increases, the performance of catalytic ozonation reaches a maximum beyond which no further enhancement can be achieved. For example, in this study TiO<sub>2</sub> did not yield any significant increase in DEP removal as its dosage increased from 1 to 2 g L<sup>-1</sup> and further increase of AC dosage beyond 2.6 g L<sup>-1</sup> did not bring any additional removal of DEP (data not shown). This could be explained by increased competition between the “catalyst” and DEP molecules towards the reactive species in solution (e.g. •OH) and the catalyst becomes inhibitor when its dosage is significantly high rather than initiator and promotor of radicals [58].

**Figure 8:** Effect of catalyst dosages on the removal of DEP by catalytic ozonation (pH=7, [DEP]<sub>0</sub>=200 mg L<sup>-1</sup>, [O<sub>3</sub>]<sub>in</sub>=45 g/m<sup>3</sup>NTP, reaction time=25min)

#### 2.2.3.2. O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>

DEP removal with O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> was investigated at different molar ratios ROF = [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>]. According to Figure 9, as ROF increased from 0.1 to 5, DEP degradation also increased significantly but a further increase to ROF=10 resulted in only little improvement. This might be attributed to increased competition between hydroxyl radicals and iron species (Equation 10) as well as reactions between ferric ions and H<sub>2</sub>O<sub>2</sub> (Equations 11-12) [59] leading to a very fast consumption of H<sub>2</sub>O<sub>2</sub> and •OH by side reactions rather than by DEP. According to the results obtained in this study, a ratio of [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] equal to 5 could suitably be selected for DEP degradation; higher ROF values will not lead to any significant improvement of DEP degradation but will rather lead to wasted materials.





**Figure 9:** Effect of ROF= $[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0$  ratio on DEP removal by  $\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+}$  (pH =7;  $[\text{O}_3]_{\text{in}} = 45 \text{ g/m}^3\text{NTP}$ )

#### 2.2.3.3. UV/TiO<sub>2</sub>

It is well established that TiO<sub>2</sub> dosage has great effect on the performance of heterogeneous photocatalytic processes [37, 60]. In this study, the effect of TiO<sub>2</sub> dosage, described by a pseudo-first-order rate constant  $k$ , after 3h of irradiation is depicted in Figure 10. The figure shows that as TiO<sub>2</sub> dosage increased from 0 to 1 g L<sup>-1</sup>, the rate constant,  $k$ , has considerably increased from almost zero to about  $9.5 \times 10^{-3} \text{ min}^{-1}$ . This increase could be explained by increased number of photocatalyst surface active sites available for the photocatalytic reaction to take place via the photoexcited holes and DEP molecules. However, as the TiO<sub>2</sub> dosage increased above 1 g L<sup>-1</sup>, the rate constant,  $k$ , was reduced. This reduction was explained by unfavourable light scattering, poor light penetration to the whole volume of solution, and loss in surface area due to agglomeration at high solid concentration [60, 61]. According to the results here, the optimal TiO<sub>2</sub> dosage for DEP degradation by photocatalysis was 1 g L<sup>-1</sup>.

**Figure 10:** Effect of TiO<sub>2</sub> dosage on the pseudo-first-order rate constant,  $k$ , of photocatalytic degradation of DEP

## 4. Conclusions

This study shows that the main mechanism for DEP oxidation is via hydroxyl radicals. This was supported by computational chemistry calculation, radical scavenger experiments, and LC/MS/MS analysis of reaction products. A carefully selected AOP could lead to complete removal of DEP at very short times. Out of the processes studied,  $\text{O}_3/\text{Al}_2\text{O}_3$  appeared as the most efficient and cheapest process for DEP removal. Overall, ozone-based AOPs have been found more efficient than the other

AOPs by several folds in certain cases. The degradation of DEP with UV or H<sub>2</sub>O<sub>2</sub> alone was poor. Ozone alone at low pHs was also not effective but as pH increased to 7 or above, the degradation of DEP by ozone alone was high (at least 70%). The Fenton process on its own was not effective for DEP removal but when combined with ozone, a significant improvement was observed. This study also showed that other operating conditions such as initial DEP concentration, ozone concentration, and catalyst dosage play significant roles in the removal of DEP. Although, the O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> process appeared as the most efficient and the cheapest in comparison to the other AOPs, more detailed cost evaluation at industrial scale in addition to considerations such as process maintainability, availability of materials and energy, skill level of operating personnel, life cycle assessment, and carbon footprint are required to be able to make proper decision on the most suitable AOP.

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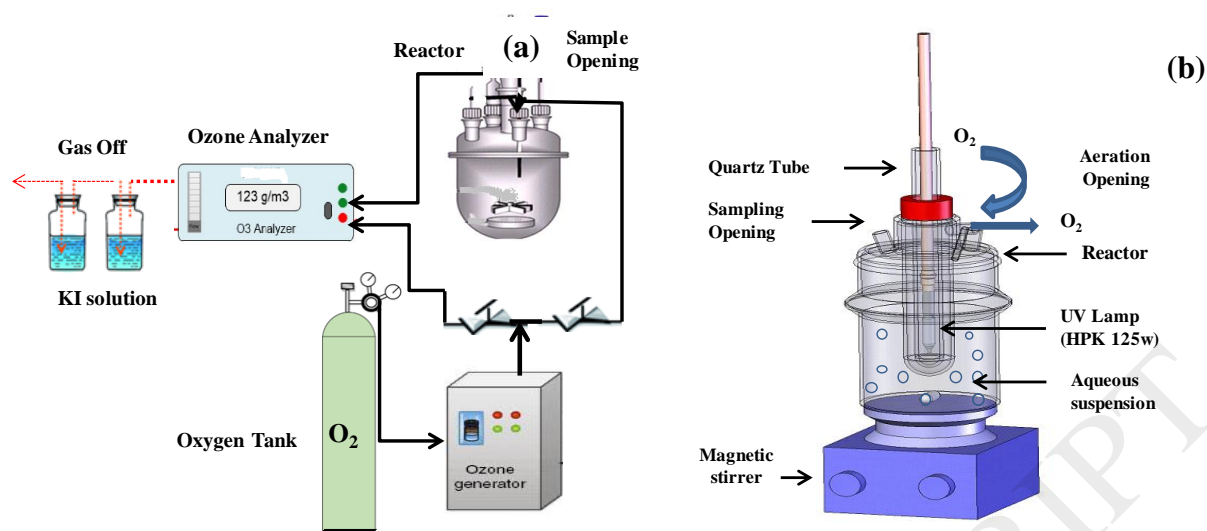
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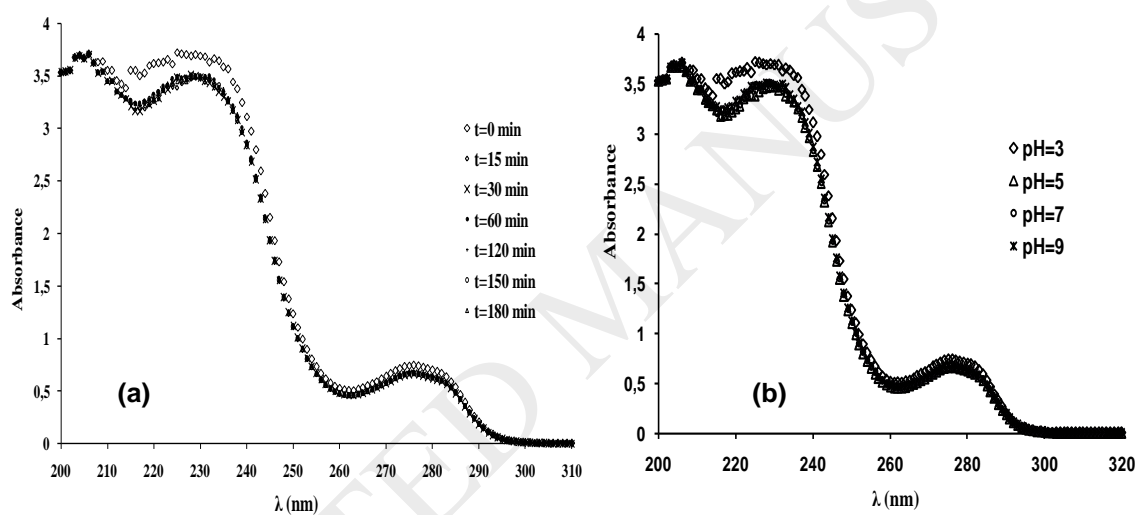
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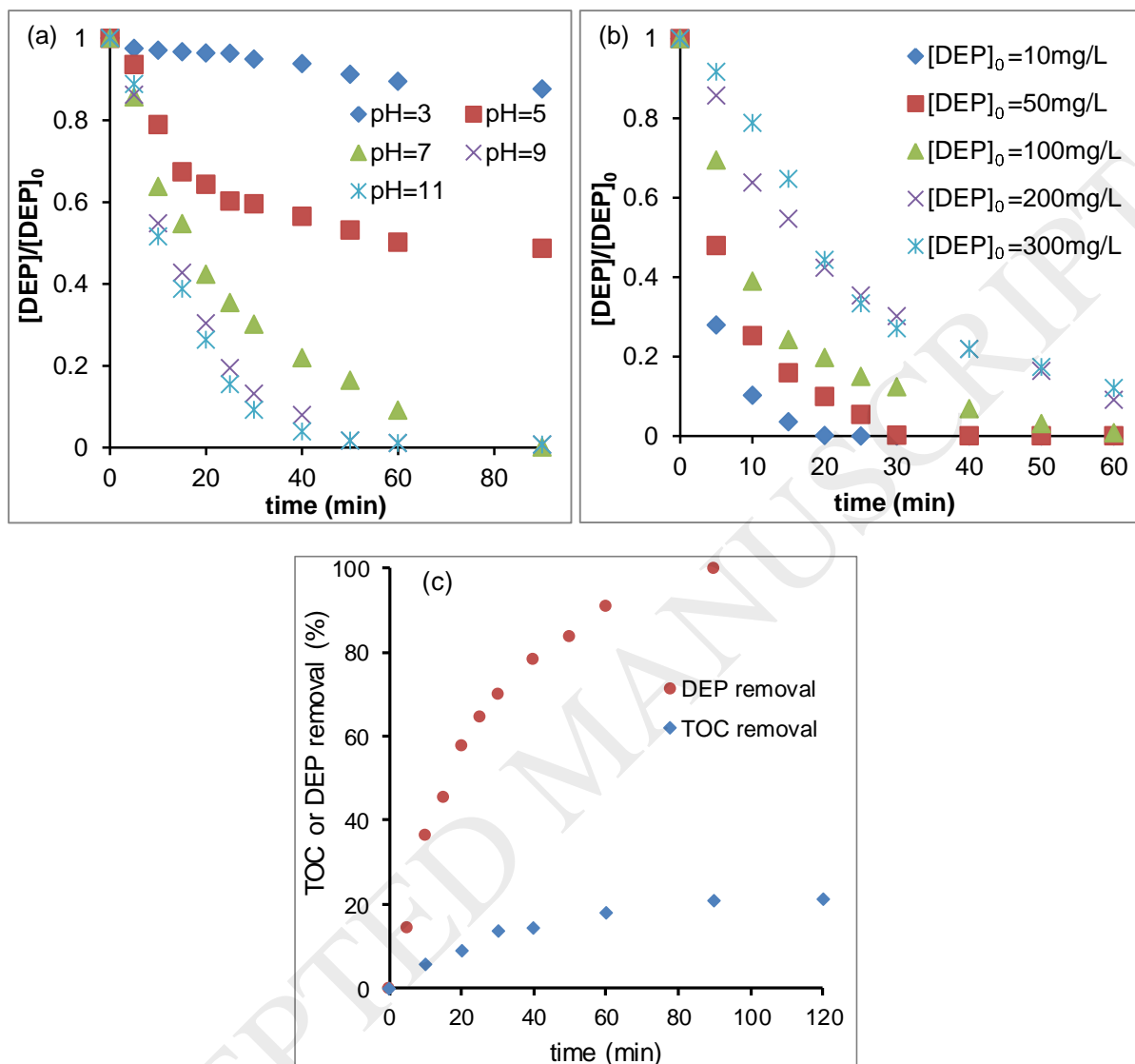
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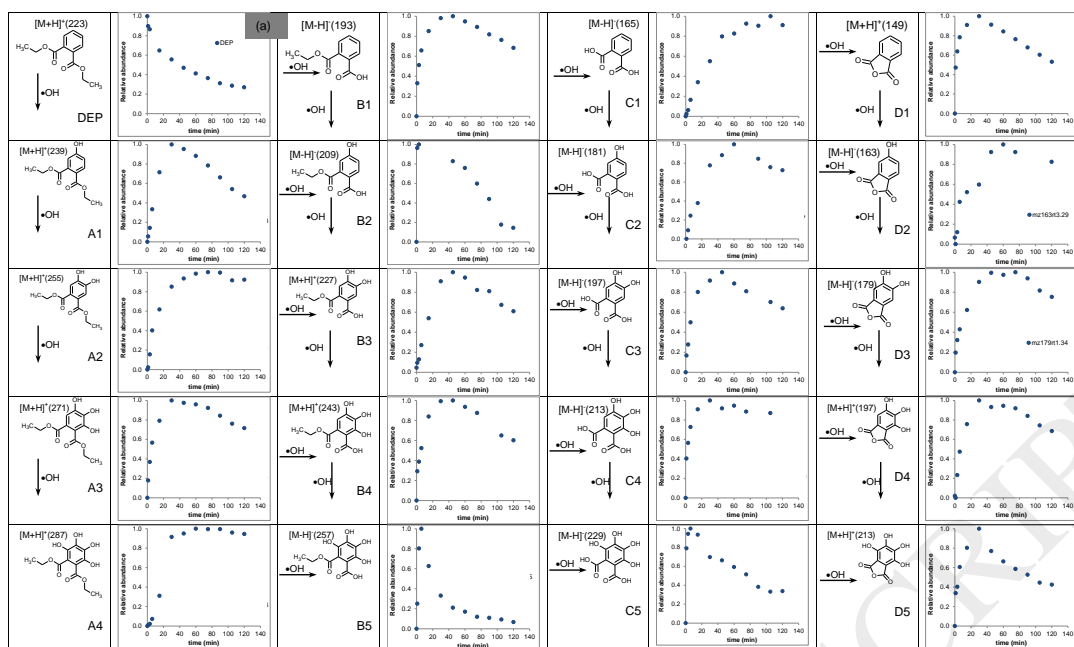
**Figure 2:** Experimental set-ups: (a) catalytic ozonation system; (b) Photocatalytic reactor with mercury UV lamp (HPK 125W)

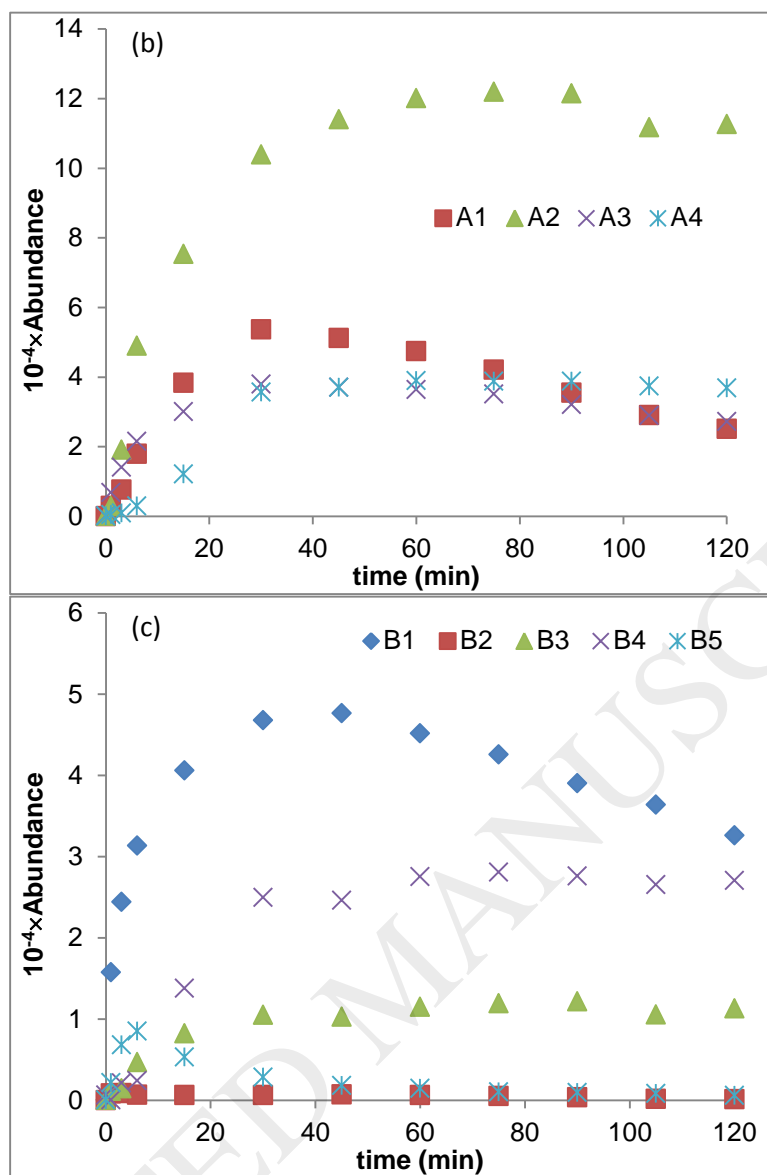


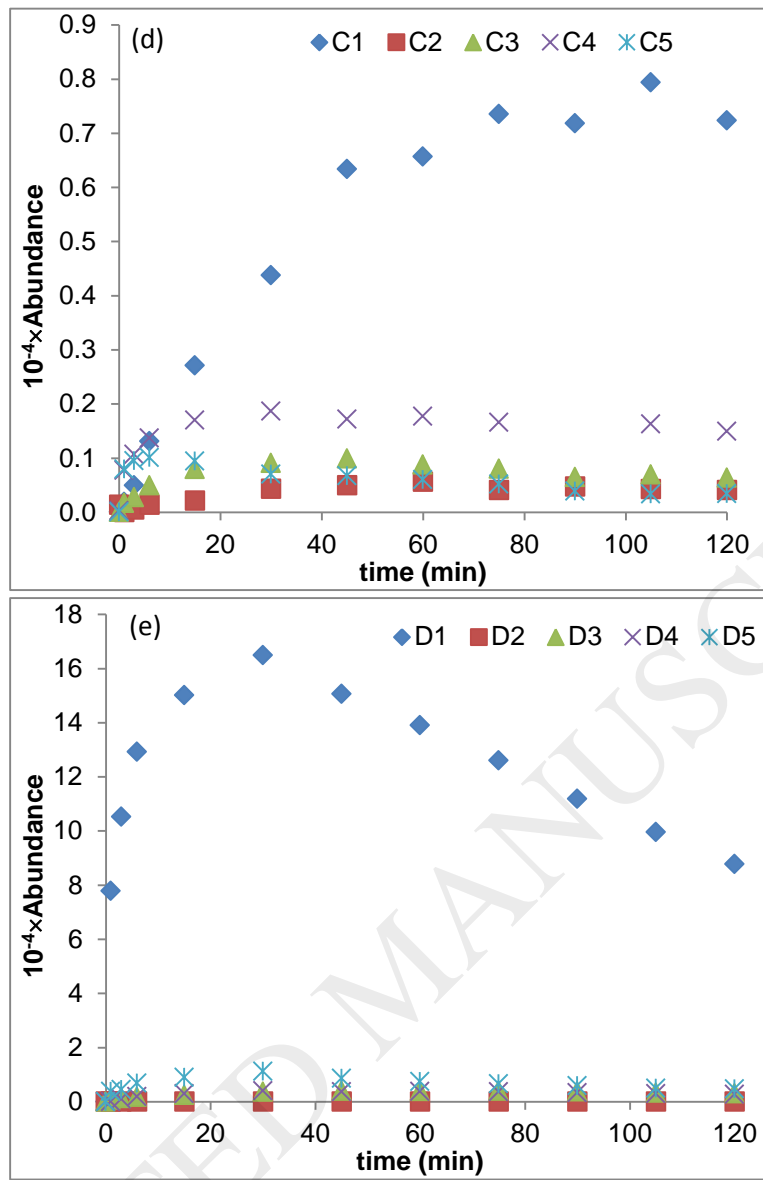
**Figure 2:** UV/Vis absorption spectra of aqueous DEP solutions during photolysis: (a) as function of time (pH=7); (b) as function of pH (irradiation time=3h)

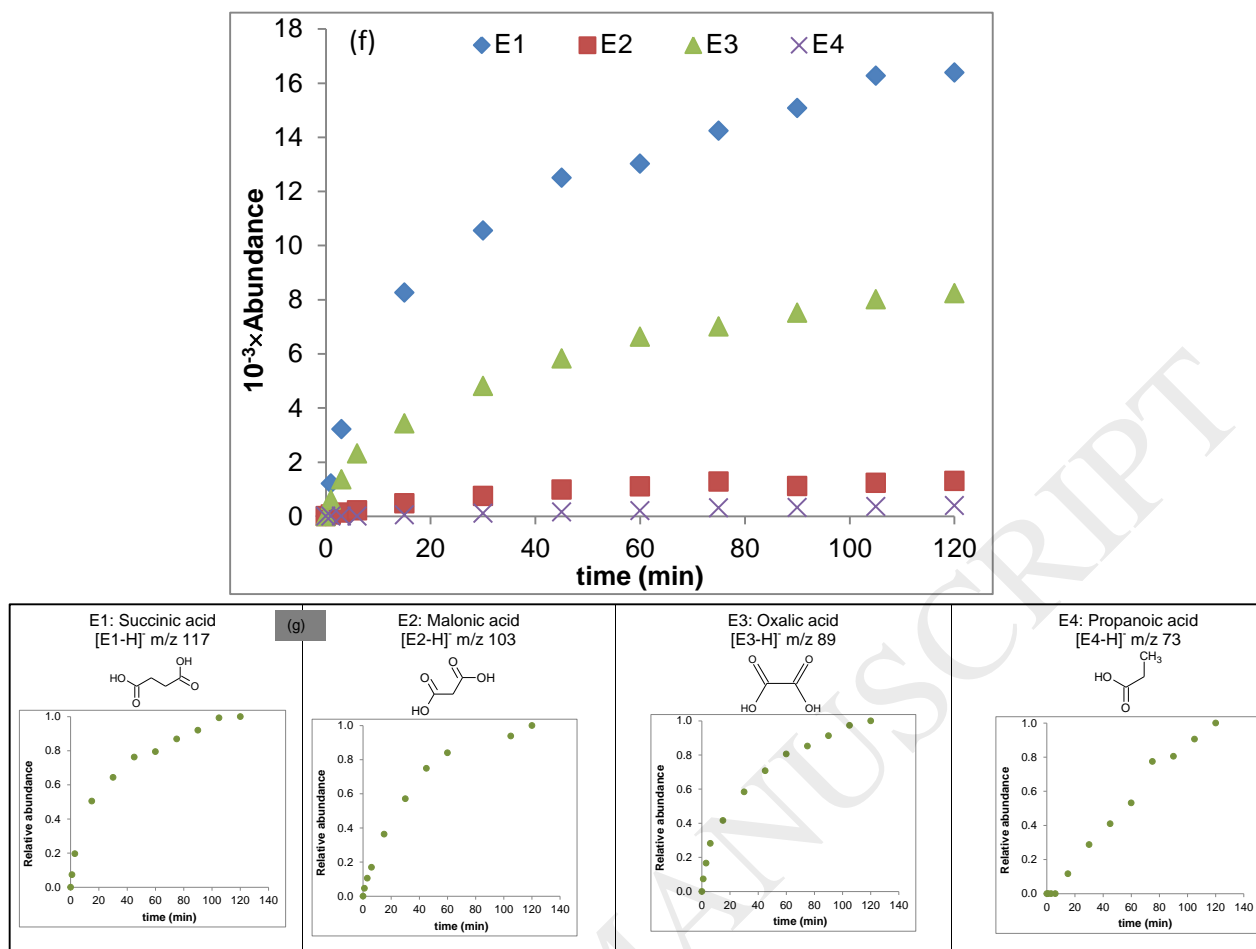


**Figure 3:** Removal efficiency of DEP by ozone: (a) At different pH values ( $[DEP]_0 = 200 \text{ mg L}^{-1}$ ,  $C_{O_3\text{liquid}} = 0.98 \times 10^{-4} \text{ M}$ ); (b): At different initial DEP concentrations ( $\text{pH} = 7$ ,  $C_{O_3\text{liquid}} = 0.98 \times 10^{-4} \text{ M}$ ); (c) Total Organic Carbon (TOC) removal ( $\text{pH} = 7$ ,  $[DEP]_0 = 200 \text{ mg L}^{-1}$ ).  $T=20\pm 1^\circ\text{C}$ .

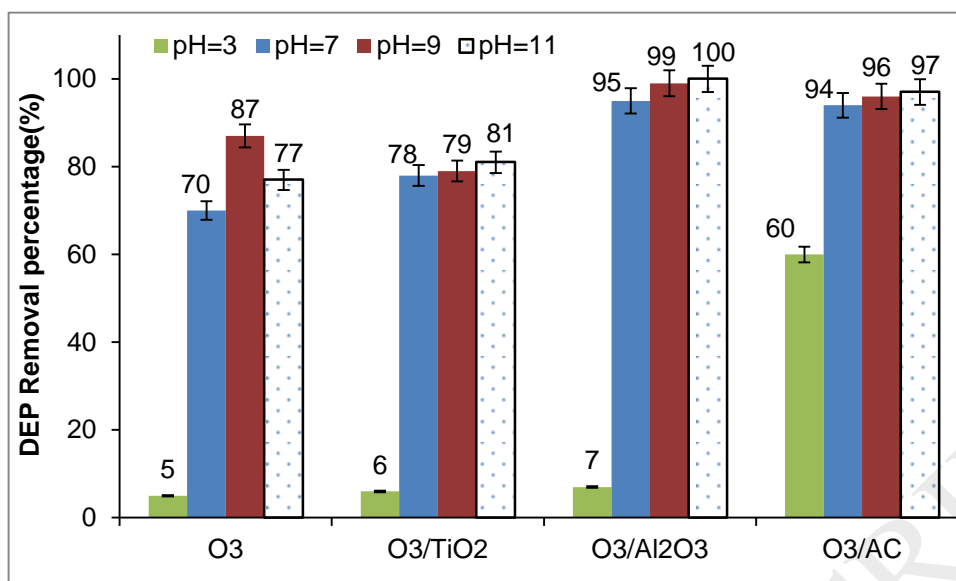






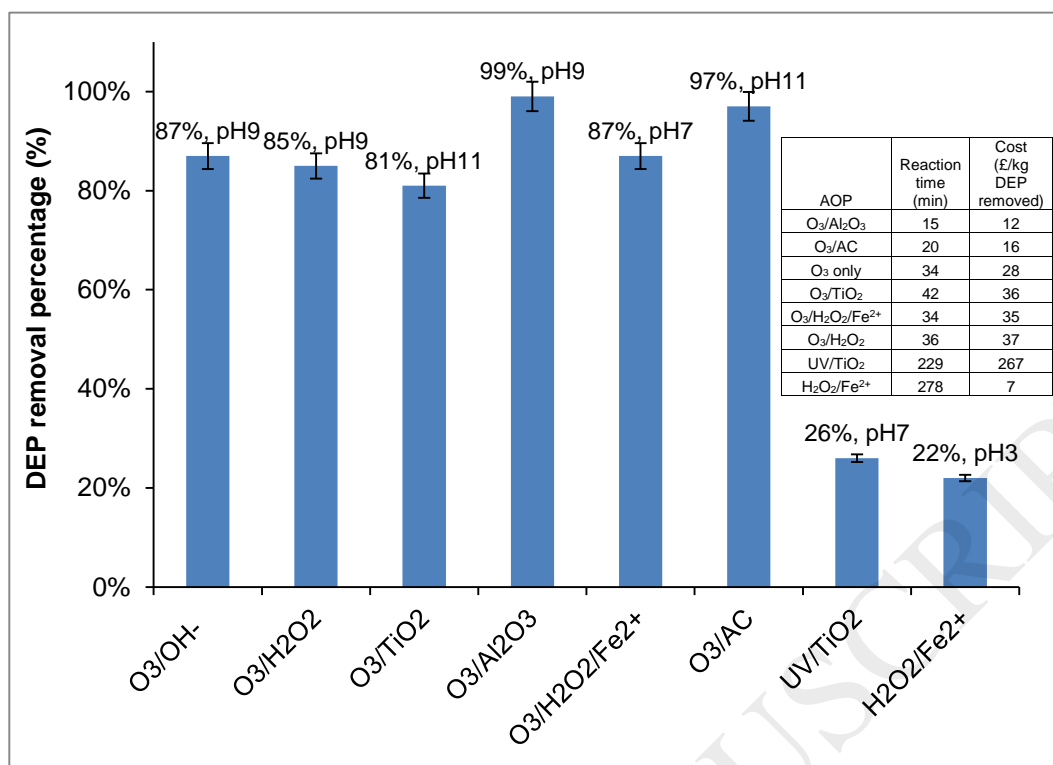


**Figure 4:** Proposed mechanism for  $\bullet\text{OH}$  attack on DEP using ozone (pH=7) and the changes of relative and absolute abundance values of each product as function of time

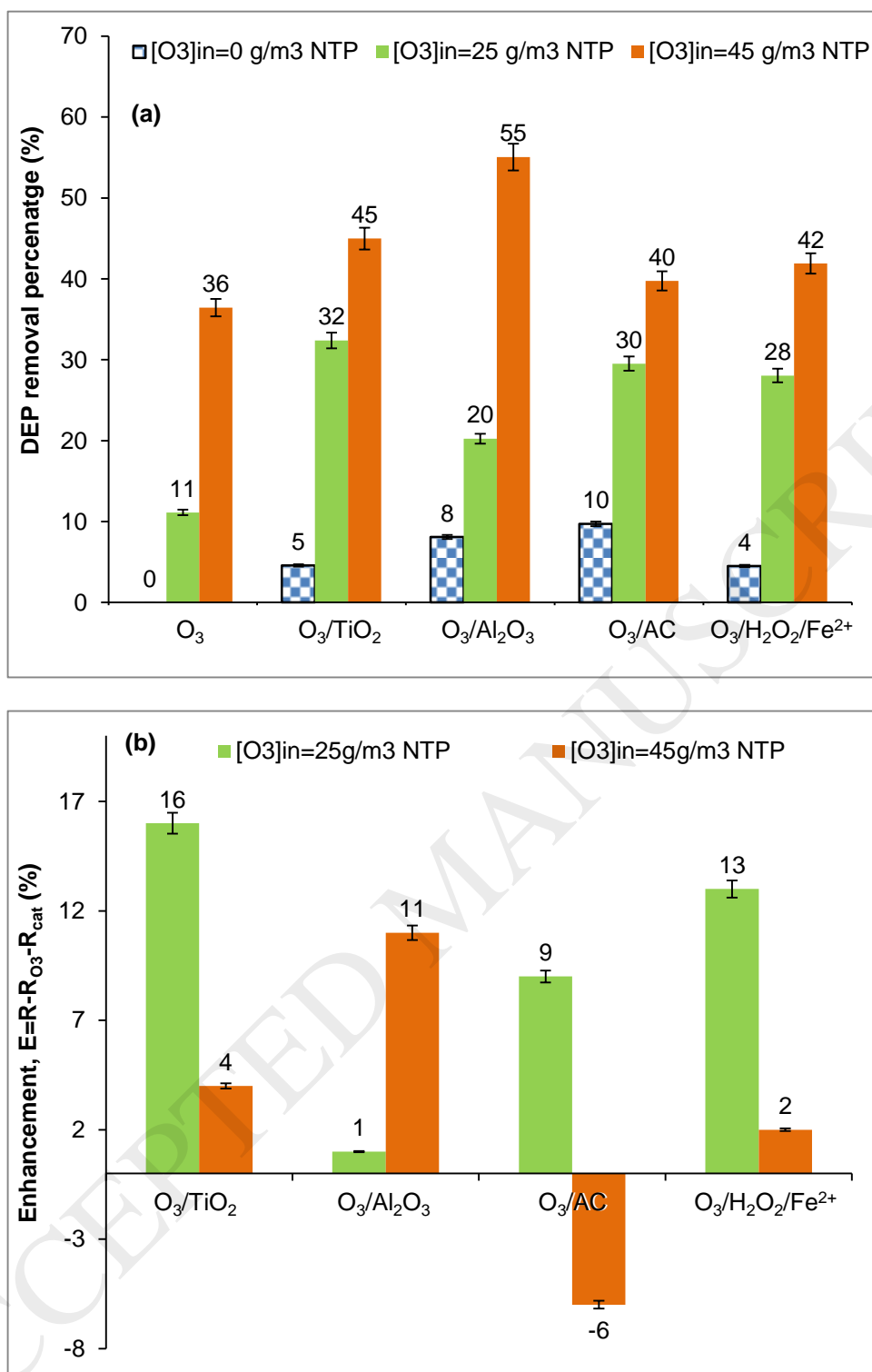


**Figure 5:** Effect of pH on the removal percentages of DEP by heterogeneous catalytic ozonation (reaction time is 30 min and the other operating conditions are as in Table 1)

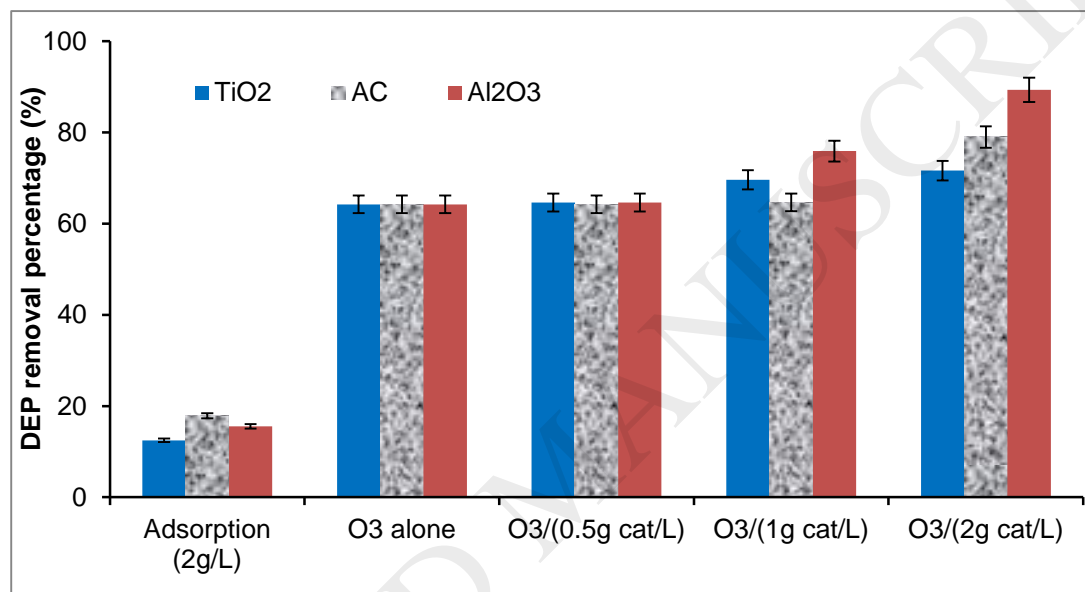




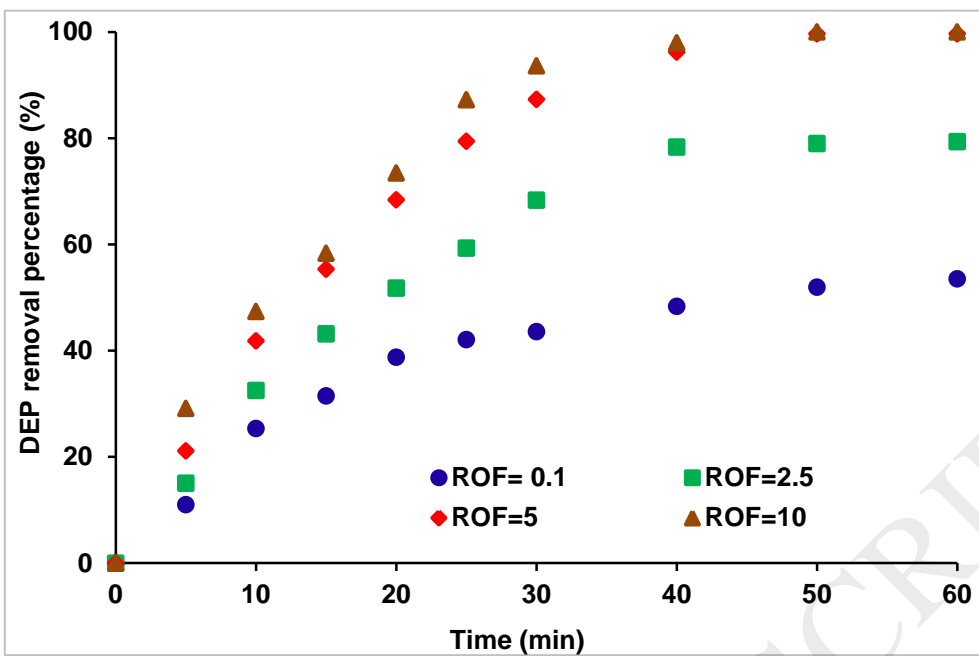
**Figure 6:** Maximum DEP removal percentages at best pH for each AOP (operating conditions are as in Table 1). Inset table: cost estimation of each AOP based on a 90% DEP removal.



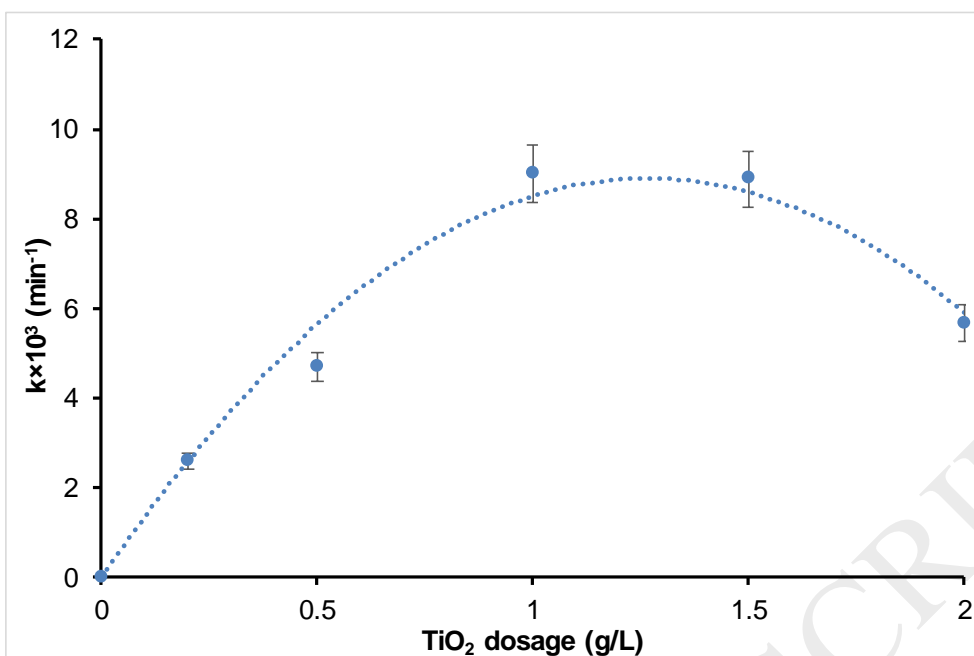
**Figure 7:** Effect of inlet ozone gas concentration  $[O_3]_{in}$  on (a) DEP removal by catalytic ozonation; (b) enhancement due to combined  $O_3$ /catalyst (pH = 7;  $[DEP]_0 = 200 \text{ mg L}^{-1}$ ; reaction time = 10 min,  $T=20\pm 1^\circ\text{C}$ ).



**Figure 8:** Effect of catalyst dosages on the removal of DEP by catalytic ozonation (pH=7,  $[\text{DEP}]_0=200 \text{ mg L}^{-1}$ ,  $[\text{O}_3]_{\text{in}}=45 \text{ g m}^{-3} \text{ NTP}$ , reaction time=25min,  $T=20\pm 1^\circ\text{C}$ )



**Figure 9:** Effect of  $ROF=[H_2O_2]_0/[Fe^{2+}]_0$  ratio on DEP removal by  $O_3/H_2O_2/Fe^{2+}$  ( $pH = 7$ ;  $[O_3]_{in} = 45 \text{ g m}^{-3} \text{ NTP}$ ,  $T=20\pm 1^\circ\text{C}$ )



**Figure10:** Effect of TiO<sub>2</sub> dosage on the pseudo-first-order rate constant, k, of photocatalytic degradation of DEP

## Tables

**Table 4 :** Comparison of DEP removal with different AOPs (reaction time=30 min, T=20±1°C)

Process	Initial pH	[DE P] <sub>0</sub> (mg L <sup>-1</sup> )	[O <sub>3</sub> ] <sub>in</sub> (g m <sup>-3</sup> NTP)	[Fe (II)] <sub>0</sub> (mol L <sup>-1</sup> )	[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> (mol L <sup>-1</sup> )	TiO <sub>2</sub> Dosage (g L <sup>-1</sup> )	Al <sub>2</sub> O <sub>3</sub> Dosage (g L <sup>-1</sup> )	AC Dosage (g L <sup>-1</sup> )	DEP removal percentage (%)
O <sub>3</sub>	pH = 2	200	45	0	0	0	0	0	1
O <sub>3</sub>	pH = 3	200	45	0	0	0	0	0	5
O <sub>3</sub>	pH = 5	200	45	0	0	0	0	0	37
O <sub>3</sub>	pH = 7	200	45	0	0	0	0	0	70
O <sub>3</sub>	pH = 9	200	45	0	0	0	0	0	87
O <sub>3</sub>	pH = 11	200	45	0	0	0	0	0	77
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	pH = 3	200	45	0	2.5 × 10 <sup>-2</sup>	0	0	0	5
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	pH = 5	200	45	0	2.5 × 10 <sup>-2</sup>	0	0	0	41
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	pH = 7	200	45	0	2.5 × 10 <sup>-2</sup>	0	0	0	81

O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	pH= 9	200	45	0	2.5×10 <sup>-2</sup>	0	0	0	85
O <sub>3</sub> /TiO <sub>2</sub>	pH= 3	200	45	0	0	2	0	0	6
O <sub>3</sub> /TiO <sub>2</sub>	pH= 5	200	45	0	0	2	0	0	19
O <sub>3</sub> /TiO <sub>2</sub>	pH= 7	200	45	0	0	2	0	0	78
O <sub>3</sub> /TiO <sub>2</sub>	pH= 9	200	45	0	0	2	0	0	79
O <sub>3</sub> /TiO <sub>2</sub>	pH= 11	200	45	0	0	2	0	0	81
O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	pH= 3	200	45	0	0	0	2	0	7
O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	pH= 5	200	45	0	0	0	2	0	19
O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	pH= 7	200	45	0	0	0	2	0	95
O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	pH= 9	200	45	0	0	0	2	0	99
O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	pH= 11	200	45	0	0	0	2	0	100
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	pH= 3	200	45	5×10 <sup>-3</sup>	2.5×10 <sup>-2</sup>	0	0	0	36
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	pH= 7	200	45	5×10 <sup>-3</sup>	2.5×10 <sup>-2</sup>	0	0	0	87
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	pH= 9	200	45	5×10 <sup>-3</sup>	2.5×10 <sup>-2</sup>	0	0	0	64
O <sub>3</sub> /AC	pH= 2	200	45	0	0	0	0	2.6	60
O <sub>3</sub> /AC	pH= 5	200	45	0	0	0	0	2.6	81
O <sub>3</sub> /AC	pH= 7	200	45	0	0	0	0	2.6	94
O <sub>3</sub> /AC	pH= 9	200	45	0	0	0	0	2.6	96
O <sub>3</sub> /AC	pH = 11	200	45	0	0	0	0	2.6	97
UV/TiO <sub>2</sub>	pH= 2	150	0	0	0	1	0	0	19
UV/TiO <sub>2</sub>	pH= 5	150	0	0	0	1	0	0	22
UV/TiO <sub>2</sub>	pH= 7	150	0	0	0	1	0	0	26
UV/TiO <sub>2</sub>	pH= 9	150	0	0	0	1	0	0	24
Fenton	pH= 3	200	0	5×10 <sup>-3</sup>	2.5×10 <sup>-2</sup>	0	0	0	22
Fenton	pH= 7	200	0	5×10 <sup>-3</sup>	2.5×10 <sup>-2</sup>	0	0	0	12
Fenton	pH= 9	200	0	5×10 <sup>-3</sup>	2.5×10 <sup>-2</sup>	0	0	0	11

**Table 5 :** Effect of DEP initial concentration on removal percentages by each AOP (reaction time=15 min, pH=7, other operating conditions are as in Table 1)

[DEP] <sub>0</sub> (mgL <sup>-1</sup> )	O <sub>3</sub> alone	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> /TiO <sub>2</sub>	O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	O <sub>3</sub> /AC	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	UV/TiO <sub>2</sub>
<b>10</b>	84	98	100	100	100	100	44

<b>50</b>	69	79	86	97	88	86	30
<b>100</b>	57	65	71	90	68	69	25
<b>200</b>	45	51	53	71	64	55	9

**Table 6 :** Overall pseudo-first-order rate constants ( $k_{overall}$ ) ( $[DEP]_0=200 \text{ mg L}^{-1}$ ;  $[O_3]_{in}=45 \text{ g m}^{-3}$  NTP,  $\text{pH}=7$ ,  $T=20\pm 1^\circ\text{C}$ )

Process	$k_{overall} (\text{min}^{-1})$
O <sub>3</sub> alone	0.039
O <sub>3</sub> /AC	0.069
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	0.053
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup>	0.076
O <sub>3</sub> /TiO <sub>2</sub>	0.050
O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.093
UV/TiO <sub>2</sub>	0.009