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Estimation of Hydroxyl Free Radicals Produced by Atmospheric Air Cold Plasma with Salicylic Acid Trapping

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Salicylic acid is used as a scavenger to quantify free hydroxyl radicals (•OH) produced from a cold plasma process. High-performance liquid chromatography revealed that salicylic acid was decomposed to 2,3-dihydroxybenzoic acid (2,3-DHB) and 2,5-dihydroxybenzoic acid (2,5-DHB). The concentrations of 2,3-DHB and 2,5-DHB were the highest when the concentration of salicylic acid was > 8,000 mg/L. Quantifying 2,3-DHB and 2,5-DHB concentrations revealed the association between the •OH concentration and the reaction time by using the following first-order equation: [•OH] = 0.01713t + 0.0311. Additionally, the rate of •OH formation in relation to different cold plasma conditions was also determined.

Keywords: Hydroxyl free radical, Salicylic acid, Cold plasma.

INTRODUCTION

Cold plasma with a high-voltage electrical barrier induces high oxidation potential, which has a wide application in wastewater treatment due to its ability to produce reactive oxygen species such as ozone, hydrogen peroxide, and free hydroxyl radicals (•OH) [1-4]. In particular, •OH are considered strong non-selective oxidants (E° = 2.8 V) [5]. Therefore, analyzing the formation rate of •OH based on the cold plasma environment has its significance.

Several techniques have been developed for indirectly quantifying •OH, for example, ESR spin-trapping with nitrone 5,5-dimethyl-1-pyrroline-*N*-oxide or 3,5-dibromo-4-nitrosobenzene sulfonate [6,7], Fricke dosimetry [8,9], iodide dosimetry [10], dimethyl sulfoxide dosimetry [11], terephthalate dosimetry [12-14], and through salicylic acid [15-17]. These methods involve the quantification of reaction products, which are indirectly related to •OH participating in the reaction. The main differences between these methods are the reactant (scavenger) used, reaction products determined and process specificity.

In the cold plasma process, •OH may undergo recombination, affecting in the correct estimation of •OH. Therefore, while quantifying •OH in reaction systems, maximum accessibility of the reactant to •OH must be ensured. Using salicylic acid decomposition for indirect quantification of •OH has several advantages, such as (i) specificity, *i.e.*, measured hydroxylated products are produced by •OH, with no intermediate products [16] and (ii) salicylic acid and •OH produces products that can be easily separated through HPLC (Fig. 1) [15,16].

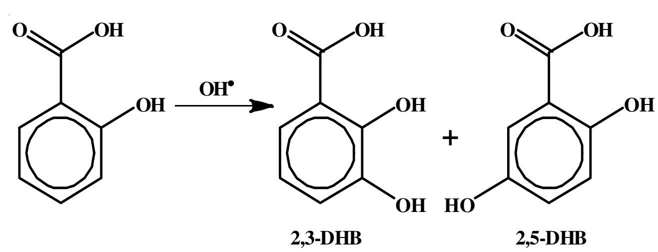

Fig. 1. Product of salicylic acid reaction with •OH radicals

The reaction products of salicylic acid and •OH are based on the hydroxylation of the third and fifth positions of the aromatic ring (Fig. 1). HPLC revealed that the main reaction products are 2,5-dihydroxybenzoic acid (2,5-DHB) and 2,3-dihydroxybenzoic acid (2,3-DHB). Formed the quantity of these reaction products helps to determine the quantity of •OH in a 1:1 molar ratio.

EXPERIMENTAL

Analytical purity grade of solvents, chemicals and salicylic acid were obtained from Merck, U.S.A. and used without further purification. All the solutions were prepared prior to carrying out experiments and kept at 60 ºC in a thermostatic device (Kewei MH-100, China) to ensure salicylic acid does not crystallize. The determination of the reaction products of salicylic acid was made with a HPLC Model HP 1100 using diode-array detector Agilent (U.S.A.).

Air cold plasma DBD reactor: The reactor consists of a high-voltage pulse generator attached to an electrode system in a thin layer of water. Ozone generation and its dissolution in water are ensured through air infusion (2-4 L/min) inside and outside the quartz tube of plasma chambers by using a pump. To efficiently degrade salicylic acid, a metered pump was used in the reactor for circulating wastewater at a speed of 1.2 L/min.

For dielectric barrier discharge (DBD), two electrodes are separated with an insulating dielectric barrier. In this study, a plasma DBD reactor consisting of two electrodes was used, namely a stainless steel electrode placed in the centre (21 mm diameter) and a copper electrode (HV) wrapped around the quartz tube (34 mm diameter). These coaxial electrodes were fixed on a plastic base insulated with Teflon. For removing water from the plasma reactor, a hole was drilled on the base. The insulating glass tubes had a high voltage to produce electrical sparks, which evenly spread around the pipe without damaging it. The electrodes were connected to a high voltage source of approximately > 10 kV. The sparks that are discharged in air between the outer surface of the water layer and inner glass tube produce DBD cold plasma between these layers.

Atmospheric air cold plasma DBD treatment: The inner electrode supplied water, which was flowed downward onto the outer surface of pipe wall, forming a 0.5-1 mm thin film based on the pump velocity. DBD plasma was obtained in the reactor chamber through adjustment of the two electrodes to produce a voltage of approximately > 10 kV). Thus, DBD air-cold plasma was formed by using UV, ozone and other reactive reagents, such as $^{\bullet}OH$, $^{\bullet}H$ and H_2O_2 [1-4]. The aforementioned active components are considerably strong oxidizing agents, which can be used for degrading pollutants in wastewater. Fig. 2 presents the structure of plasma DBD obtained from the atmospheric air cold plasma reactor.

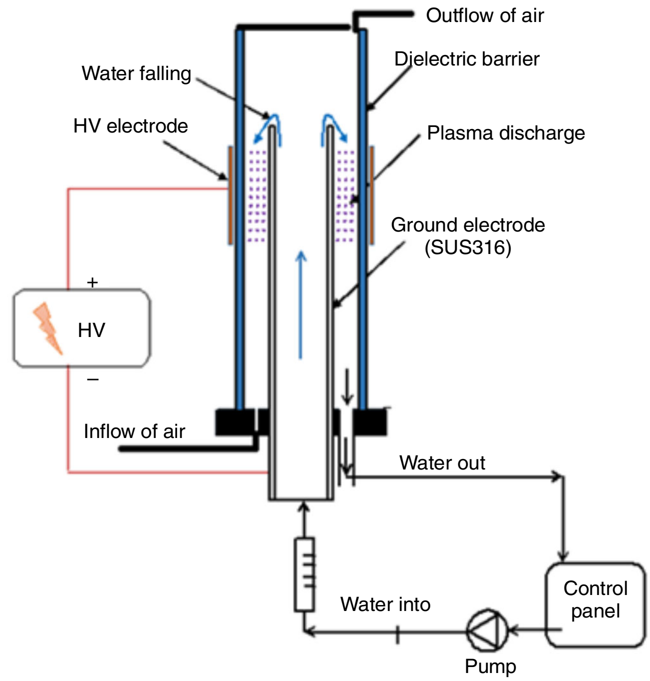

Fig. 2. Schematics of batch reactor configuration for plasma treatment

Determination of 2,3-DHB and 2,5-DHB concentration: The concentrations of 2,3-DHB and 2,5-DHB in the samples were determined by using HPLC. The HPLC instrument consisted of a detector (diode array), column of Hypersil C18 (200 × 4 mm), mobile phase of phosphate phosphoric and methanol in the ratio 55:45 (v/v). The pressure and pH were maintained at 210 bar and 2.5, respectively.

Procedure: HPLC was performed on the solution (5 µL) obtained from the reactor. For calculating the percentage of 2,3-DHB and 2,5-DHB in the reactor, retention time (t_R), peak height and peak area were determined. The following parameters were used for analyzing the HPLC: flow rate of 0.35 mL/min and sample pump volume of 5.0 µL; measurement signal of 245 and 360 nm and t_R of 3.3 and 3.2 min were maintained for 2,3-DHB and 2,5-DHB, respectively.

RESULTS AND DISCUSSION

$^{\bullet}$OH Formation rate in cold plasma: Applied power, voltage and solution circulation rate were 16 mA, 19 kV and 415 mL/min, respectively. The concentrations of salicylic acid ranged from 1,000 to 10,000 mg/L. After 30 min of treatment, the concentration of reaction products are determined.

As shown in Fig. 3, the reaction of salicylic acid with $^{\bullet}OH$ depends on the third and fifth positions of the aromatic ring. The reaction products are 2,5-DHB and 2,3-DHB. In all the cases, the amount of 2,5-DHB was more than that of 2,3-DHB because attacking the $^{\bullet}OH$ that are at fifth position is easier. Moreover, this result is consistent with the results of Ai *et al*. [18]. However, Jen *et al*. [19] showed that the concentration of 2,3-DHB is higher than that of 2,5-DHB. Some studies have suggested that the ratio of 2,5-DHB and 2,3-DHB is based on the nature of oxidation. Oxidation produces a greater proportion of 2,5-DHB, whereas biological oxidation produces a greater proportion of 2,3-DHB [20-22]. Moreover, the results show that under the same plasma conditions and time, increasing the initial concentration of salicylic acid increases the concentration of the resulting in decomposition products. This is because a low concentration of salicylic acid does not guarantee its maximum exposure to $^{\bullet}OH$ molecules to induce decomposition reaction. As the half-life of free radical OH is short (approximately 3.7×10^{-9} s [2]), they may automatically disappear or form H_2O_2 through combination reaction if not exposed to salicylic acid [2,23-25]:

$$^{\bullet}OH + {^{\bullet}OH} \longrightarrow H_2O_2$$

As shown in Fig. 3, 2,5-DHB and 2,3-DHB reached the maximum concentrations of 65.6 mg/L (0.426 mmol/L) and

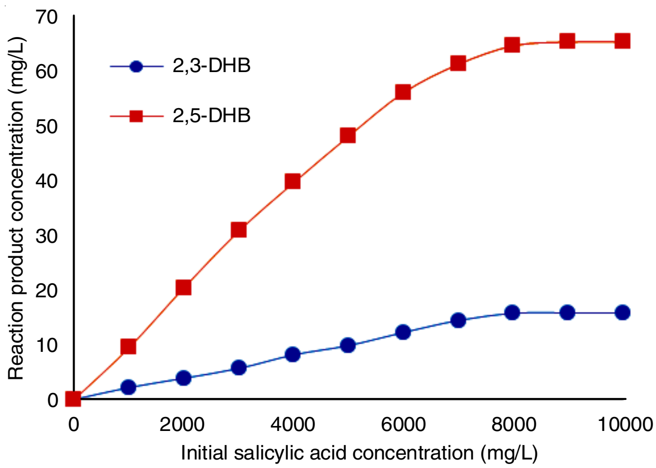

Fig. 3. Concentration of salicylic acid decomposition products at 0.5 h

15.9 mg/L (0.103 mmol/L), respectively, when the initial concentration of salicylic acid was >8,000 mg/L. The resulting $^{\bullet}$OH concentration was calculated through the addition of molarities of 2,5-DHB and 2,3-DHB:

$$[^{\bullet}\text{OH}] = [2,5\text{-DHB}] + [2,3\text{-DHB}]$$

$$[^{\bullet}\text{OH}] = 0.426 + 0.103 = 0.529 \text{ (mmol/L)}$$

At a plasma reaction time of 30 min, the average rate of $^{\bullet}$OH formation from the cold plasma process at voltage conditions of U = 19 kV and I = 16 mA was:

$$v_{^{\bullet}\text{OH}} = 0.018 \text{ (mmol/L min)}$$

Relationship between $^{\bullet}$OH concentration and treatment time: When the initial salicylic acid concentration was >8,000 mg/L, $^{\bullet}$OH optimally reacted with salicylic acid. Therefore, to analyze the association between $^{\bullet}$OH concentration and the treatment time, an initial salicylic acid concentration of 9,000 mg/L was selected. The experimental conditions were as follows: initial salicylic acid concentration of 9,000 mg/L, U of 19 kV, and I of 16 mA. The concentrations of the reaction products are shown in Fig. 4.

The concentrations of 2,3-DHB and 2,5-DHB steadily increased at all intervals according to the first-order equations

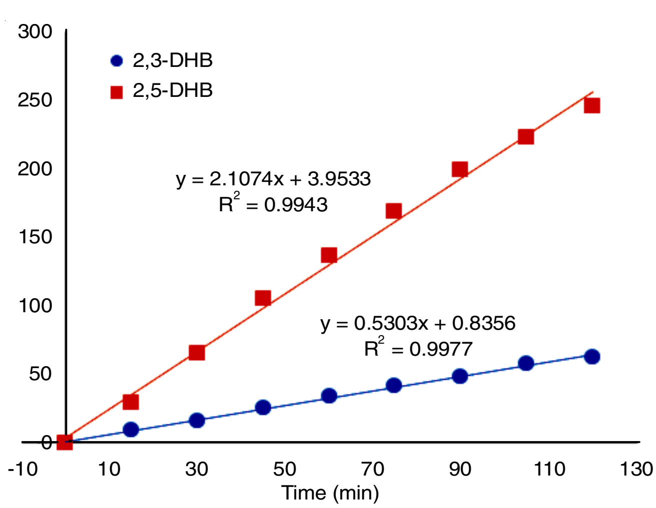

Fig. 4. Concentration of salicylic acid decomposition products at different times

y = 0.5303t + 0.8356 and y = 0.5303t + 0.8356, respectively. Accordingly, an equation can be developed to express the relationship between $^{\bullet}$OH concentration and treatment time (t) as follows:

$$[^{\bullet}\text{OH}] = \frac{[2,3-\text{DHB}]_t + 2,5-\text{DHB}]_t}{154} \text{ (mmol/L)}$$

$$\Leftrightarrow [^{\bullet}\text{OH}] = 0.01713\text{t} + 0.0311 \text{ (mmol/L)}$$

Effect of energy input on the rate of $^{\bullet}$OH formation: Three different cold plasma power generation modes, namely 1, 2 and 3 with voltage and amperage of 16, 19 and 21 kV and 10, 16 and 22 mA, respectively were used to decompose salicylic acid, with a constant initial concentration. The treatment time was maintained at 30 min. The concentrations of the reaction products are shown in Fig. 5. As shown in Fig. 5, when the input energy increased, the number of $^{\bullet}$OH also increased, leading to increase the concentrations of 2,3-DHB and 2,5-DHB. Thus, the rates of $^{\bullet}$OH formation in modes 1, 2 and 3 were 0.009, 0.018 and 0.023 mmol/L min, respectively.

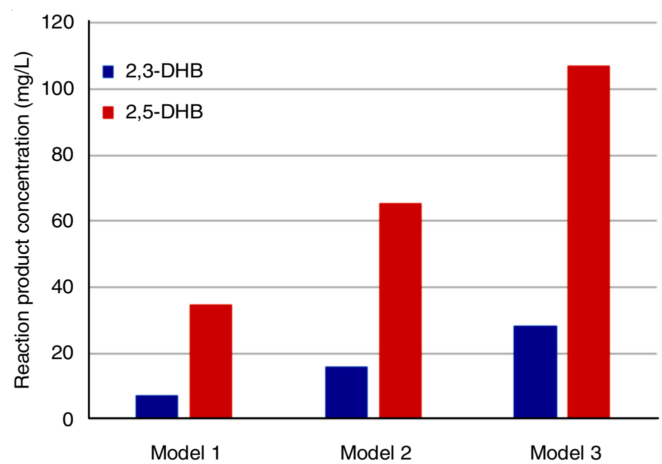

Fig. 5. Concentration of salicylic acid decomposition products in different plasma modes

Conclusion

Estimation of hydroxyl free radicals produced by atmospheric air cold plasma using salicylic acid was studied. The amount of hydroxyl free radical produced by cold plasma (DBD) was proportional to the reaction products of hydroxyl free radical and salicylic acid in reactor, being 2,3-DHB and 2,5-DHB. The main factors influencing the rate of the hydroxyl radical formation were estimated. Experimental results showed that the concentrations of 2,3-DHB and 2,5-DHB reach maximum when the initial salicylic acid concentration is > 8000 mg/L. During a plasma reaction time of 30 min, the average rate of formation of the $^{\bullet}$OH radicals in the cold plasma process under the conditions like U: 19 kV and I: 16 mA is:

$$v_{^{\bullet}\text{OH}} = 0.018 \text{ (mmol/L min)}$$

The relationship between the OH radical concentration and the reaction time has been established, obeying the first order equation:

$$[^{\bullet}\text{OH}] = 0.01713\text{t} + 0.0311$$

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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