



The interaction mechanism and characteristic evaluation of ethylbenzene/chlorobenzene binary mixtures treated by ozone-assisted UV_{254nm} photodegradation



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ABSTRACT

In the present study, we investigated ozone-assisted photodegradation (UV_{254nm}) of two common VOCs in a mixture, ethylbenzene (EB) and chlorobenzene (CB). Our results demonstrated that the photodegradation method was most efficient when ozone was introduced into the reaction system. When using this system, a significant combined effect from ozone and hydroxyl radicals was observed in the conversion of targets. The Cl radicals could suppress ozone and hydroxyl radical reactions, and thus the inhibition on EB conversion caused by higher relative humidity (RH) levels was not present. When the ratio of ozone to VOCs was 2 and RH was 75–80%, many lighter carbonyls (benzoic acid, benzaldehyde, formic acid, etc.) were observed. Under these conditions their contributions to the carbon mass balance was 43.2%. According to the toxicity results, the optimal reaction condition was the same as the condition which generated the largest amount of total organic carbon. Here, the main product was chlorophenol and thus must be controlled.

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1. Introduction

The continual release of toxic volatile organic compounds (VOCs) into the atmosphere from a variety of sources (industrial facilities, transports, aerosolized paints, domestic activities, etc.) has resulted in the gradual deterioration of the atmospheric environment [1]. More stringent VOC emission regulations have been enacted due to associated human health risks and environmental impacts. These new regulations have motivated research on new methods for preventing and removing VOCs.

Since 1970, the Environmental Protection Agency (EPA) has tracked the efficacy of methods to control VOCs. Conventional physical and chemical VOC removal processes, including absorption, adsorption, condensation and thermal oxidation, are relatively expensive and/or generate secondary pollutants. Bio-treatment has been widely used for VOC control in recent years and has several benefits. Bio-treatment is highly efficient, low cost and does not produce hazardous residues [2,3]. However, some VOCs are ill-suited for bio-treatment due to their physical properties (e.g., low water solubility or high toxicity) which require large

bioreactors and significantly reduce removal efficiencies [4,5]. Therefore, suitable pretreatments are being developed to break the technical bottleneck and broaden bio-treatment applications.

Advanced oxidation processes (AOPs), such as ultraviolet (UV) photolysis or photocatalysis, are regarded as effective mineralizing or partially oxidizing methods for most VOCs. These methods are even effective when dealing with recalcitrant compounds [6]. In such processes, strong oxidizing species (e.g., hydroxyl radical and ozone) react with absorbed organic pollutants producing carbon dioxide. If total mineralization is not achieved then other organic by-products are also produced. These intermediates are more water soluble and biodegradable than the parent compounds and can be efficiently removed by subsequent bio-treatments [7,8].

The utilization rate of light energy is significantly lower in direct UV photodegradation systems, especially the traditional UV source-system (wavelengths of 254 nm or 365 nm). Because of this, several technologies (such as TiO₂-assisted) have been tried to obtain higher light utilization efficiencies [9]. Ozone-assisted photodegradation is a novel technology and has already been shown to successfully control several hydrophobic and recalcitrant VOCs [10]. Besides the soluble and biodegradable by-products, the residual ozone in such systems influences the growth of microorganisms in subsequent biotreatments (lower concentrations would

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stimulate and higher concentrations would inhibit) [11,12]. Due to ozone's multiple effects, the direct photolysis systems that employ ozone are receiving increasing amounts of attention.

Despite the fact that most industrial VOC emissions are mixtures of different compounds, VOC mixture removal studies are relatively scarce. This scarcity extends to studies that investigate ozone-assisted photodegradation. A few studies have dealt with the photocatalytic degradation of VOC mixtures. It has also been reported that the photocatalytic removal of aromatic compounds was affected by the presence of other compounds [13,14]. For example, in toluene, acetone and *p*-xylene mixtures, toluene degradation was enhanced in the ternary mixture, while degradation of acetone and *p*-xylene was reduced [15]. In addition, the interaction mechanisms and the intermediate-characteristics of ozone-assisted photodegradation have not been clearly defined. Therefore, there is considerable interest in developing an ozone-assisted photodegradation approach for the removal of VOC mixtures.

The present work focuses on investigating ozone-assisted photodegradation of ethylbenzene (EB) and chlorobenzene (CB) in a lab-scale continuous gas reactor. Continuous mode experiments were performed using different inlet VOCs concentrations and relative humidity (RH) levels. There are four main aims of this study: (1) to determine the UV absorption of different compounds using photonic efficiency, (2) to test the influence of RH on the degradation of VOC mixtures, (3) to determine how a binary mixture influences individual reactivity with degradation compounds and (4) to determine the carbon balance of the VOC mixture after photodegradation and the characteristics (ecotoxicity and the influence on cell surface) of the intermediates formed. Preliminary results suggested that the ozone-assisted method may be a promising technology for the efficient removal of recalcitrant/insoluble VOC mixtures.

2. Materials and methods

2.1. Chemicals

The VOCs used in this study, EB and CB (analytical grade), were purchased from J&K Chemical. The purified air and oxygen (99.99%) was supplied by Jingong Gas Company (Hangzhou, China). All other chemicals were of the highest purity commercially available.

2.2. Experiment set-up

A custom-made spiral quartz column (150 cm³, total length: 300 mm; inner diameter: 10 mm) equipped with a special low-pressure mercury vapor lamp (18 W, Electrical Light Sources Research Institute, Beijing, China) was used to investigate the ozone-assisted photodegradation of the VOC mixture. The main wavelength of 254 nm and the light intensity of 0.224 mW m⁻² from 1 m were measured by the National Center of Supervision and Inspection on Electric Light Source Quality (Shanghai). Since the distance between the lamp surface and the reactant was shorter than 10 cm, the light intensity was kept constant during the duration of the study. All experiments were conducted at a stable room temperature (20 °C). Gas sampling points were located at the reactor's inlet and outlet.

A continuous gaseous stream flow of EB and CB was generated using two different spargers filled with pure liquid EB and CB. A constant air flow was passed over the spargers, and humidified air mixtures were used to regulate the RH of the experiments. The target humidity, EB concentrations and CB concentrations were obtained by the adjustment of gas flow rates using mass flow controllers. Different ozone ratios were generated by an adjustable

concentration ozone producer (Ican-CYF-3, Rongxin Electronic Equipment Company, Hangzhou, China) and introduced into the mixtures. The final stream gas humidity, EB or CB concentration as well as ozone concentration were measured using a humidity meter (Testo 625, Germany), a gas chromatograph (GC, Agilent 6890, USA) and the on-line ozone detector CPR-G6 (Shanmeishui-me Co. Ltd., Beijing, China) using the parameters we have previously reported [16].

Gaseous and liquid-absorbed samples were collected from the reactor's inlet and outlet ports by an automatic gas sampler (LaoYing 3072, Qingdao, China) with a sample volume of 19.98 L (Standard conditions of 0 °C and 101.32 kPa). Three bottles connected in series were filled with absorption solution (50 mL each) and used to capture any photodegradation products. There were four selected types of absorption solutions, and each type was used every run. (1) Deionized water was used to measure soluble intermediates, expressed as soluble total organic carbon (TOC), and was measured by the Shimadzu TOC-VCPH (Shimadzu, Kyoto, Japan); (2) 0.1 M NaOH solution used to measure CO₂ amounts, which was expressed as inorganic carbon (IC) measured by a Shimadzu TOC-VCPH (Shimadzu, Kyoto, Japan); (3) a mixture of acetone and hexane (1:1 volume ratio) was used to detect the intermediates by GC-MS (Agilent 7000A); (4) 0.025 M phosphate buffer solution was used to determine the toxicity of intermediates from ozone-assisted photodegradation. For the analysis of intermediates, the following method was applied. GC was equipped with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and interfaced directly to the mass spectrometer. The GC column was operated at a temperature of 50 °C for 2 min and then the temperature was increased at 20 °C min⁻¹ to 280 °C and held at 280 °C for 5 min. All tests were carried out in triplicate. Prior to all experiments, the reactor was purged with purified air for 30 min to decontaminate the quartz column and the lamp.

2.3. Toxicity assays

Zebrafish (*Danio rerio*) were obtained from the Institute of Hydrobiology, at the Chinese Academy of Science (Wuhan, China). These fish were maintained and propagated in our lab. Different absorption solutions (obtained under different reaction conditions) were individually added to the cultural medium to ensure equality of final concentrations. The measurement of acute toxicity induced in the zebrafish was performed according to the standard determination for acute substance toxicity for freshwater fish. The 50% effect concentrations for mortality (Lethal concentration-50%, LC₅₀) were calculated using the Sigmoid Fit function in ORIGIN 8.0.

The toxicity test for zebrafish embryos strictly followed the OECD (Organization for Economic Cooperation and Development) guidelines (1998). Fish eggs were collected and rinsed three times in reconstituted water to remove any residue from the egg's surface. Fertilized eggs were selected for exposure experiments after visual inspection using a stereomicroscope. The fish eggs were transferred into a 24-well plate, such that each well contained one embryo. Twenty wells were filled with 2 mL of a treatment solution and the remaining four wells were filled with 2 mL reconstituted water to act as controls. The treatment solution contained one of the following compounds: CB, EB, chlorophenol or acetophenone; the latter two are the main intermediates of CB and EB as reported in our previous study [16]. All of the wells were covered with transparent plastic film and maintained at 26 ± 1 °C under a 10/14 h light/dark cycle. The zebrafish embryo development from blastula to early larval stages was monitored at specified time intervals (24, 48, 72, 48 and 96 h) using an inverted microscope (8–50×) (IMT 2, Olympus Corporation, Tokyo, Japan). Endpoints used for assessing developmental toxicity were recorded and described for both control and treated embryos.

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