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Indirect Determination of Hydroxyl Radicals in Fine Particle Mist Generated from an Odor Control Technology via HPLC

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Size distribution analysis of microsized water particle mist generated from an odor control technology showed the majority of particles to be in the low micron range. The indirect detection and determination of hydroxyl radicals generated by their reaction with benzene to produce phenol was performed through UV-Vis spectrophotometry (UV-Vis) and high performance liquid chromatography (HPLC). These techniques gave verification of the presence of hydroxyl radical species in the water samples collected via this odor control technology. This technology is currently being utilized at various wastewater treatment plants.

Keywords Ozone, Odor Control, Hydrogen Sulfide, Hydroxyl Radical, Benzene, Oxidation

INTRODUCTION

The hydroxyl radical, $^{\bullet}OH$, is one of the most reactive species belonging to the reactive oxygen species family, ROS. Hydroxyl radicals are generated by several methods such as the decomposition of hydrogen peroxides by photolysis or in atmospheric chemistry by the reaction of water with excited atomic oxygen (Mopper and Zhou 1990; Zhou and Mopper 1990). Hydroxyl radicals have been shown to enhance corrosion due to their reaction with water and oxygen, and are also highly reactive with pollutants and can cause cellular damage (Page et al. 2010). Hydroxyl radicals are widely used in the treatment of drinking, industrial, and wastewater due to their effectiveness in destroying organic chemicals, as they are electrophiles that react rapidly and nonselectively with nearly all electron-rich compounds (Stasinakis 2008).

The instability of these hydroxyl radicals makes their direct detection difficult as they react rapidly with their surroundings (He et al. 1988; Otsuka et al. 1992). Because the direct detection of hydroxyl radicals is complex, several indirect determination methods have been studied including the direct hydroxylation from benzene to phenol (Bahidsky and Hronec 2004), a time-gated luminescence detection (Page et al. 2010), monitoring of photo production rates (Takeda et al. 2004), trace determination (Li et al. 1997), photochemical production (Joseph et al. 2010), advanced oxidation with salicylic acid trapping with liquid chromatography (Jen et al. 1997), and photolysis of Fe(III) pyruvate complexes among others (Chen and Mopper 2000; Kilinc 2005; Nakatani et al. 2007; Stokes et al. 1994; Wang et al., 2006a; Wang et al. 2006b; White and Yu-Ping, 2000). A widely used indirect technique involves the reaction of hydroxyl radicals with benzene resulting in the formation of phenol. The reaction mechanism is stoichiometric, where one molecule of phenol is generated per each hydroxyl radical reacting with one molecule of benzene (Blakrishnan and Reddy 1970; White and Yu-Ping 2000).

During this study, the indirect determination of the hydroxyl radical by its reaction with benzene was applied to aid in the determination of the chemical mechanism of the OhxyPhogg process. This odor control technology, OhxyPhogg, claims to generate a hydroxyl radical fine particle mist as stated by the patent, which utilizes an air, ozone, and water mixture to oxidize hydrogen sulfide and other odorous compounds such as mercaptans and amines. This system utilizes a 3-fluid nozzle patented by Vapex Environmental Technologies, Oviedo, FL, USA. This nozzle combines water, air and ozone molecules to generate microsized water particles. Previous studies show that the microsized water particles provide large surface areas for both adsorption and reaction of pollutants in the atmosphere. It has been observed that organic solutes such as polycyclic aromatic hydrocarbons, pesticides, and alkanes are found at concentrations higher than those expected from their corresponding gas-liquid-phase equilibria (Glotfelty et al. 1990), which was hypothesized to result from surface adsorption on fog droplets (Valsaraj et al. 1993).

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NOTE: OHxyPhogg was a trademarked name for Vapex units under a licensing agreement with Parkson Corporation

Recent work on naphthalene vapors also showed that small water droplets in the micrometer range had higher concentrations of these vapors than the large droplets (Raja and Valsaraj 2003).

Furthermore, it is also recognized that the smaller the size of droplets the higher the internal pressure. According to the Young–Laplace equation, for a bubble with diameter 1 μm at 298 K, the internal pressure is about 390 kPa (Agarwal et al. 2011). Hydroxyl radicals and shock waves can be generated at the gas–liquid interface due to pyrolytic decomposition that takes place within the collapsing microsized water particle (Kimura and Ando 2002). Consequently, the decomposition of ozone for producing hydroxyl radicals is accelerated in the case of water containing ozone microbubbles (Takahashi et al. 2007). Due to this phenomenon, microsized mists of gases with oxidizing ability, such as ozone, have been applied to various water treatment processes since the ozone microbubbles have high solubility and improved disinfection ability due to the generation of hydroxyl radicals and/or pressure waves (Sumikura et al. 2007).

During this investigation, the analysis of droplet size created from the fine particle mist was studied to corroborate the claim that the OhxyPhogg technology can indeed produce micron-sized water particles. Further studies were performed to verify and quantify the presence of hydroxyl radicals. For this study, the analyzed samples were collections of the resulting hydroxyl radical fine particle mist after a mixture of saturated aqueous benzene, ozone, and air was sprayed through the nozzle. Phenol is formed as a stable product of this reaction and thus the quantification could be performed. Therefore, the purpose of this study was to apply an indirect method for the detection of hydroxyl radicals supposedly generated in the fine, microsized water mist.

EXPERIMENTAL

Materials and Reagents

Phenol (Fisher Scientific, 99%, Fair Lawn, NJ, USA) was used to prepare standard phenol solutions using saturated aqueous benzene as the solvent. The saturated aqueous benzene solution with a concentration of 2.23×10^{-2} M was prepared using benzene obtained from Sigma Aldrich (99%, Saint Louis, MO, USA). All aqueous solutions of phenol and benzene were prepared using triple-distilled water with 18 ΩM resistivity (Barnstead B-Pure). Acetonitrile (Fisher Scientific, HPLC grade, Fair Lawn, NJ, USA) and triple-distilled water from a B-Pure Barnstead purification system producing ~18 ΩM cm water were used as the eluent solutions for HPLC. Water samples collected from the experimental setup were analyzed as received. All chemicals and solvents used were of reagent grade and were used without further purification unless specified. A DC-III droplet measurement technology (KLDLABS incorporated, Huntington Station, NY, USA) was used to measure the droplet size distribution of the generated mist in the reactor.

Methods

UV-Vis spectrophotometry was performed using a Varian Cary 50 spectrophotometer (Santa Clara, CA, USA). The data interval was set under a minimum ratio of spectral band width (SBW) of 3:1. A quartz cuvette with dimensions of 10-mm path length and 4-mm path width was used for all UV-Vis experiments.

The HPLC experiments were performed using a Perkin-Elmer series 200 HPLC (Santa Clara, CA, USA) consisting of a series 200 binary pump, a series 200 UV-Vis detector with deuterium lamp set at a maximum wavelength of 273 nm, a series 200 autosampler, and a series 200 vacuum degasser. The analytical column used was a Zorbax (Agilent) SB-C18 column. The mobile phase was $CH_3CN:H_2O = 50:50$ (v/v) with a flow rate of 1 cm^3/ min. A 50-μdm^3 portion of the sample was injected with a 50-μdm^3 gas-tight syringe.

Determination of Phenol in Standard Solutions

Ten concentrations of aqueous phenol in saturated aqueous benzene solution (2.23×10^{-2} M) were prepared via serial dilution (Arnold et al. 1958); 5.00×10^{-5} M, 3.00×10^{-5} M, 1.00×10^{-5} M, 5.00×10^{-6} M, 3.00×10^{-6} M, 1.00×10^{-6} M, 7.00×10^{-7} M, 5.00×10^{-7} M, 3.00×10^{-7} M, and 1.00×10^{-7} M. These solutions were used as HPLC standards. These standards were then studied on the HPLC after conditioning the column for 60 min. The solvent, 2.23×10^{-2} M aqueous benzene, was also analyzed via HPLC to determine its elution time. A calibration curve was constructed using the 10 standard solutions of phenol in order to indirectly quantify the hydroxyl radicals present in the water samples collected from the reactor.

Apparatus and Sampling

The experimental apparatus was designed as shown in Figure 1. The water collection apparatus was a steady-state flow-through system, which consisted of a black, thick polyethylene cylinder that was divided into four chambers designated C-1, C-2, C-3, and C-4, respectively. Each of the chambers was separated by an acrylic disk with an 8.5-inch diameter opening in the middle to allow the passage of the fine particle mist. Each chamber had a condenser designed to condense the mist particles for easier sample collection and a valve that allowed for the collection of these samples. At the head of the cylinder, the odor control technology generated a mist that was injected into the space with the patented 3-fluid nozzle (Erb and Resch 2000).

This nozzle combines ozone with a rapid application of microsized water particles that generates a mist of hydroxyl radicals. This mist was then dispersed through the open space with subsequent passage through the 8.5-inch disk holes for complete dispersion into the entire reactor. For experimental purposes, the water line was replaced with a line containing a saturated aqueous benzene solution with a fluid flow rate of about 2 gal h^{-1}. The saturated aqueous benzene solution was sprayed through the nozzle to create the mist and was allowed

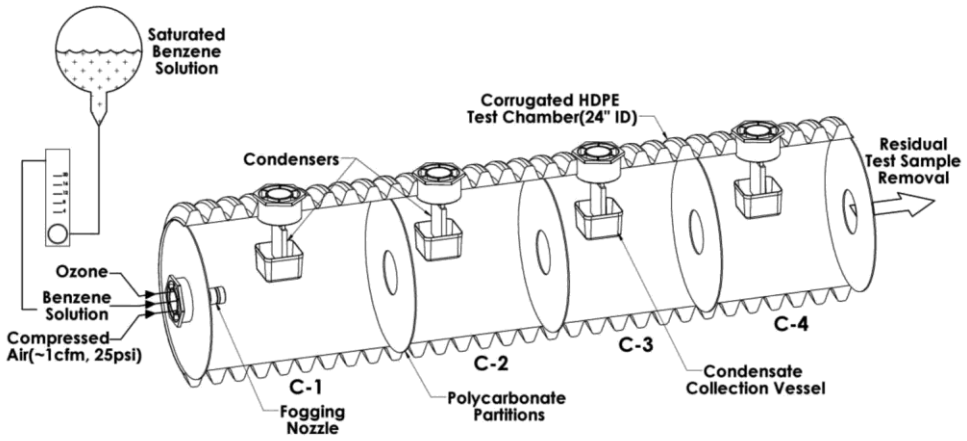


FIGURE 1. Diagram of the experimental system showing the patented nozzle connected to a cylindrical collection unit divided into four chambers.

to react with ozone and air in the first reaction chamber. The reaction time was measured from the point when the ozone reached a steady concentration of approximately 13,000 ppm. The resulting mixture of microsized water particle mist then traveled through the four chambers as the bigger droplets collapsed at the bottom of the reactor. The reaction was allowed to take place for 2 h before the condensed samples from each of the four chambers were collected as illustrated in Figure 1.

RESULTS

Droplet Size Analysis

The DC-III probe was inserted in the headspace in each of the four chambers to obtain the size distribution of the microsized water droplets in the fine particle mist. Figure 2 illustrates the observed volume mean diameter and the size of the particles in the headspace of each of the chambers. Over 90% of these particles are in the range of 10–60 μm. The largest particles were observed in chamber 1 and were found to have an average diameter of 55.22 μm, whereas the smallest particles with an average diameter of 13.90 μm were observed in chamber 4 as shown in Figure 2. The size of these droplets demonstrated a decreasing trend going from chamber 1 (closest to the nozzle) to chamber 4 (furthest from the nozzle), as only the smaller droplets travel through the reactor unit, whereas the bigger droplets condense out at the bottom of each chamber.

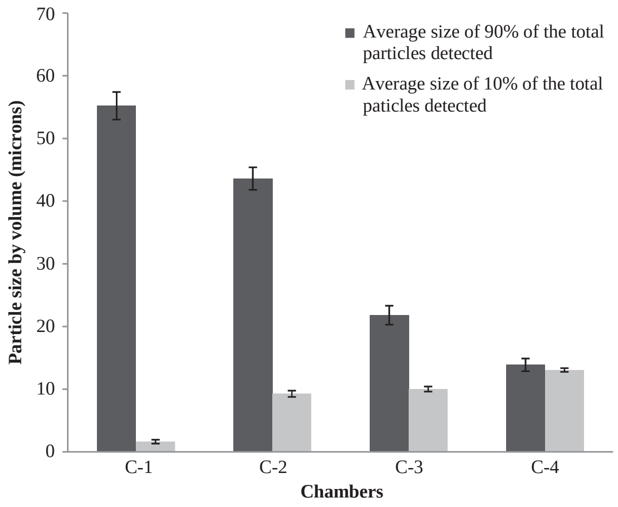


FIGURE 2. Size distribution of the microsized fine particle mist in the four reaction chambers.

UV-Vis

A UV-Visible spectrograph was used for the identification of the phenol generated by the reaction of benzene and hydroxyl radicals. For this experiment, standard solutions with various concentrations of phenol in aqueous benzene were prepared in the range of 50–500 parts-per-million (ppm). The saturated benzene concentration utilized was 5.0×10^{-3} M and it was used as the solvent for the preparation of the standard mixtures. The maximum absorption wavelengths recorded were 270 nm for phenol and 250 nm for benzene which when compared to literature, were very similar with values of 270.75 nm or 273.75 nm for phenol and 254.75 nm for benzene (Zhang et al. 2006). These wavelengths were also utilized for the initial parameters in the HPLC analysis. The UV-Vis absorbance spectrum of a standard solution is shown in Figure 3a, and Figure 3b shows the absorbance spectra of the samples collected from the reactor.

HPLC Results of the Standard Solutions

The first step in the quantification of the amount of hydroxyl radicals produced was to generate a calibration curve of known standard solutions. Ten different solutions of phenol

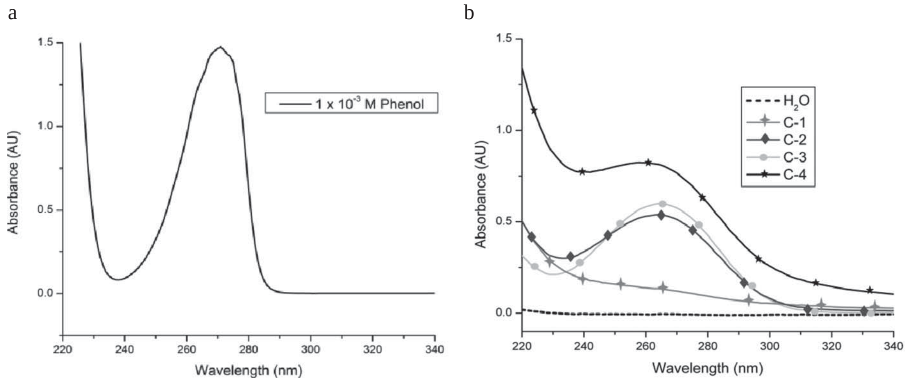


FIGURE 3. UV-Vis spectrum of (a) standard phenol solution and (b) blank and water samples from each of the four reaction chambers.

in saturated benzene were used as the standard solutions and were analyzed via HPLC. Retention times of 2.6 min and 4.4 min were observed for phenol and benzene, respectively.

Figure 4 shows the chromatograms of the standard solutions used for the calibration curve. The area of the peak associated with phenol was analyzed for each solution and a plot of phenol concentration versus peak area was constructed. A best fit line was plotted through the data points resulting in R^2-value of 0.99998. The line equation:

$$A = 5.23 \times 10^{-9} \times C - 29.07 \qquad [1]$$

where A is the peak area in μV^{*}s and C is the concentration in molarity, was then used to determine the phenol concentration in the various fine particle mist samples from the reactor.

HPLC Results of the Reactor Samples

The four experimental samples collected, one from each chamber, were examined via HPLC using the same parameters as for the standard solutions. Phenol had a retention time of 2.6 min as shown in Figure 5, and the retention time of benzene was observed at approximately 4.5 min. The area under the phenol peak was substituted into the linear equation from the calibration curve to solve for the phenol concentration in each of the four reactor samples. Chamber three, C-3, had the highest concentration of phenol followed by C-4, C-2, and C-1, respectively, as shown in Table 1. All four samples were within the linear dynamic range of the calibration curve. The calculated hydroxyl radical concentrations in terms of molarity and parts per million are as also shown in Table 1.

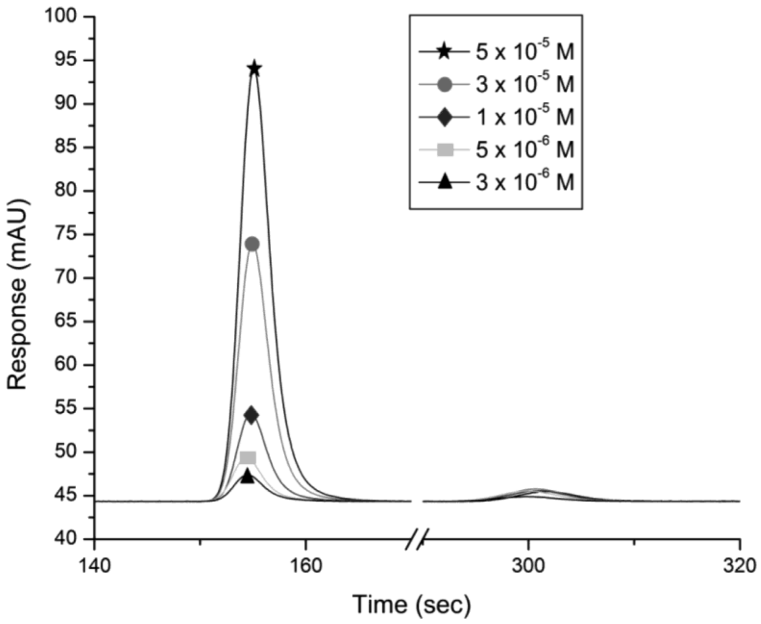


FIGURE 4. HPLC chromatograms of the standard phenol solutions (a) 5.00×10^{-5} M, (b) 3.00×10^{-5} M, (c) 1.00×10^{-5} M, (d) 5.00×10^{-6} M, and (e) 3.00×10^{-6} M.

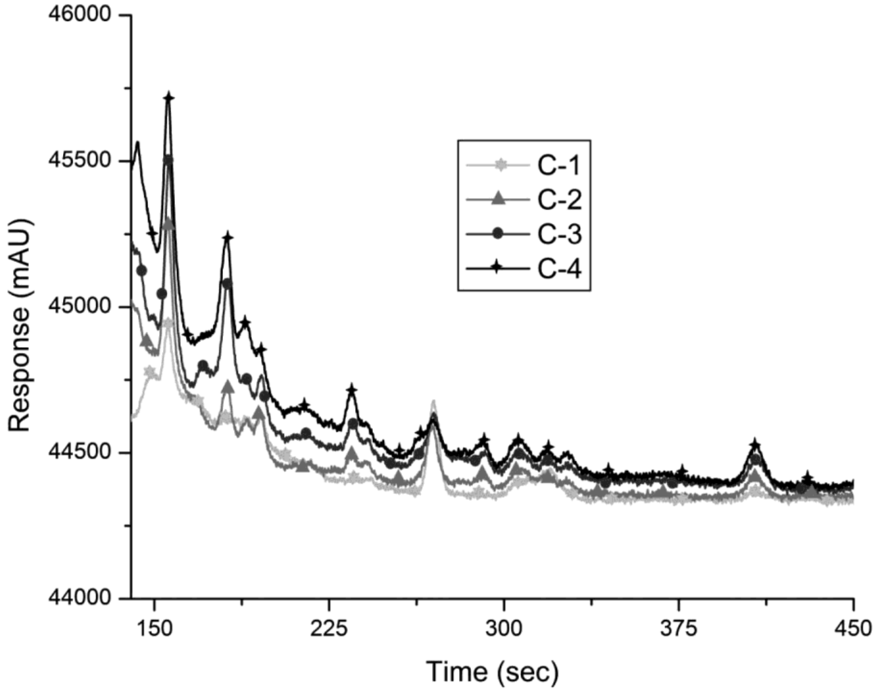


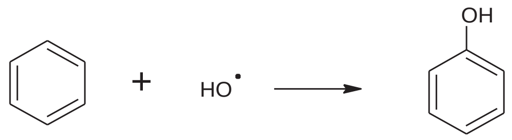
FIGURE 5. HPLC chromatogram overlay of the experimental samples collected from each of the four chambers showing the retention time of phenol along with aqueous saturated benzene solution.

TABLE 1. Calculated Concentrations of Hydroxyl Radicals in Each of the Four Reaction Chambers Based on HPLC Analysis

Reaction Chamber	Peak area (μV*s)	Peak height (μV)	$[^{\bullet}OH]$ (M)	$[^{\bullet}OH]$ (ppm)
C1	1281.83	316.59	2.62×10^{-7}	0.0247 ± 0.0121
C2	2766.35	698.85	5.59×10^{-7}	0.0526 ± 0.0163
C3	4085.23	939.48	8.23×10^{-7}	0.0774 ± 0.0108
C4	3758.3	888.12	7.57×10^{-7}	0.0713 ± 0.0098

DISCUSSION

The hydroxyl radicals generated from the odor control technology were verified using UV-Vis and were quantified via HPLC. The generated hydroxyl radicals reacted with benzene to form phenol as the major product as shown in Equation [2]. The 1:1 stoichiometry of hydroxyl radical to phenol allows a straightforward quantitation of the hydroxyl radicals formed.



[2]

Although ozone is also known to react with benzene, the reaction kinetics are considerably slower than the reaction of benzene with the hydroxyl radicals (Beltran 2004). These reactions are reported to have reaction rates of 12 M^{-1} s^{-1} and 41.2 M^{-1} s^{-1}, respectively (Beltran 2004; Mehta et al. 1989; Tully et al. 1981). Moreover, the ozone concentration monitored in all chambers during the collection of samples and the generation of the fine particle mist remained constant. In that regard, we are fairly confident that the phenol concentration determined can be attributed to the reaction with hydroxyl radicals and not with ozone. In general, the hydroxyl radical concentrations were observed to be in the low parts per million range. As expected, C-3 and C-4 showed the highest radical concentrations since the smallest microsized water droplets were present in those chambers, as the larger particulates could not pass across the holes in the separation disks.

CONCLUSIONS AND FUTURE PERSPECTIVES

This study investigated an odor control technology, OhxyPhogg, which has recently been developed and is

NOTE: OHxyPhogg was a trademarked name for Vapex units under a licensing agreement with Parkson Corporation

currently being used in the United States. The experimental results showed that the system does generate a micro-sized hydroxyl radical mist via the patented atomizing nozzle. Successful indirect detection and quantification of the hydroxyl radicals was performed through UV-Vis and HPLC. The detection limit based on the calibration curve was determined to be 1.00×10^{-7} M, which was adequate for the detection range of the collected reactor samples.

A detailed test of the reaction conditions at various pH levels to examine the optimum generation and efficiency of this hydroxyl radical mist upon its reaction with hydrogen sulfide gas is currently being investigated. The optimum reaction ratio of ozone to hydrogen sulfide with and without the presence of water is also being explored.

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