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Heterogeneous catalytic ozonation of diethyl phthalate

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ABSTRACT

Diethyl phthalate (DEP) is one of the phthalate esters having wide industrial applications, but its occurrence in the aquatic environment has been linked to disruption of the endocrine system. In this study, the removal of DEP with ozone alone (OA) and heterogeneous catalytic ozonation (HCO) with activated carbon (AC) was investigated. Results show that the addition of AC was effective to achieve almost 100% degradation of DEP in about 30 min using 2.86 g AC/L as compared to over 80 min without AC. It was also found that radical reactions were the main mechanism by which DEP was degraded and adsorption contributed significantly to the removal of DEP by OAC. Indeed, after 60 min, adsorption alone achieved about 75% removal, whilst OA achieved 92% removal. In contrast, as expected molecular ozone reactions were relatively insignificant. The contribution of adsorption and radical reactions to the overall removal of DEP were of similar rates at the beginning of the experiments but the latter declined due to competitive reactions. The notable decrease of DEP removal rate observed in the presence of radical scavenger tert-butanol (tb) indicates that the reaction between DEP and ·OH proceeds mainly in the bulk of the aqueous phase. Moreover, the experimental results also revealed that in the absence of tb and after 40 min, almost 100% removal was observed as compared to only 64% when tb was added to the solution. This confirms that radical reactions play an important role in DEP removal by the OAC process. A model taking into account the various reactions in the bulk solution and on the surface of AC was developed and was found to predict well the experimental data. This study proves that HCO was effective to remove DEP and the changes of the contributory mechanisms underpinning the process were determined as function of time.

Keywords: Endocrine disruptors; Diethyl phthalate; Ozone; Heterogeneous catalytic ozonation; Activated carbon

1. Introduction

Phthalates are a group of refractory organics used as additives in the manufacturing of plastics, polyvinyl acetates, celluloses, polyurethanes and polyvinyl chloride. They are also widely used in paints, adhesives, cardboard, lubricants and fragrances [1]. Great concern about the effects of these compounds in nature has arisen as a result of their

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endocrine-disrupting properties [2,3]. Most of the studies on the endocrine-disrupting effects of chemicals in nature are based on their effects on the reproduction of fish and on changes in their genital structures. Several investigations have established that phthalates are teratogenic at high dosages and have potential risk on human male reproductive health [4]. Some of the phthalates are suspected to be carcinogenic, and there are indications that low-molecular weight phthalates are liver carcinogenic [5].

Since phthalates are weakly bound to the plastic structure [6] and as these products become wastes, which are generally disposed of in landfill sites, they are exposed to photochemical, thermal and microbial degradation resulting in phthalate esters easily leaching out by water and becoming ubiquitous pollutants [7,8]. The occurrence of phthalate esters in municipal landfill leachates has been widely reported [7,9–12]. Phthalates have also been detected in other environments including air, soils and natural waters [1,13].

The short-chained esters such as diethyl phthalate (DEP), which mainly come from the discharge of wastewater, and leaching and volatilization from plastic products during their usage and after disposal [14], are among the most frequently identified phthalate esters in diverse environmental samples including surface marine waters, freshwaters [1,5,15], landfill leachates [8,16,17] and sediments [18–20]. Moreover, DEP, the phthalate that we focus on in this study, has been found to have diverse acute and chronic toxic effects on several species at different trophic levels, as well as endocrine-disrupting properties [1,3,21]. In addition, due to its tendency to persist in the environment and bioaccumulate in organisms, DEP is listed as one of the 129 Priority Pollutants regulated by the US Environmental Protection Agency (EPA) [22].

Research studies have shown that DEP is difficult to degrade biologically or photochemically [1,23]. Hence, to reduce its potential harmful effects on humans and the environment, it is important to degrade and remove DEP from wastewaters before discharge in the environment using better and more effective treatment methods. Indeed, a number of advanced oxidation processes (AOPs) including UV/H_2O_2 [24], UV/H_2O_2/Fe^{2+} [25] and photocatalytic [26,27] 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 [28–30], DEP degradation with ozone-based AOPs merit studying since these processes produce hydroxyl radicals in sufficient quantities capable to degrade organic molecules in water.

One of the ozone-based AOPs is heterogeneous catalytic ozonation (HCO), which has been found effective for the removal of several organic compounds from drinking water and wastewater and also enhances molecular ozone reactions [31–33]. Research on the removal of DEP using HCO is scarce, with only a very recent study suggesting HCO degradation of DEP [34,35]. However, the optimum operating conditions still need to be determined, in order to reduce the cost of the HCO treatment and to improve the extent of phthalates removal. Moreover, it is very important to understand the effects of the operating conditions on the nature of the reactions and mechanisms contributing to DEP degradation resulting from O_3/catalyst interaction. Thus, this study was carried out to evaluate the removal of DEP using HCO in aqueous solution under various reaction conditions with activated carbon (AC) as a catalyst. In addition, the mechanisms underpinning DEP removal and their changes as function of time were suggested and discussed in the present study.

2. Experimental

2.1. Chemicals

All chemicals were of reagent grade and used without further purification. Milli-Q/RO water (resistivity $> 18\,\mathrm{M\Omega\,cm}$) was used for solution preparations. DEP (CAS no: 84-66-2, purity: 99.5%, molecular mass: 222.2 g/mol, solubility in water: 1.1 g/L, log K_{ow}: 2.65) was purchased from Sigma–Aldrich, UK. Working aqueous solutions at different initial DEP concentrations in the range 10–200 mg/L were prepared by dilution from a stock solution (200 mg/L). Other chemicals used in this study were tert-butanol (tb) (Fisher Scientific, UK): radical scavenger, potassium indigo trisulphonate (Sigma Aldrich, UK): ozone quenching reagent, acetonitrile (Fisher Scientific, UK): HPLC mobile phase, sodium hydroxide and hydrochloric acid (Fisher Scientific, UK): pH adjusting solutions, and sodium hydrogen carbonate, potassium iodate, diaminoethane tetra-acetic acid disodium salt, starch (soluble), zinc chloride sodium sulphite anhydrous, sulphamic acid and potassium iodide all from Fisher Scientific, UK and were of purity of at least 99% and cobalt (II) sulphate heptahydrate (Sigma–Aldrich, UK) were used in the iodometric titration method and in the determination of gas/liquid specific surface area experiments. AC was a gift from Chemviron, UK. The AC was sieved to the required particle sizes of 1 and 2 mm. Particles of the AC were washed thoroughly with Milli-Q water and then oven dried over night at 110˚C. All dried AC were stored in dry plastic containers firmly closed until use.

2.2. Catalyst characterisation

BET surface area, pore size distribution and volume were determined by liquid nitrogen adsorption/desorption at 77 K using Nova 4000e Analyzer. The point of zero charge of AC was also determined using mass titration [36]. Briefly, the methodology involved preparing in Erlenmeyer flasks solutions at three different initial pH values (3.29, 6.85 and 10.89) and at each pH, AC was added at six mass percentages between 0.05 and 10%. A 0.01 M $NaNO_3$ solution was used as the background electrolyte. All flasks were sealed with laboratory Parafilm and placed in an incubator shaker (Innova 44 series) for 24 h before the final pH was measured. The speed of the incubator shaker was adjusted to 250 rpm and the temperature was fixed at 25˚C.

2.3. Catalytic ozonation experiments

The experiments were carried out in a semi-batch jacketed glass reactor (700 mL) fed with ozone in oxygen through a glass sinter gas diffuser (Fig. 1). A magnetic stirrer was used to ensure well mixing of the reactor to prevent coalescence of gas bubbles. A peristaltic pump was used to circulate, in a closed loop, the aqueous solution through a vertical fixed-bed of the catalyst (glass column diameter: 2.76 cm, height: 15.5 cm). The pH was fixed at values within the range 2–11 and in some experiments tb (a radical scavenger) was added to the solution at a concentration of 0.2 M. Ozone was produced using a BMT 803 generator (BMT-Messtechnik, Germany) fed by dry pure oxygen and its concentration was measured by an ultraviolet gas ozone analyzer (BMT 963) based on the absorbance at 254 nm. A calibrated variable-area-gas flow meter fitted with a needle throttle valve was used to measure and control the gas flow rate. Off-gas ozone was passed through sodium aluminosilicate particles to destroy any residual ozone in the gas effluent before being exhausted in a fume hood. The gas flow rate was 400 mL/min and the inlet ozone concentration was fixed at a constant value within the range 25–80 g/m^3 and normal temperature and pressure (NTP): 0˚C and 1 atm. All experiments were conducted at room temperature of 20 ± 1˚C. Liquid samples were collected as function of time using a syringe fitted with a 10 cm needle. Each sample was immediately placed into a vial after being filtered with a syringe filter (25 mm GHP GF 0.45 μm) and was exposed to a gentle stream of air for about 15 s to quench any residual ozone so to stop the reaction before analysis. Ozone quenching was also done by 0.05 g of 0.1 M sodium thiosulphate solution and no difference was obtained with the air quenching method, so the latter was adopted because of simplicity. Control experiments using 2 g inert glass beads (2 mm) instead of AC were also carried out.

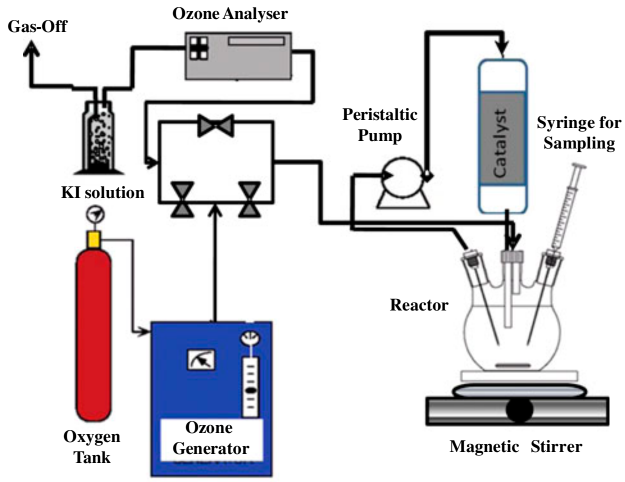

Fig. 1. Experimental set-up of ozone/AC system.

2.4. DEP adsorption experiments

Adsorption experiments were performed in the same reactor as the main experiment by circulating in a closed-loop mode the DEP solution at an initial concentration C_0 through the packed bed ($m_{AC} = 2$ g) but without supply of the gas. The volume of the solution was 0.7 L and four DEP concentrations (10, 50, 100 and 200 mg/L) at initial pH 7 were used. These solutions were mixed at room temperature until equilibrium was reached (i.e. until no change in solution concentration was observed). The samples were withdrawn at regular time intervals to determine the remained DEP concentrations. The capacity of carbon, q, was calculated by $q = V \times (C_0 - C)/m_{AC},$ where V is the solution volume, C_0 and C are the initial and final DEP concentrations and m_{AC} is the mass of AC. Langmuir and Freundlich models were applied to describe the adsorption isotherm.

2.5. Gas/liquid ozone mass transfer parameters

Ozone mass transfer parameters including the mass transfer coefficient, k_L, and the specific interfacial area, a, were determined using Danckwerts' plot for oxygen absorption in sodium sulphite solutions containing different concentrations of cobalt catalyst [37,38]. The oxygen absorption rate was calculated from the decrease of sulphite concentration as function of time by $R_{O_2} = 0.5 \times V \times \Delta[SO_3^{2-}]/\Delta t$.

Sulphite concentration was determined by standard iodometric titration method with potassium iodide-iodate titrant in the presence of a starch indicator [39]. The ozone mass transfer coefficient k_L, was then calculated from the obtained experimental value of oxygen mass transfer coefficient, k_{LO2}, by $k_L = k_{LO_2} (D_{O_3}/D_{O_2})^{0.5}$, where D_{O_3} and D_{O_2} are ozone and oxygen diffusivities, respectively.

2.6. Analytical methods

DEP concentration was analysed using a high-performance liquid chromatograph (Agilent 1200 Series) with a diode array detector (Agilent G1315D) at 276.5 nm. A reversed phase Zorbax Eclipse XDB-C18 column (4.6 mm × 150 mm, 5 µm) was used, the mobile phase was an isochratic 65%v acetonitrile: 35%v water at a flow rate of 1 mL/min, the column temperature was set at 30˚C, the injection volume was 20 µL and the analysis cycle was 10 min (retention time of DEP was about 3.5 min). Ozone concentration in the liquid phase was determined using the indigo colorimetric method [39]. A diode array UV/Vis spectrophotometer (HP8453, Agilent, UK) was used to measure the absorbance of indigo solution at 600 nm.

3. Results and discussion

3.1. AC characterisation and adsorption isotherm

Table 1 shows the results of the textural and chemical characterisation of the AC used in this study. The N_2 adsorption–desorption isotherms at 77 K showed that the AC is microporous and also contained mesopores as indicated by the shape and hysteresis loop of the nitrogen isotherms. The results shown in Table 1 are comparable to those reported in the literature for AC [40,41].

The adsorption isotherm of DEP on AC was also determined at pH 7 and the Langmuir model (i.e. $q^* = Q_m bC/(1 + bC)$) was found to describe well the data. The Langmuir parameters Q_m and b were determined by least-square best curve fit and their values were 89.49 mg/g (or 4.03×10^{-4} mol/g) and 0.332 L/mg (or 7.40×10^4 L/mol), respectively. The maximum adsorption capacity Q_m corresponds to complete monolayer coverage and at this value, it is possible to calculate the surface occupied by DEP as: $S_{occ}(m^2/g) = Q_m \times S_{DEP} \times N_A$, where S_{DEP} is the surface of a DEP molecule estimated at $6.62 \times 10^{-19}\,m^2$ and N_A is the Avogadro number. A coverage of only 18% was calculated. The reason for this low coverage may due to the microporous nature of the AC and its narrow mean pore size in comparison with the size of DEP molecule.

Table 1
Chemical/physical characteristics of AC

BET surface area (m^2/g)	932.58 (±4%)
Specific pore volume (cm^3/g)	0.54 (±1%)
Average pore radius (Å)	11.55 (±3%)
pH_{pzc}	10.68

3.2. Determination of ozone mass transfer coefficient, k_L, interfacial area, a and ozone to DEP ratio, v

The reaction of sulphite with oxygen in the presence of cobalt catalyst is assumed of first order when the concentration of sulphite is greater than 0.5 M [38] and the kinetic constant k_1 is directly proportional to cobalt concentration (i.e. $k_1 = \alpha[Co^{2+}]$) in the range 10^{-7}–10^{-3} mol Co^{2+}/L [42]. Under these conditions, the oxygen absorption rate may be described by Eq. (1), which is derived from the well-known Danckwerts' plot. The value of the constant, α, was initially determined from experiments carried out in a stirred cell with a known interfacial area ($A = 65.97\,cm^2$) by plotting the $R^2_{O_2}$ as function of [Co^{2+}]; a value of α equal to $7.28 \times 10^5\,L\,m^2/s\,mol$ was determined. Once the value of α was known, oxygen absorption experiments on the main reactor were carried out and using the same procedure, the interfacial area, a, and oxygen mass transfer coefficient, k_{LO_2}, were determined; their values were 33.84 m^2/m^3 and 5.04×10^{-4} m/s, respectively. The ozone mass transfer coefficient k_L was then calculated and its value was 4.88×10^{-4} m/s.

$$R^2_{O_2} = \alpha(AC^*_{O_2})^2 D_{O_2}[Co^{2+}] + (AC^*_{O_2}k_L)^2 \tag{1}$$

where R_{O_2} is the oxygen absorption rate (mol/s), A is the interfacial area (m^2), D_{O_2} and $C^*_{O_2}$ are the oxygen diffusivity and solubility determined from Linek and Vacek [43].

Under the experimental conditions used in this study (i.e. pH 7, $C = 200$ mg/L and $C_{O_3} = 60\,g/m^3$ NTP), the absorption of ozone in the DEP solution fell within the diffusional kinetic regime since Hatta number satisfied the condition $0.02 < Ha < 0.3$ and the aqueous ozone concentration was zero [37,44]. The conditions of having both interfacial area and liquid holdup high, so the reaction was sufficiently fast to hold the ozone concentration close to zero in the bulk liquid as discussed in Charpentier [37], were also satisfied. Given that the volumetric mass transfer coefficient, k_La, was determined, it was possible to determine the overall ratio of ozone used to DEP removed, v (Eq. (2)).

$$N_{O_3} = Ek_LaC^*_{O_3} = -v\frac{dC}{dt} \tag{2}$$

where the enhancement factor $E = 1$ because $Ha < 0.3$ and $C^*_{O_3}$ is the equilibrium ozone concentration determined using the equation developed by Roth and Sullivan [45]; C is DEP concentration; and t is time.

Integration of Eq. (2) between the initial time and a time t leads to Eq. (3). A plot of the left-hand side (LHS) term of Eq. (3) against time leads to a straight line with a slope $s = k_LaC^*_{O_3}/v$. The value of the slope s was then used to determine the ratio v by $v = k_LaC^*_{O_3}/s$. At pH 7, a value of v equal to 4.5 was obtained in this study. This ratio is higher than one, a generally reported stoichiometric ratio for ozone reactions with organics, possibly due to ozone consumption by other reactions including its autodecomposition, radical reactions and reactions with oxidation products.

$$C_0 - C = \frac{k_LaC^*_{O_3}}{v}t \tag{3}$$

3.3. Effect of inlet ozone gas concentration (C_{AGin}) on DEP removal

The inlet ozone gas concentration (C_{AGin}) is one of the main variables of importance in ozone systems since it affects ozone mass transfer rates and solubility [46]. In addition, C_{AGin} does not only affect the dissolved ozone concentration but also the formation of hydroxyl radicals and hence the potential for the formation of toxic oxidation by-products [47]. In this study, the effect of C_{AGin} on DEP removal with ozone alone (OA) and ozone/AC (OAC) systems was investigated by bubbling ozone at different gas concentrations into the DEP solution. As shown in Fig. 2(A) and (B)), in both systems, DEP removal increased by increasing ozone concentration but further increase beyond 60 g/m^3 NTP had no significant effect. The experimental set at 200 mg/L of DEP at various influent ozone gas concentrations was carried out in duplicates and over 95% confidence level in results was obtained. The coefficient of variation values varied in the range of 1–5% indicating good reproducibility of the experimental runs. The experimental results revealed that for OA, a 90% reduction in DEP concentration was achieved at decreasing times (t_{90}) of approximately 70, 60 and 50 min for increased inlet ozone gas concentrations of 45, 60 and 80 g/m^3 NTP, respectively, but a much longer time of about 150 min was needed to achieve the same degradation percentage when C_{AGin} was 25 g/m^3 NTP. Similarly for OAC, increased C_{AGin} led to faster removal of DEP but t_{90} values were much shorter than those for OA (43, 40, 28 and 27 min for C_{AGin} of 35, 45, 60 and 80 g/m^3 NTP, respectively) (Fig. 2(C)). Increasing ozone gas concentration results in increased aqueous ozone concentration, which leads to increased direct and indirect reaction rates, hence the overall rate. This is expected because an increase in the influent ozone gas concentration results in an increase in aqueous ozone concentration which either directly reacts with DEP or decomposes to produce ($OH^·$) which in turn reacts with DEP molecule. Obviously, increasing the inlet ozone gas concentration would lead to higher reaction kinetics by increasing the ozone mass transfer to the liquid phase and also the ozone saturation concentration in the reactor [48].

The results also clearly indicate that OAC was more effective for the removal of DEP. Besides, the effect of C_{AGin} on DEP removal was less pronounced for OAC as for OA and contrary to OA, when C_{AGin} reached 60 g/m^3 NTP; the increase of the gas concentration had only little effect on DEP removal with OAC.

3.4. Effect of pH

The removal of DEP by OA and OAC was performed at different pH values (Fig. 3). For both systems, the results show that DEP was removed by ozonation but the degradation kinetics depended strongly on pH. Remarkably, at pH 2, OA did not remove DEP (only 5% removal after 1 h), but when OAC was used, a significant removal was observed (75% removal after 1 h). On the other hand, when the pH increased to five and then up to 11, the removal of DEP has significantly increased. After 60 min treatment, DEP removal by OA increased from 63 to 92% at pH values of five and seven, respectively (Fig. 3(A)). At these pHs and after 60 min, the removal by OAC was almost 100% (Fig. 3 (B)). In addition, Fig. 3 shows that increasing the pH beyond seven had weaker effect on the removal of DEP. 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 [49]. 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 OH^- is enhanced at high pH [50].

According to literature on catalytic ozone decomposition [44], the following mechanisms of surface

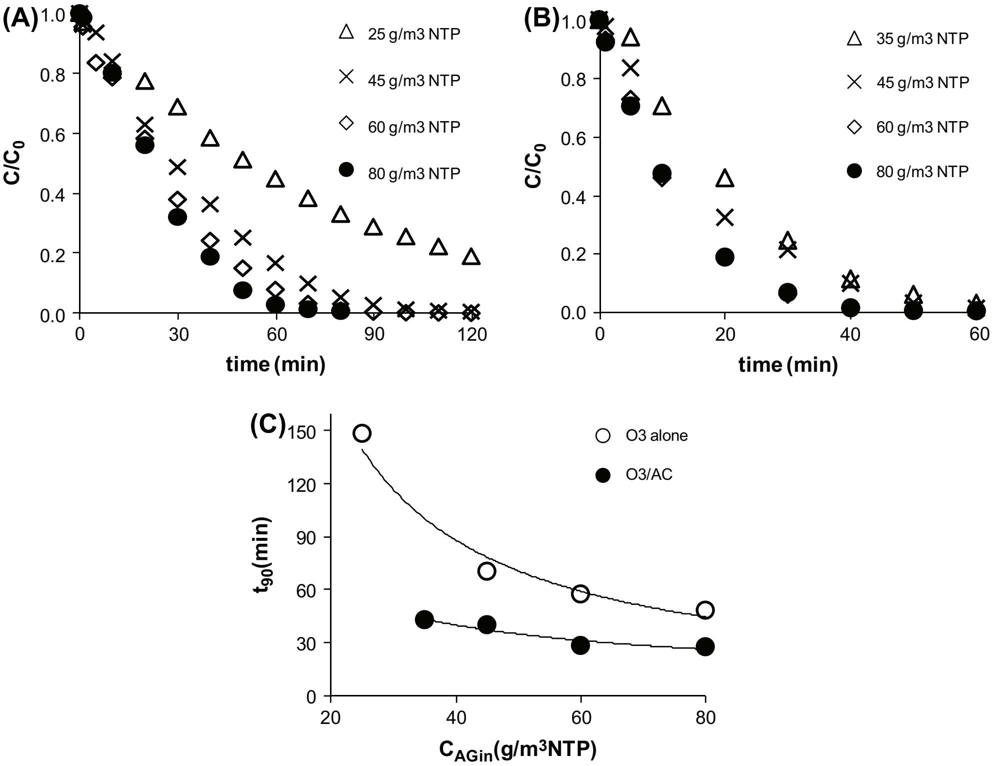

Fig. 2. Effect of inlet ozone gas concentration on DEP removal ($C_0 = 200$ mg/L; pH = 7): (A) O_3 alone, (B) O_3/AC (AC dose = 2.86 g/L) and (C) effect of C_{AGin} on the time taken to achieve 90% removal (t_{90}).

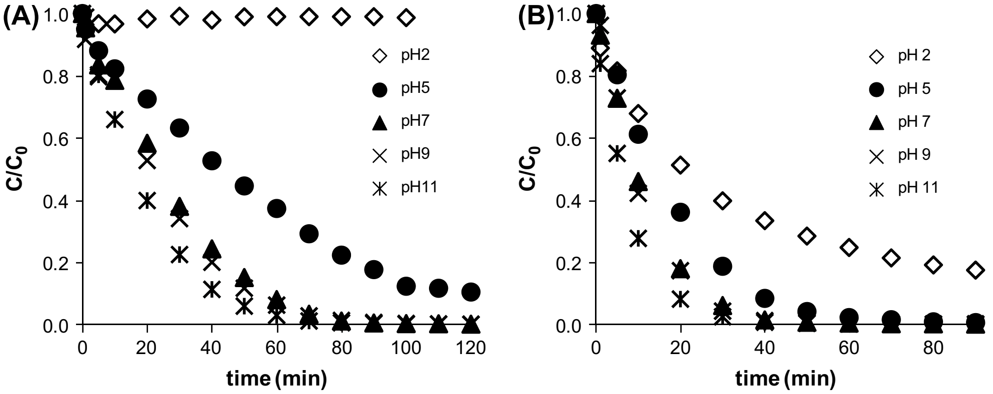

Fig. 3. Effect of solution pH on DEP removal ($C_0 = 200$ mg/L, $C_{AGin} = 60$ g/m^3 NTP): (A) O_3 alone, (B) O_3/AC (AC dose = 2.86 g/L).

reactions, that take place during heterogeneous ozonation under conditions where external and internal diffusion rates are very fast and hence do not affect the true kinetics, are proposed:

3.4.1. Homogenous decomposition

For pH 2–6:

$$O_3 + AC \leftrightarrow O_3 - AC$$

$$O_3 - AC \leftrightarrow O - AC + O_2$$

$$O_3 + O - AC \leftrightarrow 2O_2 - AC$$

In addition, for pH > 6:

$$OH^- + AC \leftrightarrow OH - AC$$

$$O_3 + OH - AC \leftrightarrow {}^{\cdot}O_3 - AC + HO^{\cdot}$$

$${}^{\cdot}O_3 - AC \leftrightarrow {}^{\cdot}O - AC + O_2$$

$$O_3 + {}^{\cdot}O - AC \leftrightarrow O_2^{\cdot -} - AC + O_2$$

$$O_3 + {}^{\cdot}O - AC \leftrightarrow O_2^{\cdot -} - AC + O_2$$

As shown above, the transformation of ozone into hydroxyl radicals ($^{\cdot}OH$) is enhanced by the AC; DEP removal by OAC was higher. Furthermore, at low pH level, molecular ozone is directly adsorbed on AC active sites, whereas at neutral and basic solutions, ozone reacts with adsorbed hydroxyl groups. This is due to the fact that in acidic medium and in the presence of AC, the initiation step of ozone decomposition is the same as in the gas phase and does not depend on the concentration of OH^- ions, whereas in neutral and basic media, ozone decomposition rate constant is a function of solution pH [51]. Thus, low DEP removal rate was observed at pH 2.

On the other hand, the formation of hydrogen peroxide and the generation of OH^- ions in OAC system, due to the reduction of ozone on AC surface, were confirmed by several studies [52,53] and lead to the initiation of the ozone decomposition into $^{\cdot}OH$ increasing the oxidation rate of the contaminants. Consequently, at pH 2, H_2O_2 reacts very slowly with molecular ozone, and only at pH values above five, a strong acceleration of ozone decomposition by H_2O_2 is observed [30]. As a result, an increase in the elimination performance of DEP by the OAC system was observed for pH values higher than five, explained by the presence of higher concentration of HO_2^- resulting from the formation of H_2O_2 on surface active sites and its subsequent dissociation.

Moreover, the highly basic character of the used AC ($pH_{pzc} = 10.68$) may have a significant effect not only in initiating ozone decomposition at neutral or basic medium, but also in improving molecular ozone adsorption on the catalyst surface at low pH levels [53].

3.5. Effect of initial DEP concentration

Fig. 4 shows the effect of initial DEP concentration (C_0) on DEP removal by OA and OAC. It can be observed that the concentration profiles follow similar trends at the various C_0 values for OA and OAC. Clearly as the initial DEP concentration increased, the removal of DEP by OA or OAC becomes more difficult. For OA, the times required to achieve 90% removal (t_{90}) were 8, 18, 30 and 57 min for C_0 values of 10, 50, 100 and 200 mg/L, respectively, when compared to only 5, 13, 13 and 28 min for OAC at the same respective C_0 values. This indicates that the addition of AC has almost doubled the performance of the system for all initial DEP concentrations though the removal rate declined as C_0 increased. This means that catalytic ozonation (OAC) achieves only a limited amount of DEP at the highest initial DEP concentration, because an increase of the initial DEP concentration corresponds to an increase of by-product concentration in the solution. Then the available ozone (the ozone was supplied to the reactor at a constant ozone rate (24 mg/min)) at all C_0 values will be consumed both for oxidation of intermediates and also for continuing degradation of the original DEP. This means that 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 [54].

3.6. Effect of catalyst dose

Since the dose of catalyst is a critical parameter that affects the dissolved ozone transformation into radical species and adsorption of the organic species [32,53], ozonation experiments were carried out by varying AC doses from zero to 2.86 g/L. Inert glass beads of similar sizes to the AC were used for the control experiments (i.e. zero AC dose). Fig. 5 shows that the removal of DEP progressively increased as the dose of AC increased. Naturally, as the dose of AC increased, active sites for DEP adsorption and production of radical species responsible for the oxidation of DEP also increased, which explains the observed results. The figure also shows that the addition of AC was effective to achieve almost 100% degradation of DEP in about 30 min using 2.86 g AC/L as compared to over 80 min without AC. On the other hand, adsorption of DEP on AC was of comparable kinetics to OA only within the first 15 min before it became slow. After 60 min, adsorption alone achieved about 75% removal, while OA achieved 92% removal. It is clear from these results that both adsorption and oxidation contributed to DEP removal during the catalytic ozonation process. Calculations of the mass of DEP removed by OA, OAC and adsorption separately revealed that at times less than 5 min, the sum of the mass removed by OA and adsorption equalled that removed by OAC. The contribution of adsorption to the overall removal was 36%. However, at times higher than 5 min, the same calculation revealed that the sum of OA and adsorption gave only 80% of the observed removal by OAC. The remaining 20% removal may due to radical reactions resulting from ozone decomposition in the presence of AC. The

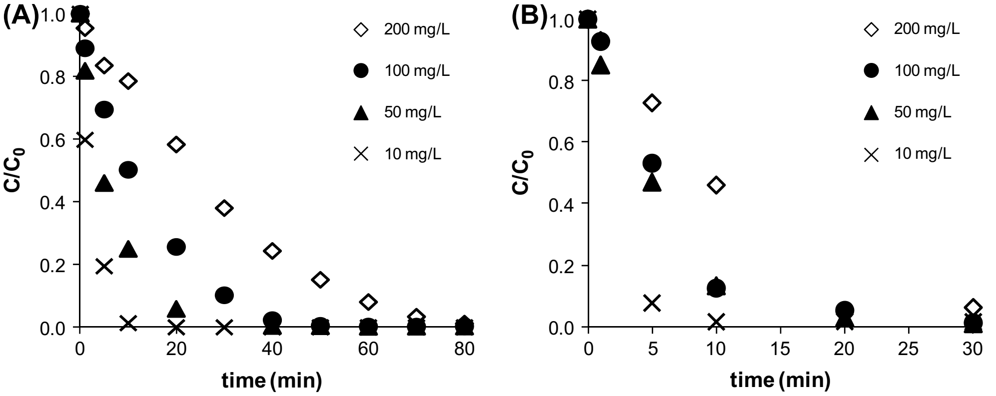

Fig. 4. Effect of initial DEP concentration on DEP removal ($C_{AGin} = 60\,g/m^3$ NTP, pH = 7.0); (A) OA, (B) OAC (AC dose = 2.86 g/L).

contribution of adsorption, OA and catalytic radical reactions to the overall observed removal by OAC is 40, 40 and 20%, respectively. So, for OAC, AC can act as an adsorbent material, a radical initiator or reaction support as also observed by Sanchez-Polo et al. [53]. Therefore, the dose of AC should be well optimised to favour the removal of water contaminants at the lowest ozone dose hence reducing treatment costs.

3.7. Effect of tb and contribution of adsorption, molecular ozone and radical reactions

It has been reported in previous studies that ozone decomposition in the presence of AC leads to the generation of •OH [52,53]. The contribution of ·OH to the overall reaction may be studied by the addition to the solution of a radical scavenger such as tb, which is a well-known radical scavenger used in ozone studies [55] since it reacts very rapidly with hydroxyl radicals ($k_{OH,t\text{-}BuOH} = 6 \times 10^8\,M^{-1}\,s^{-1}$) but very slowly with ozone ($k_{O3,t\text{-}BuOH} = 0.003\,M^{-1}\,s^{-1}$) [50,56]. In this study, tb (0.2 M) was used to investigate its effect on DEP removal and hence the contribution of ·OH to the overall DEP removal. Fig. 6 clearly shows that following addition of tb, the removal rate of DEP declined significantly. Indeed, in the absence of tb and after 40 min, almost 100% removal was observed as compared to only 64% when tb was added to the solution. This confirms that radical reactions play an important role in DEP removal by the OAC process as also observed by de Oliveira et al. [34]. However, the elimination efficiency of catalytic ozonation (OAC) in the presence of tb was still higher than that of ozonation alone with tb (results are not shown), which implies the existence of other pathways, namely catalytic oxidation and adsorption.

The contribution of adsorption, ozone and radical reactions at pH 7 and within the time of complete removal of DEP by OAC (i.e. $t < 50$ min—see Fig. 6) to the overall DEP removal rate is depicted in Fig. 7. The adsorption contribution was determined from experiments carried out with AC only (i.e. no ozone) while the contribution of ozone reactions was determined from the difference between OAC with tb experiments and adsorption experiments. Besides, the contribution of all radical reactions was determined from the difference between OAC experiments and OAC with tb experiments. It should be noted that tb did not affect the adsorption of DEP on AC (results are not shown here). Fig. 7(A) shows that the contribution of ozone reactions is significantly low as com-

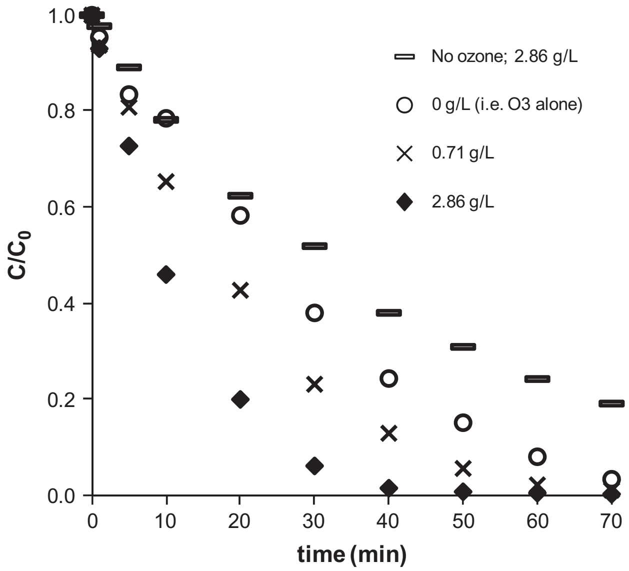

Fig. 5. Effect of catalyst dose on DEP removal ($C_0 = 200$ mg/L; pH = 7.0, $C_{AGin} = 60\,g/m^3$ NTP, $d_p = 2$ mm).

pared to adsorption and radical reactions. Other studies have also shown that DEP degradation with molecular ozone is very difficult [28,29,54]. In contrast, the contribution of radical reactions increased rapidly as time increased up to a maximum at time 25 min after which DEP removal by radical reactions decreased slowly. The ascendant part of the radical contribution (i.e. $t < 25$ min) is only slightly above the adsorption curves, which indicates that both mechanisms have comparable rates during this part of the process. In Fig. 7(A), the descendent part of the radical curve, which started after about 25 min at which 88% DEP has already been removed, may be explained by consumption of the formed radicals, which ought to have a sustained rate since ozone was supplied at constant rate, by the products of the main reaction. As DEP depleted significantly after about 25 min, radical reactions with the products overcame the main reaction, hence its decline as observed in Fig. 7(A).

In HCO, radical reactions may take place in the bulk of solution as well as on the surface of the catalyst [53]. The contribution of the bulk radical reactions may be determined from the difference between the contribution of all radical reactions as determined above and the contribution of the surface radical reaction determined from experiments carried out at the lowest pH at which bulk radical reactions are insignificant. It was found that experiments at pH 7 with tb and those at pH 2 gave the same results indicating inhibition of radical reactions under both conditions and proving the validity of the preceding method for the determination of the contribution of surface and bulk radical reactions. Fig. 7(B) shows that about 75% of radical reactions took place in the bulk solution during the first 30 min of reaction, at which 94% DEP has been removed, followed by an increase to 100% marking the end of reaction.

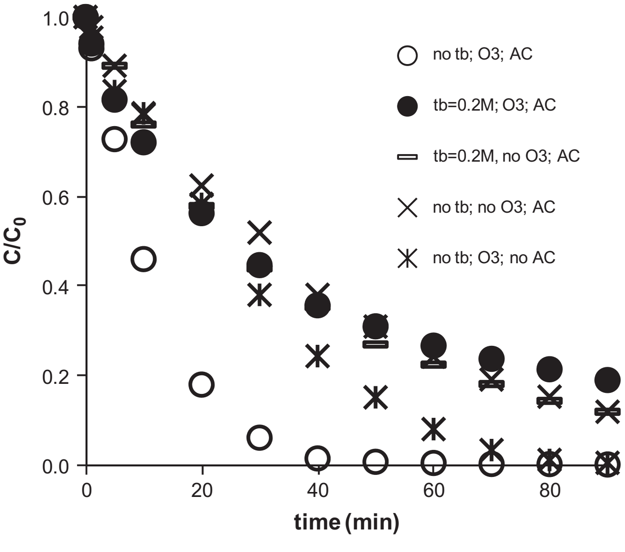

Fig. 6. Effect of t-butanol on DEP removal ($C_0 = 200$ mg/L; pH = 7; $C_{AGin} = 60\,g/m^3$ NTP; $d_p = 2$ mm; AC dose = 2.86 g/L).

3.8. Kinetics study

The experimental results reported previously demonstrate that the mechanisms for the enhancement of ozonation efficiency include a synergistic effect of indirect oxidative reaction by hydroxyl radicals in the bulk liquid phase and oxidation reactions on the surface of AC in addition to adsorption phenomena. 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. A simplified second-order reaction set taking place in the bulk liquid phase and on the catalyst surface is as follows.

3.8.1. Homogeneous reactions

$$\mathrm{DEP} + \mathrm{O_3} \overset{K_{\mathrm{O_3-home}}}{\longrightarrow} \text{products}$$

$$-\frac{d[\mathrm{DEP}]}{dt} = k_{\mathrm{O_3-homo}}[\mathrm{O_3}][\mathrm{DEP}] \quad (4)$$

$$\mathrm{DEP} + {}^{\bullet}\mathrm{OH} \overset{K_{\mathrm{OH-home}}}{\longrightarrow} \text{products}$$

$$-\frac{d[\mathrm{DEP}]}{dt} = k_{\mathrm{OH-homo}}[{}^{\bullet}\mathrm{OH}][\mathrm{DEP}] \quad (5)$$

3.8.2. Heterogeneous reactions

The surface charge of the AC is dependent on the pH but since its pH_{pzc} is high ($pH_{pzc} = 10.68$) as compared to the pH values used in most of the experiments of this study; it was assumed that the net surface charge of the carbon was positive and contained the functional groups ($-OH_2^+$). The sorption of DEP may result from the interaction of the oxygen donor atoms of DEP molecule with these groups to form a surface complex (SOHDEP; where S represents the carbon surface) by coordination of the DEP molecule and the release of protons from the AC surface. The release of protons was confirmed by decreased pH in adsorption experiments carried out without control of pH. The heterogeneous reactions follow.

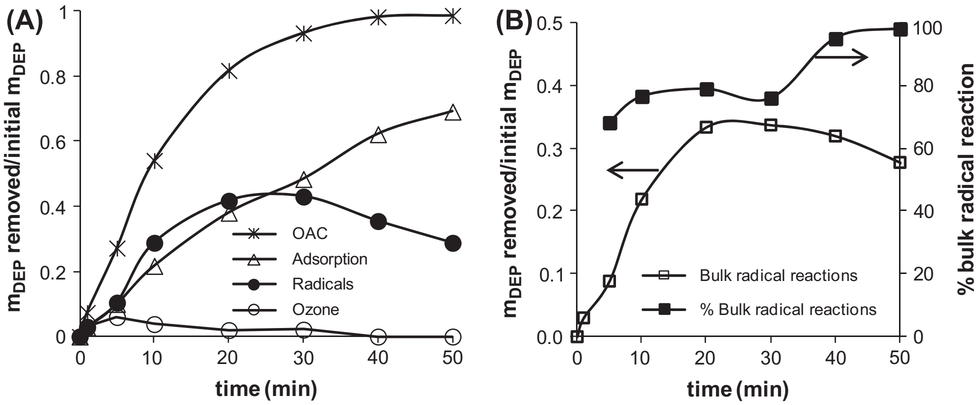

Fig. 7. (A): Contribution of radical reactions, ozone and adsorption to the overall removal of DEP by OAC; (B): Contribution of bulk radical reactions. ($C_0 = 200$ mg/L; pH = 7; $C_{AGin} = 60$ g/m^3 NTP; $d_p = 2$ mm; AC dose = 2.86 g/L when used).

$$\mathrm{SOH_2^+} + \mathrm{DEP} \underset{k_{\mathrm{Des}}}{\overset{k_{\mathrm{Ads}}}{\rightleftarrows}} \mathrm{SOHDEP} + \mathrm{H^+} \frac{d[\mathrm{DEP}]}{dt} = -k_{\mathrm{Ads}}\{\mathrm{SOH_2^+}\}[\mathrm{DEP}] + k_{\mathrm{Des}}\{\mathrm{SOHDEP}\}\{\mathrm{H^+}\} \tag{6}$$

It should be noted that at equilibrium, the forward and backward rates are equal, which lead to:

$$K_{\mathrm{Ads/Des}} = \frac{k_{\mathrm{Ads}}}{k_{\mathrm{Des}}} = \frac{\{\mathrm{SOHDEP}\}\{\mathrm{H^+}\}}{\{\mathrm{SOH_2^+}\}[\mathrm{DEP}]} \tag{7}$$

The formed surface complex SOHDEP may decompose by surface reactions with the adsorbed ozone and ozone-generated hydroxyl radicals as shown by Eqs. (8) and (9).

$$\mathrm{SOHDEP} + \mathrm{O_3} \xrightarrow{k_{\mathrm{O_3\text{-}het}}} \text{products} \qquad -\frac{d\{\mathrm{SOHDEP}\}}{dt} = k_{\mathrm{O_3-het}}\{\mathrm{SOHDEP}\}\{\mathrm{O_3}\} \tag{8}$$

$$\mathrm{SOHDEP} + {}^{\cdot}\mathrm{OH} \xrightarrow{k_{\mathrm{OH\text{-}het}}} \text{products} \qquad -\frac{d\{\mathrm{SOHDEP}\}}{dt} = k_{\mathrm{OH-het}}\{\mathrm{SOHDEP}\}\{{}^{\cdot}\mathrm{OH}\} \tag{9}$$

Since ozone was supplied continuously to the reactor at a constant rate, it can be assumed that its concentration on the solid surface is proportional to its concentration in the bulk phase as $\{O_3\} = \alpha_{\mathrm{O_3}}[\mathrm{O_3}]$. Besides, since ozone is the main species for the production of hydroxyl radicals, their concentration can also be assumed proportional to the concentration of ozone on the solid surface and consequently is proportional to the bulk ozone concentration as $\{{}^{\cdot}\mathrm{OH}\} = \alpha_{\mathrm{OH}}[\mathrm{O_3}]$. Hence, the reaction rates can be written as:

$$-\frac{d\{\mathrm{SOHDEP}\}}{dt} = k_{\mathrm{O_3-het}}\alpha_{\mathrm{O_3}}\{\mathrm{SOHDEP}\}[\mathrm{O_3}] \tag{10}$$

$$-\frac{d\{\mathrm{SOHDEP}\}}{dt} = k_{\mathrm{OH-het}}\alpha_{\mathrm{OH}}\{\mathrm{SOHDEP}\}[\mathrm{O_3}] \tag{11}$$

The overall rate describing the change of concentration of the complex SOHDEP is given by:

$$\frac{d\{\mathrm{SOHDEP}\}_{\mathrm{overall}}}{dt} = k_{\mathrm{Ads}}\{\mathrm{SOH_2^+}\}[\mathrm{DEP}] - (k_{\mathrm{Des}}\{\mathrm{H^+}\} + (k_{\mathrm{O_3-het}}\alpha_{\mathrm{O3}} + k_{\mathrm{OH-het}}\alpha_{\mathrm{OH}})[\mathrm{O_3}])\{\mathrm{SOHDEP}\} \tag{12}$$

Applying the quasi steady-state approximation for the intermediate complex SOHDEP (i.e. d{SOHDEP}$_{\mathrm{overall}}/dt \approx 0$) yields:

$$\{\mathrm{SOHDEP}\} = \frac{k_{\mathrm{Ads}}\{\mathrm{SOH_2^+}\}[\mathrm{DEP}]}{k_{\mathrm{Des}}\{\mathrm{H^+}\} + (k_{\mathrm{O_3-het}}\alpha_{\mathrm{O3}} + k_{\mathrm{OH-het}}\alpha_{\mathrm{OH}})[\mathrm{O_3}]} \tag{13}$$

On the other hand, the overall rate describing the changes of DEP bulk concentration is:

$$\frac{d[\mathrm{DEP}]_{\mathrm{overall}}}{dt} = \left(-k_{\mathrm{O_3-homo}}[\mathrm{O_3}] - k_{\mathrm{OH-homo}}[{}^{\cdot}\mathrm{OH}] - k_{\mathrm{Ads}}\{\mathrm{SOH_2^+}\}\right) \times [\mathrm{DEP}] + k_{\mathrm{Des}}\{\mathrm{SOHDEP}\}\{\mathrm{H^+}\} \tag{14}$$

Substituting Eq. (13) into Eq. (14) gives:

$$\frac{d[\mathrm{DEP}]_{\mathrm{overall}}}{dt} = \begin{pmatrix} -k_{\mathrm{O_3-homo}}[O_3] - k_{\mathrm{OH-homo}}[{}^{\cdot}\mathrm{OH}] - \\ k_{\mathrm{Ads}}\{\mathrm{SOH_2^+}\}\left(1 - \frac{k_{\mathrm{Des}}\{\mathrm{H^+}\}}{k_{\mathrm{Des}}\{\mathrm{H^+}\} + \left(k_{\mathrm{O_3-het}}\alpha_{\mathrm{O3}} + k_{\mathrm{OH-het}}\alpha_{\mathrm{OH}}\right)[\mathrm{O_3}]}\right) \end{pmatrix} \times [\mathrm{DEP}] \tag{15}$$

The overall removal rate of DEP can be simplified to:

$$\frac{d[\mathrm{DEP}]_{\mathrm{overall}}}{dt} = -k_{\mathrm{overall}}[\mathrm{DEP}] \tag{16}$$

where:

$$k_{\mathrm{overall}} = k_{\mathrm{homo}} + k_{\mathrm{het}}\{\mathrm{SOH}_2^+\} \tag{17}$$

$$k_{\mathrm{homo}} = k_{\mathrm{O_3-homo}}[\mathrm{O_3}] + k_{\mathrm{OH-homo}}[^{\cdot}\mathrm{OH}] \tag{18}$$

$$k_{\mathrm{het}} = k_{\mathrm{Ads}}\left(1 - \frac{k_{Des}\{\mathrm{H}^+\}}{k_{\mathrm{Des}}\{\mathrm{H}^+\} + (k_{\mathrm{O_3-het}}\alpha_{\mathrm{O3}} + k_{\mathrm{OH-het}}\alpha_{\mathrm{OH}})[\mathrm{O_3}]}\right) \tag{19}$$

The surface proton concentration, $\{H^+\}$, may be calculated by the Boltzmann distribution equation: $\{\mathrm{H}^+\} = [\mathrm{H}^+]\exp(-\frac{ze\psi}{kT})$, where z is the ion charge (+1 for H^+); e is the charge of an electron = 1.602×10^{-19} C; k is Boltzmann constant =1.3805×10^{-23} J/K; T is temperature in Kelvin; ψ is the surface potential, which can be approximated from its relationship with the surface charge, σ, by the simplified Grahame equation $\psi = \frac{\sigma\lambda_D}{\varepsilon\varepsilon_0}$.

Integration of Eq. (16) 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:

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

A plot of the LHS as function of time would lead to a straight line with a slope k_{overall}. The model was found to predict very well the results obtained in this study within a relative error of about 10%. Table 2 shows the effect of pH on 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. Clearly the table shows that as the pH increased k_{overall} also increased, which is in agreement with the discussion presented earlier. Besides increased generation of hydroxyl radicals in the bulk solution as a result of increased pH, Eq. 19 also predicts that the heterogeneous rate constant, k_{het}, increases following an increase in pH (i.e. the second term between parentheses becomes smaller when $\{H^+\}$ becomes smaller as a result of reduced $[H^+]$ in the bulk solution). Hence, the effect of pH is of twofold: it increases hydroxyl radicals in the bulk solution and also increases the heterogeneous rate constant on the surface of the AC.

Table 2
Overall rate constants of DEP removal by OAC process at various pHs ($C_0 = 200$ mg/L; $C_{\mathrm{AGin}} = 60$ g/m^3 NTP; $d_p = 2$ mm; AC dose = 2.86 g/L)

pH	k_{overall} (min^{-1})	R^2
2	0.026	0.983
5	0.060	0.998
7	0.097	0.996
9	0.104	0.996

4. Conclusions

The results obtained in this study clearly indicate that HCO using AC outperformed OA for the removal of DEP. For both systems, the pH and ozone concentration played an important role in enhancing the removal rates. The degradation rate and removal efficiency of DEP can also be affected by the dose of the catalyst and initial DEP concentration too. Experiments with the radical scavenger tb revealed that DEP was removed mainly through radical reactions and the contribution of adsorption was significant in the O_3/AC process. This resulted in increased removal rates when the catalyst dose increased. At pH 7, it was found that 4.5 moles of ozone reacted with one mole of DEP. The contributions of adsorption and molecular ozone and radical reactions to the overall removal process were determined. It was found that adsorption and radical reactions had similar rates within the first 25 min followed by a decline in radical reaction contribution. On the other hand, molecular ozone reaction contribution was relatively insignificant. The study also revealed that most of the radical reactions took place within the bulk of the aqueous phase. A model taking into account of the various reactions in the bulk solution and on the surface of AC was developed and was found to predict well the experimental data. This study shows that catalytic ozonation promoted by AC is suitable for phthalates removal from aqueous solutions.

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