



Research article

Removal of diethyl phthalate from water by ozone microbubbles in a pilot plant



Abdisa Jabesa, Pallab Ghosh*

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India

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ABSTRACT

Ozone microbubbles (OMBs) were used to remove diethyl phthalate (DEP) from water in a pilot plant. The removal of DEP and the mineralization efficiency were investigated under various reaction conditions. The removal of DEP by OMBs was very effective at the high pH and high ozone generation rates. Almost complete mineralization of DEP could be achieved at the high pH. The contribution of $\cdot\text{OH}$ was computed by using a hydroxyl radical scavenger (i.e. *t*-BuOH). In neutral and alkaline media, the reaction of DEP with $\cdot\text{OH}$ dominated over its direct reaction with ozone. The overall oxidation reaction fitted a second-order kinetic model. The overall rate constant and the volumetric mass transfer coefficient of ozone slightly increased with increasing pH. The results indicate that the OMBs were efficient in terms of the reduction of concentration of DEP and its complete mineralization.

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1. Introduction

The environmental fate of phthalates is considerably important due to their effects on the health of human beings and animals. Phthalates are synthetic compounds, which are widely used in different industrial applications, predominantly as additives in plastics to improve their mechanical properties during post-processing. They are also present in cosmetics, solvents, lubricants, toys, disposable medical packages and insecticide carriers (Abdel daiem et al., 2012; Khan et al., 2015). They are ubiquitous and persistent organic pollutants in the environment and pose serious problems due to their widespread occurrence. The annual worldwide production of phthalates is about 6–8 million tons (Net et al., 2015; Xie et al., 2007). Most of the phthalates can easily escape into the environment during manufacturing, during the use of the product, and/or after the disposal of the product, because they are not chemically bonded to the polymeric matrix (Huang et al., 2013). They were classified as “priority pollutants” by the United States Environmental Protection Agency (EPA, 2014). Biodegradation is generally the desired removal method for these phthalates. However, some studies have indicated that phthalates

with long alkyl chains are poorly degraded and some of them are considered as resistant to biological treatment (Maldonado et al., 2006; Stales et al., 1997).

Diethyl phthalate (DEP) is one of the most frequently identified phthalates in diverse environments. It is used as a plasticizer in various products such as in plastic packaging and as an ingredient in more than 60 cosmetic formulations (Api, 2001). It was chosen as a model target pollutant in this work because of its high solubility in water and toxicity. The DEP molecule has a non-dissociating structure (Mansouri et al., 2013).

Several methods have been reported for the removal of DEP from water and wastewater. Some of them are ozonation (Jung et al., 2010; Legube et al., 1983), ozonation with UV irradiation (Oh et al., 2006), ozonation in presence of H_2O_2 (Wen et al., 2011), treatment with UV irradiation and H_2O_2 (Xu et al., 2007), ozonation in the presence of activated carbon (de Oliveira et al., 2011; Mansouri et al., 2013; Nahum et al., 2013), electro-peroxone process (Hou et al., 2016), photo-Fenton process (Yang et al., 2005), sonophotolysis and sonophotocatalysis (Na et al., 2012a), and membrane filtration (Bodzek et al., 2004). Most of the ozonation processes have used conventional bubbles or millibubbles. Some works (Yuan et al., 2002) show that DEP is difficult to degrade by the biological and photo-chemical methods. Hence, there is a strong need to search for effective treatment processes for the removal of DEP from water and wastewater.

* Corresponding author.

E-mail address: pallabg@iitg.ernet.in (P. Ghosh).

Affordability, high reactivity towards many pollutants, possibility of generation at the point of use, and self-decomposition to oxygen have made ozone a more promising oxidant than others (Loeb et al., 2012; von Sonntag and von Gunten, 2012). The conventional ozonation plants use ozone millibubbles, whose size depends on the gas sparger used, and usually varies in the range of 2–5 mm. Ozone is sparingly soluble in water (Johnson and Davis, 1996). As a result of their poor ability to dissolve ozone, millibubbles used in the conventional bubble column reactors require a considerable amount of the gas, thereby involving a high energy consumption (Khuntia et al., 2012a). Therefore, a better gas–liquid contactor is required that can enhance the solubility of ozone in water, perform rapid oxidation of the organic compounds, and also decrease the loss of ozone. In this regard, microbubbles can be a good alternative to the conventional millibubbles. Microbubbles have a very low terminal velocity. Due to their high curvature and consequently, high Laplace pressure, the concentration of dissolved ozone in water is more. They are very effective in increasing the rate of transfer of ozone into water (i.e. enhance the concentration of ozone in the aqueous phase). The dissolved ozone generates hydroxyl radicals ($\cdot\text{OH}$) that are highly effective in decomposing the organic molecules (An et al., 2014; Sumikura et al., 2007; Takahashi et al., 2007). $\cdot\text{OH}$ are very effectively generated by the collapse of ozone microbubbles (OMBs) in aqueous solutions (Chu et al., 2008b; Takahashi et al., 2007). The $\cdot\text{OH}$ is a more powerful oxidant than ozone. The standard redox potentials of $\cdot\text{OH}$ and ozone are 2.8 and 2.07 V, respectively (Masten and Davies, 1994). The $\cdot\text{OH}$ readily reacts with various organic compounds through electrophilic addition, electron transfer, hydrogen abstraction, and radical–radical reactions, which often leads to the complete mineralization of the organic compound (Ikehata et al., 2006; Oppenländer, 2007).

In recent years, the microbubble-aided technology has been extensively used for improving ozone-based advanced oxidation processes for water and wastewater treatment. For instance, OMBs have been used for the oxidation of phenols (Shin et al., 1999), dimethyl sulfoxide (Li et al., 2009), pollutants present in textile wastewater (Chu et al., 2008a), dyes (Chu et al., 2007; Khuntia et al., 2014b), residual pesticides (Ikeura et al., 2011), soluble organics like BTEX (i.e. benzene, toluene, ethylbenzene, and xylenes) (Walker et al., 2001), ammonia (Khuntia et al., 2012b), As(III) (Khuntia et al., 2014a), sludge (Chu et al., 2008b), and in the disinfection of *Bacillus subtilis* spores (Zhang et al., 2013) and hydroponic culture solutions (Kobayashi et al., 2011). Thus, the use of OMBs may be a good alternative method for complete degradation and mineralization of DEP present in water.

As far as we are aware, hardly any work has been reported on the use of OMBs for the removal of DEP from water in a pilot plant scale. The objective of the present work was to investigate the removal efficiency of DEP by OMBs in a pilot plant using a commercial MBG. The major parameters which influence the removal of DEP, such as its initial concentration, ozone generation rate (i.e. concentration of ozone in the gas), and the pH of reaction medium, have been studied. In addition, the contribution of hydroxyl radicals to the removal of DEP and the effect of H_2O_2 on ozonation have been investigated. The TOC of the solutions was analyzed to determine the extent of mineralization. The overall kinetic parameters of the reaction between DEP and ozone, and their variation with the pH of the medium have been determined from the experimental results. Microbubbles enhance mass transfer as compared to the conventional bubbling process. Therefore, the microbubble-based ozonation process is expected to provide a better efficiency for the removal of DEP and mineralization.

2. Experimental section

2.1. Materials used

DEP [make: Alfa Aesar (England), 99% assay], acetonitrile [make: Spectrochem (India), 99.9% assay], hydrogen peroxide [make: Merck (India), 50% assay], hydrochloric acid [make: Merck (India), 35% assay], sodium hydroxide pellets [make: Rankem (India), >98% assay], and *t*-butanol [make: Spectrochem (India), 99.5% assay] were used in this work. They were of analytical grade and used as received from their manufacturers. Stock solutions were prepared by using the Milli-Q water of a conductivity of $0.055 \mu\text{S cm}^{-1}$ (at 298 K). Standard pH solutions for pH calibration were purchased from Oakton (USA). If not stated otherwise, all aqueous solutions were initially prepared at pH 7 and the initial concentration of DEP in the aqueous solution was 0.18 mol m^{-3} .

2.2. Experimental method

The details of the experimental setup (Khuntia et al., 2012b) are shown in Fig. 1. It has an oxygen concentrator, an ozone generator, a microbubble generator (MBG), and a destructor of excess ozone. The ozonation was carried out in a polycarbonate reactor of 20 dm^3 capacity. The reactor was connected to the MBG [make: Riverforest Corp. (USA), model: AS MK-III], which operated in a continuous recirculation mode. Tap water was used to prepare the aqueous solutions. It was filtered through an iron removal cartridge [make: Eureka Forbes (India), model: Iron-Nil]. The oxygen concentrator [make: Oz-Air (India), model: HG 03] was used to isolate oxygen from air. It generated high purity oxygen from air (>98% by volume). This oxygen was fed to the ozone generator [make: Oz-Air (India), model: ISM 10 Oxy], which converted oxygen to ozone by the corona-discharge method (Ciambrone, 1976). The ozone generation rate varied in the range of $0.5\text{--}3.0 \text{ mg s}^{-1}$, as per the recommendation of the manufacturer. A rotameter ($8\text{--}80 \text{ cm}^3 \text{ s}^{-1}$) was used to measure the flow rate of the gas mixture (i.e. oxygen and ozone) coming out of the ozone generator.

The gas mixture from ozone generator was fed to the MBG. The concentration of ozone in the gas mixture that was fed to the MBG varied in the range of 0.7–2.7%, for the ozone generation rate of $0.6\text{--}2.2 \text{ mg s}^{-1}$. In the MBG, the dissolution of gas in water was achieved by applying a high pressure and the microbubbles were continuously generated by the release of pressure. The MBG produced a milky dispersion of microbubbles. Fig. 2 depicts the bubble size distribution. From Fig. 2 it can be seen that about 65% of

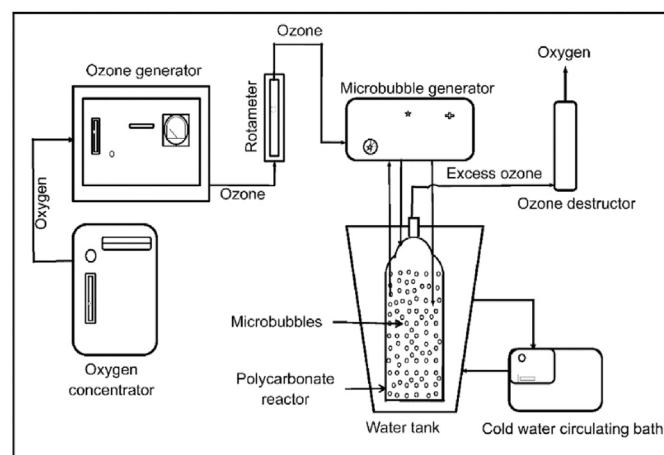


Fig. 1. Experimental setup for ozonation using microbubbles.

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