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Catalytic ozonation of model organic compounds in aqueous solution promoted by metallic oxides

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ABSTRACT

Removal of Diethyl phthalate (DEP) from water has been accomplished through catalytic ozonation promoted by TiO_2 and Al_2O_3. A laboratory setup was designed to evaluate and select the optimal oxidation process. The degradation rate is strongly dependant on the pH, initial concentrations of the phthalate, catalyst dosage, and O_3 dosage. The effect of these parameters has been studied. Results show that the addition of Al_2O_3 was effective to achieve almost 95% degradation of DEP in about 30 min using 2 $g\,L^{-1}$ as compared to over 50 min with TiO_2. It was also found that radical reactions were the main mechanism by which DEP was degraded and adsorption has a small contribution to the removal of DEP by O_3/TiO_2 and Al_2O_3 processes. Indeed, after 60 min, adsorption alone achieved only about 12.5 and 15.5% removal, respectively, in the presence of TiO_2 and Al_2O_3. Under same conditions, the kinetics of degradation was found to follow first-order reaction rules for both systems. After 1 h treatment, the rate constant of DEP removal were 0.0093 and 0.053 min^{-1} using O_3/AlO_3 and O_3/TiO_2 processes, respectively. The O_3/Al_2O_3 system proved to be the most efficient and occurs at a much higher oxidation rate than O_3/TiO_2 system and allows achieving 100% degradation of DEP (100 $mg\,L^{-1}$) in 25 min of reaction time. The notable decrease of DEP removal rate observed in the presence of radical scavenger tert-butanol indicates that the reaction between DEP and $OH^{\bullet}$ proceeds mainly in the bulk of the aqueous phase. The results of the study showed that O_3/TiO_2 and O_3/Al_2O_3 systems were effective and economic treatment processes for DEP under neutral conditions by producing higher mineralization efficiency in a relatively short ozonation time compared to ozone alone process.

Keywords: Catalytic ozonation; Diethyl phthalate; Degradation; TiO_2; Al_2O_3; catalyst

1. Introduction

The occurrence of emerging contaminants such as phthalic acid esters in the wastewater that comes from urban sewage and factories is a topic of great concern today [1,2]. Large amounts of phthalates are often leached from the plastics that are dumped at municipal landfills [3,4]. Among them, diethyl phthalate (DEP) can be highlighted, since even at very low

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concentrations its influence in the aquatic environment can be hazardous [2,3,5]. In fact, DEP is one of the important molecules in the family of phthalate esters which has wide industrial applications and is recognized to be an estrogenic chemical that cause endocrine disruption in humans [2,5,6,7]. DEP was reported to be the major proportion of micro-pollutants in the Han River that runs through Seoul, South Korea over a five-year period [8]. Therefore, DEP was chosen as a model pollutant of phthalates compounds because of its high water solubility (1,080 $mg\,L^{-1}$ at 293 K) and toxicity [9]. Several studies have shown that DEP is difficult to degrade biologically or photochemically [8,10]. Hence, to reduce its potential harmful effects on humans and the environment, it is important to degrade and remove phthalate esters from wastewaters before discharge in the environment using better and more effective treatment methods. In recent years, advanced oxidation processes (AOPs), which generate hydroxyl radicals ($^{\bullet}OH$) are a promising tool for the removal of a great variety of organic contaminants [11–15], at an acceptable cost (for e.g. 0.05–0.20 per m^3 for ozonation) [16]. Indeed, a number of AOPs including UV/H_2O_2 [17], $UV/H_2O_2/Fe^{2+}$ [5], and photocatalytic [18–20] processes have been studied and found effective for the degradation of DEP. Although, the reaction of DEP with molecular ozone was found to proceed at low rates [11,16]. Activated carbon (AC) adsorption is a relatively simple, economic, and appropriate process for removing organic compounds from drinking water. It has been observed that a hybrid process combining the high oxidation capacity of ozone and the high adsorption capacity of AC can be a fairly efficient process comparing with the conventional AOPs [5,14]. The DEP has been also decomposed by a combined system using both ozone and AC [21,22]. The enhancement was caused by the AC which acted as $HO\bullet$ radical initiator and promoter rather than adsorbent [12,14,16,20,23–29]. However, several studies reported that the degradation of organic pollutants in aqueous solution through ozonation with heterogeneous catalysts, such as metallic oxides, is another alternative to improving the removal effectiveness of the recalcitrant pollutants [25,30]. Moreover, water treatment catalysts are limited by their high cost and reuse. Thus, alternative catalysts should be investigated. Consequently, the lower cost and the reclamation make catalyzed ozonation in the presence of metal oxides more preferable in water treatment [14,31,32]. The main catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides (MnO_2, TiO_2, Al_2O_3) and also metals or metal oxides on metal oxide supports (e.g. $Cu–Al_2O_3$, $Cu–TiO_2$, $Ru–CeO_2$, $V–O/TiO_2$, and TiO_2/Al_2O_3, Fe_2O_3/Al_2O_3) [31,32]. The catalytic activity of the catalysts mentioned is mainly based on the catalytic decomposition of ozone and the enhanced generation of hydroxyl radicals [14]. However, the knowledge about the pathway and the mechanism of catalyzed ozonation were not clear. The mechanism of some catalytic ozonation reactions is not well developed, because of the lack of the experimental data in published work and complexity of the process. Furthermore, a particular catalyst is only active under certain condition and in the form of particular groups of organic compounds to be oxidized. Therefore, the generalization concerning the mechanism of the catalytic ozonation is difficult. Consequently, the current study aims at investigating the effectiveness of cooperatively employing O_3/metallic oxide in phthalate treatment. A new treatment process (O_3/ metallic oxide) is introduced by employing the TiO_2 and Al_2O_3 in the ozonation process for the elimination of DEP, chosen as model contaminant of aqueous medium. The aim of this research was to systematically investigate the removal of DEP in water when treated with ozone catalyzed by metallic oxides (TiO_2 and Al_2O_3). The scope is twofold. First, the focus is put on the effect of operational variables on DEP removal and on the ozone consumption. To the author's best knowledge, compared to the previous studies, this study successfully presented a TiO_2 and Al_2O_3 catalysts to obtain a distinguished improvement on the mineralization of DEP and its derivatives in the catalytic ozonation process. The TiO_2 Degussa (P25) and commercial Al_2O_3 catalysts were applied to catalyze the ozonation of DEP. The effect of the catalytic ozonation conditions, such as the inlet ozone concentration, pH, DEP concentration, metallic oxide dosage, and inlet ozone concentration, which may affect the efficiency of O_3-metallic oxide reactions. Second, kinetic in order to achieve optimum operational conditions, which will allow economic reactor design, process control, economical capital, and operational cost.

2. Experimental

2.1. Reagents

Diethyl phthlate DEP (CAS No. 84-66-2) has as formula $C_{12}H_{14}O_4$ (Fig. 1), in the purest form 99.5%, is available from Merck Chemical. Table 1 presents the physicochemical characteristics of DEP. The commercial Al_2O_3 catalyst (CAS No. 1344-28-1), was obtained from Sigma Aldrich (Sigma Aldrich, Germany) [33]. The used commercial alumina has a pHzc value between 9,4 and 10,1 (at 20˚C). Table 2 represents the characteristics of the two used catalysts. Used TiO_2 (P25) consists of 80% anatase and 20% rutile.

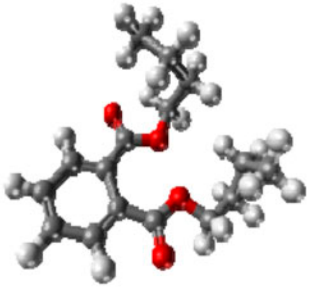

Fig. 1. Molecular structure of DEP.

Table 1
Properties of DEP

Compound	Mass molar ($g\,mol^{-1}$)	Solubility ($mg\,L^{-1}$)	Log Kow
Diethyl phthlate (DEP)	222.2	110	2.65

The pH of the phthalate solution was adjusted by using hydrochloric acid or sodium hydroxide (Merck). Tert-butanol (TBA) (CAS No. 75-65-0) which has as formula $C_4H_{10}O$ was obtained from Fisher Scientific (Fisher Scientific, Germany) and used as a radical scavenger since it is the well-known radical scavenger used in ozone studies [28,34]. Other chemicals used in this study were potassium indigo trisulfonate (Sigma Aldrich, Germany): ozone quenching reagent and acetonitrile (Fisher Scientific, Germany): HPLC mobile phase. All reagents employed were not subjected to any further treatment. Purified water was obtained using a MilliQ system (Millipore) and had a resistivity of 18.2 MΩ cm.

2.2. Laboratory setup

All experiments (ozonation chemical oxidation alone and catalyzed by metallic oxides) were performed in a well stirred, semi-batch, cylindrical glass reactor with a total volume of 2 L (Fig. 2).

The reactor fed with ozone in oxygen through a glass sinter gas diffuser. A magnetic stirrer was used to ensure well mixing in the reactor and prevented gas bubble coalescence. Ozone was produced using a SORBIOS generator (SORBIOS, Germany) fed by dry pure oxygen and its concentration was measured using an ultraviolet gas ozone analyzer (BMT 964) based on the absorbance at 254 nm. At the top, the reactor has inlets for feeding ozone and ports for withdrawing samples. Off-gas ozone was washed with KI (Potassium iodide) solution (2%) before being exhausted to the fume hood and the whole experimental system was placed under a fume cupboard. The gas flow rate was maintained constant and the input ozone concentration (C_{AGin}) was about 45 g m^{-3} NTP. All experiments were conducted at room temperature of 20 ± 1°C.

2.3. Experimental procedure and analytical methods

For every experiment conducted, the reactor was filled with 1 L of DEP aqueous solution at the desired initial concentrations. Aqueous solutions at different initial DEP concentrations C_0 (max. 200 mg L^{-1}) were used. Before catalytic ozonation experiments, suspensions of TiO_2 and Al_2O_3 (catalyst dosage max. 3 g L^{-1}) in the DEP solution were stirred 30 min at 20 ± 1°C, a sufficient time to reach DEP equilibrium concentration. Assuming that adsorption–desorption of substrate and reaction intermediates is relatively slow in comparison to the radical reactions via $OH^{\bullet}$, we suppose that the oxidation reactions to adsorption onto TiO_2 and Al_2O_3 surface of the DEP are limited [24,27]. After mixing DEP solution with a pre-determined amount of the metallic oxide particle in a glass reactor, the mixture was maintained in suspension by a magnetic stirrer. The pH values of the suspensions were adjusted to the desired values (from neutral pH

Table 2
Chemical/physical characteristics of used catalysts

	TiO_2 Degussa P25	Al_2O_3
Appearance	White solid	White solid
Molar mass ($g\,mol^{-1}$)	79.86	101.96
Density ($g\,cm^{-3}$)	3.8	3.9
*Surface area BET ($m^2\,g^{-1}$)	55	0.5–50 $m^2\,g^{-1}$
Particular size (nm)	30	21
pH_{PZC}	6.2–7.5 at 20°C	9.4–10.1 (at 20°C)

*Surface area BET: surface area determined by: (Brunauer–Emmett–Teller) Method.

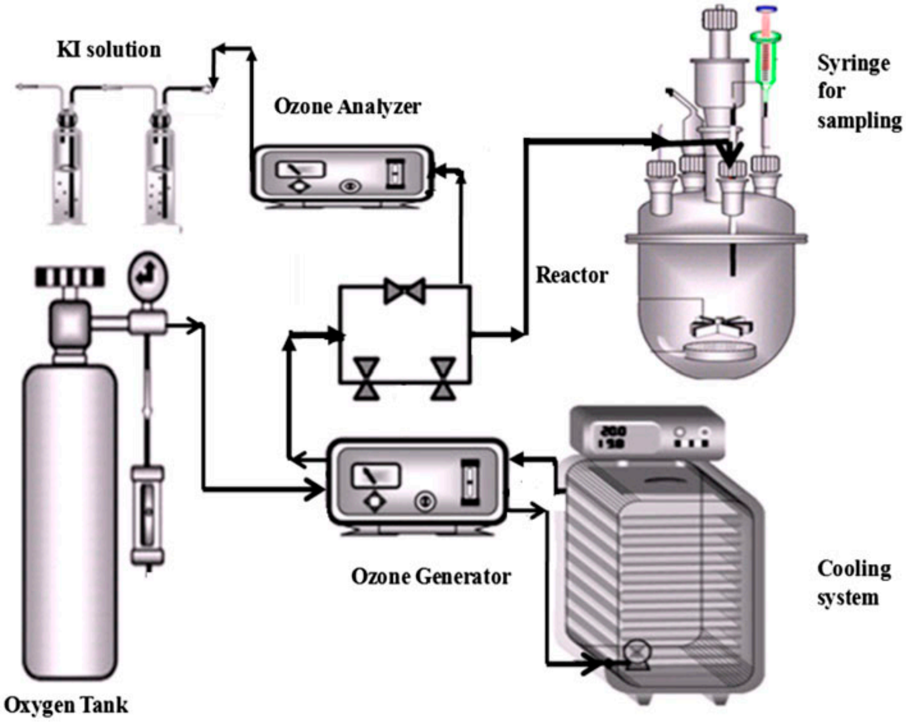

Fig. 2. Experimental set-up of ozone/metallic oxide system.

to pH 3 or pH 11) using 0.1 M HCl or NaOH. The time at which the reactor was fed with ozone was considered time zero or the beginning of the experiment. The total volume of the suspension in the reactor was 1 L for all cases. The samples were withdrawn with a syringe at given time intervals in the course of the experiments, a volume of 1 mL of sample was immediately introduced into 100 μL of a sodium thiosulfate solution $Na_2S_2O_3$ (0.1 M) to quench the O_3 reaction and filtered through 0.45-μm Teflon syringe filters to minimize any continuing adsorption of DEP after sampling. Samples were stored at 4°C for subsequent analyses. In some experiments, the radical scavenger TBA was added to the solution at DEP concentration of 200 mg L^{-1}. Samples were collected at regular time intervals and the total sampling volume was less than 5% of the experimental solution. The samples were then analyzed by the HPLC and further analyses were carried out using an Agilent 1050 HPLC (Agilent Technologies, USA) equipped with a 79855A 21—Vial auto sampler, a G1303A Vacuum Degasser, a 79853C Variable Wavelength UV detector, and a 79852A Quaternary Pump. The UV detection wavelength was 228 nm. A Gemini-NX C18 column (250 mm × 4.6 mm, i.d. 5 μm) was used. The mobile phase involves an isocratic 65% acetonitrile: 35% water at a flow rate of 1 mL/min and the injection volume was 20 μL in all samples. All experimental solutions were prepared with deionized water without other buffers.

3. Results and discussion

3.1. Removal efficiency of DEP

The DEP removing experiments of the 200 mg L^{-1} DEP in aqueous solution were performed on the adsorption on TiO_2 and Al_2O_3, conventional ozonation ((1) DEP+O_3), and catalytic ozonation, ((2) DEP+O_3+Al_2O_3 and (3) DEP+O_3+TiO_2) as shown in Fig. 3. As expected (Fig. 3(A)), the adsorption of DEP on both catalysts was insignificant (<16%), which may be due to the molecular size and steric hindrance of DEP [19]. In fact, the lowest DEP degradation efficiency appears with adsorption on Al_2O_3 and TiO_2, resulting in the removal of only 15.5 and 12.5%, respectively, of the initial DEP after 30 min. Compared with ozonation alone and that of the catalytic ozonation processes, the adsorption of DEP after 30 min is too small to contribute significantly to the degradation efficiency of DEP and can therefore be neglected.

In addition to the adsorption results, Fig. 3(B) shows how the ozone worked as oxidant agent during the DEP degradation. The conventional ozonation (without catalyst) and catalytic ozonation in presence

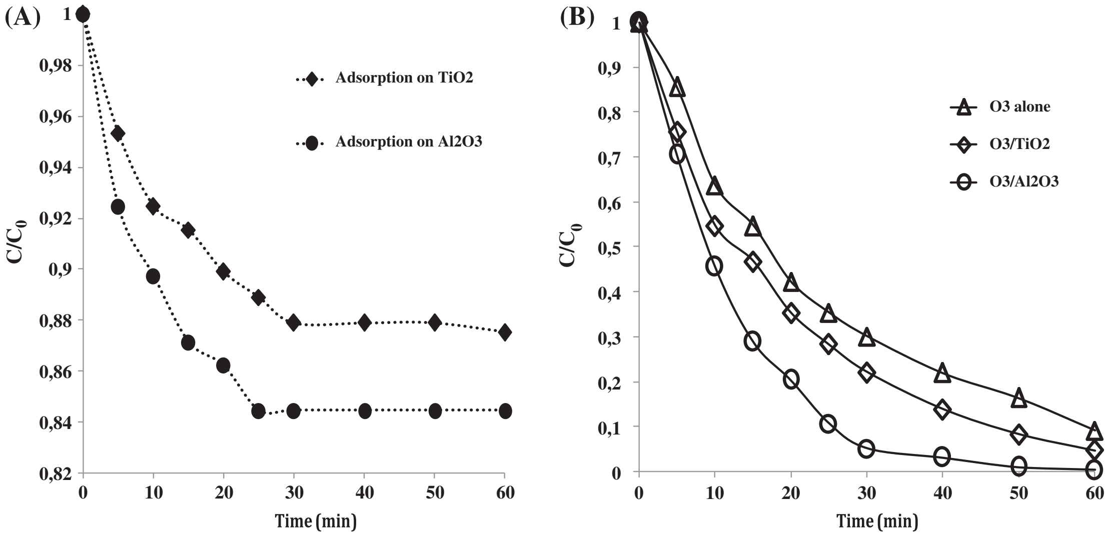

Fig. 3. Degradation efficiency of DEP in the different processes (pH 7, $C_0 = 200\ \mathrm{mg\ L^{-1}}$, $C_{\mathrm{Gin}} = 45\ \mathrm{g\ m^{-3}}$ NTP; [TiO_2] = 2 g L^{-1}); [Al_2O_3] = 2 g L^{-1}).

of TiO_2 and Al_2O_3 showed the same behavior. From the results, it is possible to observe that the removal of DEP with ozone alone after 5 min of reaction time proceeds at slow degradation rate compared to catalytic ozonation processes. It can be due to the presence of Al_2O_3 and TiO_2 in the reaction medium yielding only 9 and 5% of ozone decomposition, respectively. On the other hand, the presence of ozone in the aqueous solution leads to the decrease of DEP concentration when reaction time increases. The presence of metallic oxide catalysts significantly enhanced the degradation efficiency of DEP and the best result was obtained when Al_2O_3-catalyzed ozonation was used. In TiO_2/O_3 process, the presence of TiO_2 did not improve DEP removal (78% at 30 min oxidation time), which was lower than that in Al_2O_3/O_3 process (95% at 30 min oxidation time), because the presence of TiO_2 nanoparticles slows the transference of ozone in water.

Furthermore, as shown in Fig. 3(B), DEP is immediately decomposed in the early period of the catalytic ozonation. The degradation rate of DEP was almost identical in the presence or absence of the two catalysts because the initial oxidation of DEP was easily carried out via the direct ozonation [29]. It is well known that ozone may either react directly with organic compounds or indirectly generate $^{\bullet}$OH to dominate subsequent oxidation reactions. In the first case, ozone, one of the most powerful oxidants, favorably attacks the functional groups with high electron density due to the resonance structures of molecular ozone. Thus, DEP is hardly oxidized by ozone alone, due to the electron-withdrawing properties of COO^- groups. In the second case, the decomposition of ozone produces $^{\bullet}$OH via a chain reaction and the oxidizing potential of $^{\bullet}$OH is much higher than that of molecular ozone, which is considered unselective and more reactive toward organic compounds [21,22,34,35].

On the other hand, the removal effectiveness of catalytic ozonation in the presence of aluminum oxide was higher than that of ozonation alone, TiO_2/O_3 and adsorption on catalysts. In fact, since the surface hydroxyl groups of solid metal oxides were the active site of catalytic ozonation reaction [24], the surface charge status of surface hydroxyl groups determinates the catalytic activity in the catalytic ozonation of DEP. According to literature [24], the catalytic activity of the aluminum oxides was related to highly hydroxylated surface. The surface hydroxyl groups on the aluminum oxides were the active sites in catalytic ozonation of DEP. The higher density of surface hydroxyl groups and the stronger Brønsted acidity of the surface of Al_2O_3 compared to TiO_2 can remarkably enhance the catalytic activity. Moreover, another advantage of using the Al_2O_3 catalyst in the catalytic ozonation of DEP is easy to recover, while it is not the case when TiO_2 is used due to the small particle size of Degussa P25 TiO_2.

3.2. Effect of initial pH

The influence of initial pH on DEP degradation efficiency in aqueous solution was investigated during ozonation alone (Table 3) and metallic oxide-catalyzed ozonation (shown in Fig. 4). For all studied systems, the results show that DEP was removed by ozonation but the degradation kinetics depended strongly on pH. Remarkably, at pH = 3, ozonation alone did not remove DEP (only 4% removal after 1 h), even when metallic oxides catalysts were used, an insignificant removal was also observed (6 and 7% removal, respectively, using TiO_2 and Al_2O_3, after 1 h). On the other hand, when the pH increased to seven and then up to 11, the removal of DEP has significantly increased in all studied systems (over 60% DEP removal rate in all systems (Table 1)). At low pH, radicals play a minor role in the overall ozone reactions due to the low concentration of hydroxide ions and the decomposition of aqueous ozone is slow [29]. Due to the fact that DEP molecule has a non-dissociating structure, the efficiency of DEP removal depends only on the ozone actions at the different pH values. This suggests that radical reactions are the main pathway for DEP removal since the formation of hydroxyl radicals as a result of ozone decomposition by $^{\bullet}OH$ is enhanced at high pH [35]. Fig. 4 shows also the degradation efficiency of DEP in aqueous solution is greatly enhanced by increasing pH from 3 to 7 in O_3/TiO_2 and O_3/Al_2O_3 systems at an initial DEP concentration of 200 mg L^{-1}.

Table 3
Effect of initial pH on DEP removal rate after 20 min, in different processes

	O_3 alone	O_3/TiO_2	O_3/Al_2O_3
pH = 3	3.7	6	7.1
pH = 7	64.6	71.6	89.3
pH = 11	84.6	73.8	99.2

According to Fig. 4, the degradation efficiency of DEP in aqueous solution in O_3/TiO_2 system was 71.62% and that in O_3/Al_2O_3 ozonation system was 89.34% at pH = 7. However, when the pH solution was decreased to 3.0 by adding chloric acid, the degradation efficiency of O_3/TiO_2 and O_3/TiO_2 ozonation system was reduced to 6.08, and 7.10%, respectively (Table 3). In contrast, when the pH of the solution was raised to 11, the degradation rate of DEP in O_3/TiO_2 process was similar to that at neutral pH. Under the same experimental conditions, the degradation rate of the Al_2O_3-catalyzed ozonation system increase and was almost 100% in only 25 min.

Experimental result shows that for the higher solution pH (pH = 11), the higher degradation rate was observed (99% in 20 min using Al_2O_3 catalyst). When the solution pH was near the pH_{pzc} of the aluminum oxide (pH_{pzc} of the commercial Al_2O_3 (Sigma–Aldrich)) range between 9.4–10.1 [33]), higher activity was observed in the catalyzed ozonation process, wherein the relative $^{\bullet}OH$ concentration was much higher than in the ozonation process alone (Table 3). It is concluded that when the solution pH is close to pH_{pzc} of the aluminum oxide, the oxide exhibits the maximum effect on ozone. Therefore, and during the O_3/Al_2O_3 process, as a non-dissociation compound, DEP cannot be chelated on the surface of aluminum

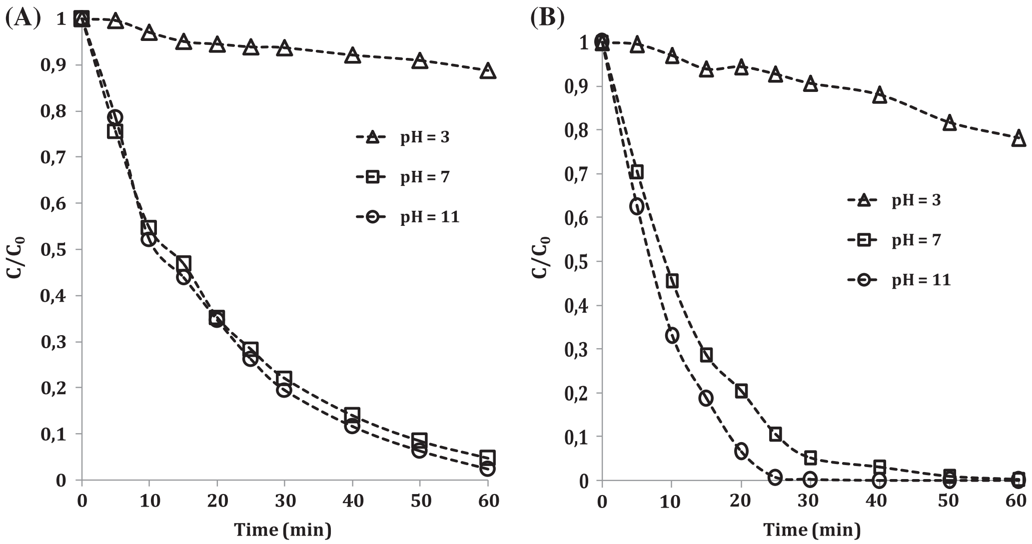

Fig. 4. Effect of solution pH on DEP removal ($C_0 = 200$ mg L^{-1}, $C_{AGin} = 45$ g m^{-3} NTP): (A) O_3/TiO_2 (TiO_2 dose = 2 g L^{-1}) and (B) O_3/Al_2O_3 (Al_2O_3 dose = 2 g L^{-1}).

oxide. Therefore, the adsorption reaction between DEP and aluminum cannot influence the effects of solution pH on catalytic ozonation of DEP. Moreover, the highly basic character of the used Al_2O_3 (pH between 9.4 and 10.1) [27] may have a significant effect in initiating ozone decomposition at neutral or basic medium, but also in improving molecular ozone adsorption on the catalyst surface (The highest DEP removal rate was observed at pH = 11 (Table 3)).

In the case of O_3/TiO_2 system, the results showed that neutral pH favored the DEP removal. The increase of initial pH up to 7 has no effect on the DEP degradation efficiency. This behavior is due to the fact that adsorption of DEP on TiO_2 particles is limited. Previous work [19], showed that after 30 min, the adsorption amounts of DEP by TiO_2 particles ($1\ g\,L^{-1}$) at pH 3, 7, and 10 were 8.1, 12.5, and 10.6%, respectively.

Moreover, it is well established that upon hydration, the TiO_2 surface develops hydroxyl groups, which can undergo a proton association or dissociation reaction:

$$\equiv TiOH + H^+ \Longleftrightarrow \equiv TiOH_2^+; \quad \text{at pH} < pH_{zpc}$$

$$\equiv TiOH + OH^- \Longleftrightarrow \equiv TiO^- + H_2O; \quad \text{at pH} > pH_{zpc}$$

where $\equiv TiOH_2{}^+$, $\equiv TiOH$ and $\equiv TiO^-$ are positive, neutral, and negative hydrous TiO_2 surface functional groups, respectively. Since DEP is a kind of unionizable compound, the adsorption density is consistent with the concentration of the surface sites $\equiv TiOH$ that can support the adsorption of DEP. It implies that DEP will be adsorbed by the greatest extent on catalyst surface under conditions in which $pH = pH_{zpc}$. In our case TiO_2 (P25), the pH_{zpc} is about pH 6.2–7.5) [24]. Moreover, according to results showed in Table 3: at pH = 11, the DEP removal rate by O_3/TiO_2 system was similar to the one reached at pH = 7 (73.8% compared to 71.6%). It should also be pointed out that high concentration of OH ions in the medium might trap CO_2 generated by the degradation of DEP and as a result, bicarbonate and carbonate were formed in the alkaline medium, which would limit the degradation rate of DEP because bicarbonate and carbonate are efficient scavengers of hydroxyl free radicals [11]. Furthermore, experimental observations showed that the pH value of the solution decreased from an initial value of 6.8 to a final value ranging from 2.8 to 3.7 in the early ozonation period (15 min), suggesting that acidic groups such as organic acids are generated in the decomposition of DEP, which can contribute to the strong scavenger effect of hydroxyl free radicals in the system and would limit the DEP degradation. Therefore, neutral pH was selected as the optimal experimental condition and there was no need for a neutralization process.

3.3. Effect of catalyst dosage

The catalyst concentration is an important parameter in catalytic ozonation [12]. The effect of increasing the catalyst concentration from 0 to 3 g/L on the degradation of DEP was analyzed. Fig. 5 shows the effect of various catalyst concentrations on the removal effectiveness of DEP by catalytic ozonation. The catalyst concentrations exert an appreciable positive influence on the removal rate. These results demonstrate the effectiveness of TiO_2 and Al_2O_3 as a catalyst in catalyzed ozonation. The removal effectiveness of DEP was enhanced by increasing the metallic oxide concentration. Higher catalyst concentrations result in more active sites for catalytic reaction. The increase in active sites is accounted for in the removal of the organic pollutant.

Fig. 5 showed also that catalyst dose exerted a positive influence on DEP conversion in catalytic ozonation process. In the case of TiO_2/O_3 system, the increase of catalyst dose did not yield any significant increase of the oxidation rate as illustrated in Fig. 5, an optimum was obtained at catalyst dose of $2\ g\,L^{-1}$. Contrary, when Al_2O_3 was used, the catalytic ozonation removal of DEP was not enhanced greatly when the catalyst dose degradation increase over $2\ g\,L^{-1}$. As adsorption experiments on Al_2O_3 showed that the

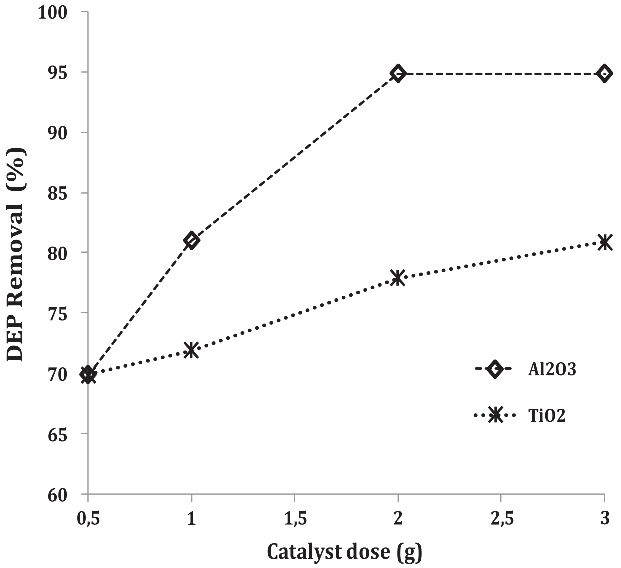

Fig. 5. Effect of catalyst dose on DEP decomposition rate after 30 mn ($C_0 = 200\ mg\,L^{-1}$; pH = 7, $C_{AGin} = 45\ g\,m^{-3}$ NTP).

degradation efficiency of DEP in aqueous solution is limited, increasing experiments using Al_2O_3 dose over 3 g L^{-1} were neglected.

3.4. Effect of initial DEP concentration

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of phthalate. Therefore, the effect of pollutant concentration on the degradation efficiency was investigated at different concentration of DEP and presented in Fig. 6.

As shown in Fig. 6, the higher the initial DEP concentration, the lower the DEP removal efficiency was obtained. The degradation efficiency reached under the two studied processes O_3/TiO_2 and O_3/Al_2O_3, 66 and 76.8% for 50 mg L^{-1} of DEP, respectively, after ozonation for 5 min, while the efficiency is only 24.3 and 29.5%, respectively, for initial DEP concentration of 200 mg L^{-1}.

For O_3/TiO_2, the times required to achieve 90% removal (t_{90}) were 17, 28, and 45 min for initial DEP concentration values of 50, 100, and 200 mg L^{-1}, respectively, as compared to only 9, 15, and 25 min for O_3/Al_2O_3 at the same respective initial DEP concentration values. This indicates that the addition of Al_2O_3 has almost the double performance on DEP removal compared to the system using TiO_2, for all initial DEP concentrations though the removal rate declined as initial DEP concentration increased. This means that catalytic ozonation using metallic oxide achieves only a limited amount of DEP at the highest initial DEP concentration, because an increase in the initial DEP concentration corresponds to an increase of by-product concentration in the solution. Therefore, the supplied ozone is shared between reactions with DEP and its intermediates. Intermediates including phthalic acid, phthalic anhydride, and 4-hydroxy phthalate in addition to hydrogen peroxide, which do react with ozone at significant rates, have been identified in DEP oxidation with ozone [26]. In fact, as mentioned before, experimental observations showed that the pH value of the solution decreased to a final value ranging from 2.8 to 3.7 suggesting that acidic groups such as organic acids are generated in the decomposition of DEP. Moreover, since the ozone was supplied to the reactor at a constant ozone rate, the available ozone at all initial DEP concentration values will be consumed both for oxidation of intermediates and also for continuing degradation of the original DEP.

3.5. Effect of ozone dosage on the DEP degradation

The purpose of catalytic ozonation is to accelerate the decomposition of ozone for generating more oxidation potential species, such as $^{\bullet}OH$. Therefore, ozone dosage is also an important factor which influences the amount and rate of $^{\bullet}OH$ production. To determine the effect of the ozone dosage on DEP removal efficiency in different oxidation processes, a series of experiments were carried out by varying ozone dosage from 0 to 45 g m^{-3} NTP. Fig. 7 indicates that the degradation rate of DEP appears to increase rapidly with ozone concentration in O_3 catalytic process. For example, DEP removal rate improved from 15.5 to 51.8 and 95% as the ozone concentration

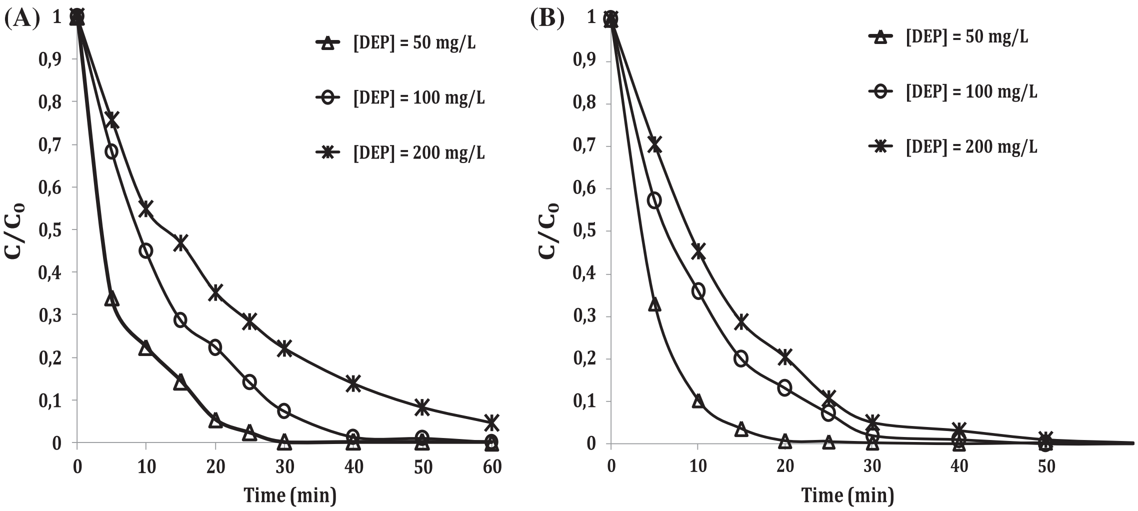

Fig. 6. Effect of initial DEP concentration on DEP removal ($C_{AGin} = 45$ g m^{-3} NTP, pH = 7.0); (A) O_3/TiO_2 (TiO_2 dose = 2 g L^{-1}) and (B) O_3/Al_2O_3 (Al_2O_3 dose = 2 g L^{-1}).

increased from 25 g m^{-3}NTP to 45 g m^{-3}NTP at 30 min, in O_3/Al_2O_3 process (catalyst dose = 2 g L^{-1}).

As shown in Fig. 7, the effect of ozone dosage on the degradation of DEP was the same as those in TiO_2/O_3 and Al_2O_3/O_3 processes. DEP removal was quickly increased with ozone dosage. However, the increase of ozone concentration considerably improved DEP removal. DEP removal rate at 30 min in TiO_2/O_3 and Al_2O_3/O_3 processes was 77.8 and 95%, respectively, with 45 g m^{-3} NTP ozone dosage compared to inlet ozone gas concentration of 25 g m^{-3} NTP, where removal rate reach only 51 and 51.8%, respectively. Thus, ozone dosage played a major role in TOC removal rate in O_3 /metallic oxide process, as it can partake in reactions, such as direct ozone reaction, ozone photolysis producing hydroxyl radicals, and ozone reaction with elections to the superoxide ion radical [25]. So, the phthalate DEP removal rate was found to increase as a function of ozone dosage. However, in practical processes, increasing ozone dosage result in significant increase of treatment costs, because ozone is very expensive. As a consequence, the use of catalyst was carried out in the ozonation experimental in order to save operation expenditure.

3.6. Effect of radical scavengers on the removal of DEP

In general, catalyzed ozonation in the presence of metal oxides, $^{\bullet}OH$ is the main reactive species during the catalyzed ozonation [30]. In order to verify whether the ozonation of DEP in the presence of aluminum and titanium oxides involves $^{\bullet}OH$, some experiments were carried out in the presence of TBA, a well-known $^{\bullet}OH$ scavenger [34]. In fact, TBA is a stronger radical scavenger, as indicated by its higher reaction rate constant with hydroxyl radicals ($k_{OH^{\bullet}}$ = 5 × 10^8 $M^{-1}s^{-1}$) [16] and with ozone alone (k_{O3} = 3 × 10^{-3} $M^{-1}s^{-1}$) [28]. TBA reacts with $^{\bullet}OH$, generating inert intermediates, thus causing the termination of the radical chain reaction. The results obtained for all experiments in the presence or absence of catalysts are presented in Fig. 8. The results show that the ozonation of DEP catalyzed by aluminum and titanium oxides is strongly inhibited in the presence of TBA, causing a primary reduction in the degradation rate, even at a very low concentration (0.1 M).

Moreover, the DEP degradation efficiency during ozonation alone decreased from 69.8 to 5.2% within 30 min oxidation time and the degradation rate of the metallic oxide-catalyzed ozonation dropped from 59 to 14.9% in the presence of Al_2O_3.

In the presence of TiO_2, the DEP removal rate decrease from 78 to 12.7% in 30 min treatment. Taking in account previous results, adsorption of DEP on TiO_2 and Al_2O_3 can cause approximate 12 5 and 15 5% disappearance of this compound at a catalyst loading of 2 g L^{-1}. Thus, the DEP removal rate of the simultaneous application of ozone and TiO_2 or Al_2O_3 was higher than the sum of the individual contributions of single ozonation and single adsorption. It is evident that removal of DEP was due to the action of

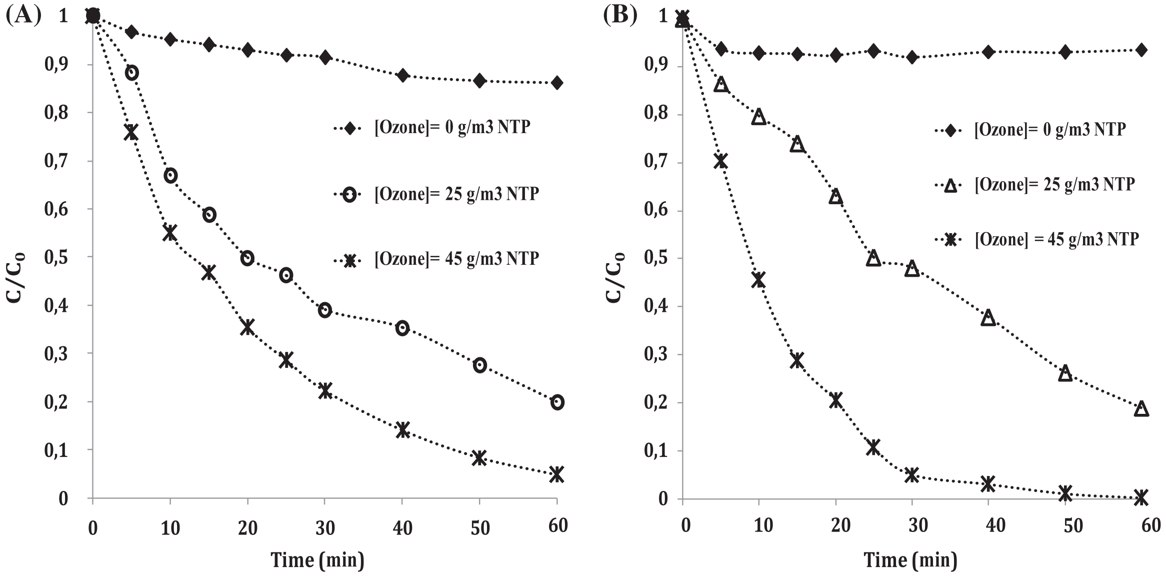

Fig. 7. Effect of inlet ozone gas concentration on DEP removal (C_0 = 200 mg L^{-1}; pH = 7): (A) O_3/TiO_2 (TiO_2 dose = 2 g L^{-1}) and (B) O_3/Al_2O_3 (Al_2O_3 dose = 2 g L^{-1}).

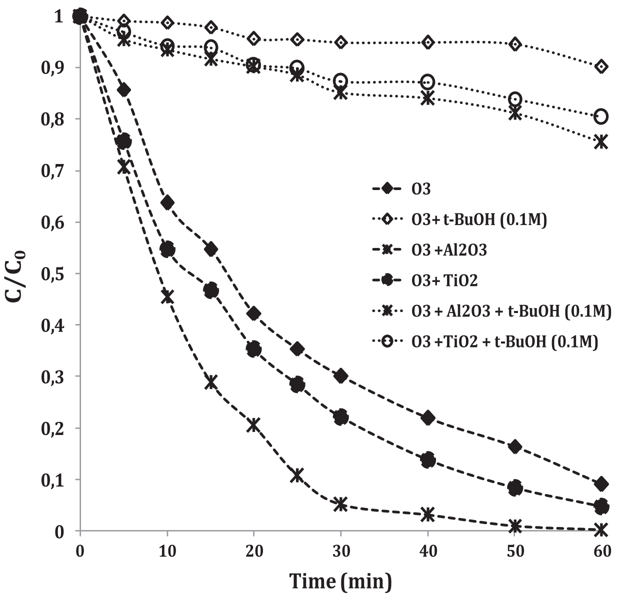

Fig. 8. Effect of TBA on DEP removal ($C_0 = 200\,mg\,L^{-1}$; $C_{AGin} = 45\,g\,m^{-3}$ NTP, pH = 7.0; TiO_2 dose = $2\,g\,L^{-1}$and Al_2O_3 dose = $2\,g\,L^{-1}$).

some ozone absorbed species or free radicals generated probably on the catalyst surface or in the aqueous bulk. Thus, twhe presence of TBA effectively inhibits radical generation in the aqueous solution at pH = 7. In fact, the experimental results indicated that the addition of TBA negatively influence the DEP degradation efficiency during both ozonation alone and metallic oxide-catalyzed ozonation. This indicates that TBA competitively traps and rapidly consumes $^{\bullet}OH$ in aqueous solution. The results also suggest that in both ozonation alone and metallic oxide-catalyzed ozonation, DEP is primarily oxidized by $OH^{\bullet}$ in aqueous solution. This experimental observation indicates also that $^{\bullet}OH$ is the main activity species during aluminum- and titanium-oxides-catalyzed ozonation process. The oxidation mechanism of DEP accrued predominantly via $^{\bullet}OH$ in the liquid bulk. However, the influence of scavenger on catalytic ozonation in the presence of catalysts was remarkably different. The effect in the presence of TiO_2 was less pronounced than the case of Al_2O_3. This observation indicates that the ability of Al_2O_3 catalytic ozone decomposition to generate $^{\bullet}OH$ is stronger than that of TiO_2. On the basis of Fig. 8, aluminum oxides can enhance ozone decomposition to generate $^{\bullet}OH$. According to scavenger experiments, ozone decomposition is enhanced in the presence of aluminum oxides. Therefore, the yield of $^{\bullet}OH$ can be improved by metallic oxides.

3.7. Kinetics study of DEP removal

In the catalytic ozonation, the oxidation of an organic compound in an aqueous solution can be due to the contribution of the reactions at the catalyst surface, bulk solution, and catalyst surface–bulk solution interface [21,22]. The boundary layer of the catalyst, (the catalyst–solution interface), can adsorb oxidants, so that the reaction is enhanced at the boundary layer [21]. Molecular ozone reaction in the bulk liquid phase was found insignificant, whereas the oxidation reaction of hydroxyl radicals was more significant because of its importance as a universal reaction. The oxidation after adsorption is specific to a given compound and is likely that it does not take place for some compounds. Thus, according to previous work [22], the overall removal rate of DEP in aqueous solution can be mathematically represented by the subsequent equation:

$$\frac{d[\mathrm{DEP}]_{\mathrm{overall}}}{dt} = -k_{\mathrm{overall}}[\mathrm{DEP}] \tag{1}$$

Integration of Eq. 1 between the initial time $t = 0$ at which the initial DEP concentration is $[\mathrm{DEP}]_0$ and a time t at which the DEP concentration is [DEP] gives:

$$Ln\left(\frac{[\mathrm{DEP}]_0}{[\mathrm{DEP}]}\right) = k_{\mathrm{overall}}t \tag{2}$$

Fig. 9. shows a plot of the left hand side of Eq. 2 as function of time would lead to a straight line with a slope k_{overall}. The model was found to predict the results very well obtained in this study with a relative error of about 10%. Fig. 9 shows the overall rate constant, k_{overall}, and the determination coefficient R^2, which was higher than 0.98 for all experiments indicating good fitting of the experimental data.

It is important to note that, as mentioned before, the ozonation reactor was operated in semi-batch mode during these experiments since ozone was continuously bubbled into the reactor solution to keep the concentration of dissolved ozone constant (0.98×10^{-4} M). The kinetics of the direct reaction of DEP with ozone was studied by performing experiments at pH = 7.0 and without TBA.

After 1 h treatment, the rate constant of DEP removal were 0.0093 and 0.053 min^{-1} using O_3/AlO_3 and O_3/TiO_2 processes, respectively. Compared to photocatalytic degradation of DEP at initial concentration of 150 $mg\,L^{-1}$ in the presence of 1 $g\,L^{-1}$ TiO_2, the rate constant was 0,009 min^{-1} and $t_{1/2}$ was around 77 min [19]. The degradation half-life of DEP by

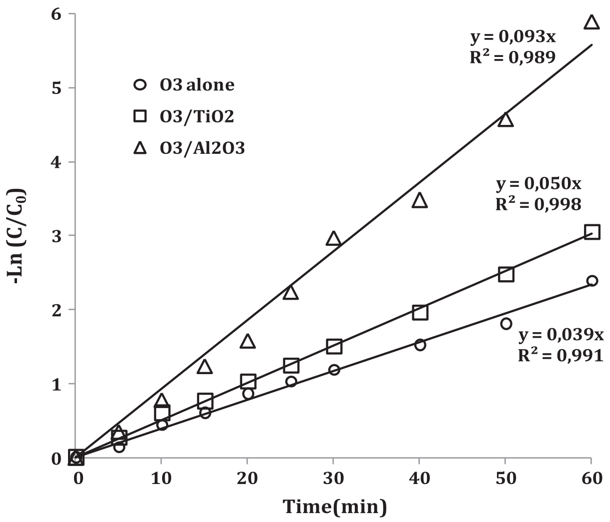

Fig. 9. Kinetic of DEP removal by heterogeneous catalytic ozonation ($C_0 = 200\ \mathrm{mg\ L^{-1}}$; $C_{\mathrm{AGin}} = 45\ \mathrm{g\ m^{-3}}$ NTP, pH = 7.0; TiO_2 dose = $2\ \mathrm{g\ L^{-1}}$and Al_2O_3 dose = $2\ \mathrm{g\ L^{-1}}$).

microbial anaerobic degradation was 15.4 days [36]. From the results, it is indicated that the degradation efficiency of catalytic ozonation was faster than that of microbial degradation and photocatalytic degradation.

4. Conclusions

In this study, the performance of employing metallic oxides (TiO_2 or Al_2O_3) as advanced oxidation for treatment of DEP by ozone was investigated. The optimum application for the treatment was conducted with respect to operational conditions, i.e. catalyst concentration, pH variance, ozone dosage, organic pollutant concentration, and reaction time. The study yielded a good value of DEP removal with O_3/Al_2O_3 (almost 95% in 30 min) system compared with other experiments conducted in the presence of TiO_2 (77.8% for the same oxidation time). At natural pH value, the performance of combined metallic oxide and ozone is more efficient for phthalate treatment than the ozone alone process. According to TBA inhibiting experiments, •OH was generated in the catalytic ozonation process in the presence of TiO_2 and Al_2O_3. By determination of DEP removal rate values, the generation of more $^{\bullet}$OH was accounted for the enhancement of DEP degradation. These experimental results confirmed that the mechanism of the catalytic ozonation promoted by TiO_2 and Al_2O_3 of DEP as pollutant model included an indirect oxidative reaction by hydroxyl radicals and a direct oxidation reaction after the ozone and DEP adsorbed on the surface of catalyst. The kinetics of the overall DEP removal reaction was corresponding to pseudo-first-order rate equation. This study shows that catalytic ozonation promoted by AC is suitable for phthalates removal from aqueous solutions.

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