Acta Scientiarum
http://www.uem.br/acta
ISSN printed: 1806-2563
ISSN on-line: 1807-8664
Doi: 10.4025/actascitechnol.v36i1.11834

Reaction of dissolved ozone in hydrogen peroxide produced during ozonization of an alkaline medium in a bubble column

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ABSTRACT. The effect of a reaction of dissolved ozone in an alkaline water solution with hydrogen peroxide was evaluated. Assays were conducted in a bubble column with a gaseous ozone concentration (mixed with oxygen) at 21 and 27 g m^{-3}. Concentration curve of dissolved ozone in the liquid revealed an ozone concentration peak in the liquid phase, subsequent decreasing concentration and constant maintenance in the stationary phase. Highest concentration was not detected for the lowest ozone concentration in the gaseous phase. Peak was due to the self-decomposition of ozone in the liquid phase and the production of hydrogen peroxide. The latter reacted with molecular dissolved ozone and decreased ozone concentration after maximum concentration.

Keywords: ozone, bubbling column, hydrogen peroxide.

Avaliação do efeito da reação de ozônio dissolvido com peróxido de hidrogênio gerado durante a ozonização de meio alcalino em uma coluna de borbulhamento

RESUMO. O presente trabalho avalia o efeito da reação de ozônio dissolvido em uma solução aquosa alcalina com peróxido de hidrogênio. Para tanto, foram realizados ensaios experimentais em uma coluna de borbulhamento com concentração de ozônio na fase gasosa (mistura com oxigênio) a 21 e 27 g m^{-3}. Verificou-se que o histórico da curva de concentração de ozônio dissolvido no líquido apresenta um pico de concentração de ozônio na fase líquida e a seguir, no tempo, esta concentração decresce, mantendo-se constante no estado estacionário. Essa concentração máxima não é detectada para a menor concentração de ozônio na fase gasosa. A presença desse pico deve-se a autodecomposição do ozônio na fase líquida, gerando o peróxido de hidrogênio, que por sua vez reage com o ozônio molecular dissolvido resultando no decréscimo da concentração do ozônio após a sua concentração máxima.

Palavras-chave: ozônio, coluna de borbulhamento, peróxido de hidrogênio.

Introduction

Ozonization of waste water involves the transference of ozone mass from the gas phase to the liquid phase, ozone's reaction with organic and inorganic pollutants in the liquid medium and the reactions of ozone self-decomposition (CHENG et al., 2003). Ozone reacts in two ways in aqueous solutions: direct oxidation of compounds by molecular ozone and indirect oxidation due to the compounds´ reaction with hydroxyl free radicals from ozone decomposition. Whereas direct reactions are often slow and highly selective, indirect reactions by radicals are non-selective and fast. Moreover, ozone decomposition is catalyzed by OH^- ions and occurs fast as pH increases. All ozone reactions occur simultaneously and are involved in the ozonization process. Direct reactions predominate in acid solutions whereas indirect reactions by free radicals form a significant section of ozonization in base pH (LANGLAIS et al., 1991). The oxidation pathway is determined by the relationship between ozone and •OH radicals concentrations and by their corresponding kinetics. Reaction constant for oxidation by ozone varies by ten orders of greatness, or rather, between 0.01 M^{-1} s^{-1} and approximately 7 x 109 M^{-1} s^{-1} (VON GUNTEN, 2003).

In the direct oxidation process, the ozone molecule reacts directly with other organic or inorganic molecules through electrophilic addition. Ozone´s electrophilic attack occurs in atoms with negative charge density or in double or triple bonds of the carbon-carbon, carbon-nitrogen and nitrogen-nitrogen type (LIN; YEH, 1993). Ozone decomposition occurs by an alkaline medium-triggered complex chain reaction and produces hydroxyl free radicals ($HO_2^\bullet$ and $HO^\bullet$). The hydroxyl radical is a powerful and non-selective oxidant that may react by three distinct mechanisms:

hydrogen abstraction, electron transference and radical addition. Secondary radicals formed during these reactions may once more react with ozone or other compounds (KUNZ et al., 2002).

Hydroxyl free radicals are more reactive and less selective than ozone in an aqueous medium. They have high reaction speeds with organic compounds at 10^9 and 10^{10} mol L^{-1} s^{-1}, coupled to a microsecond half-life, less than that of molecular ozone (GLAZE, 1986). Due to hydroxyl radicals' characteristics, ozone decomposition causes a decrease in permanence time in its molecular form when compared with radical forms. The decomposition of ozone in the aqueous phase is favored by high temperatures, pH increase and compounds that inhibit or catalyze these reactions in aqueous solutions. It should be underscored that the solution's pH is relevant since the hydroxide ions start the decomposition of ions involving the following reactions (VON GUNTEN, 2003).

i) Start

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (1)$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2 \qquad (2)$$

ii) Propagation

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \qquad (3)$$

$$pH < 8: \quad O_3^{\bullet -} + H^+ \leftrightarrow HO_3^{\bullet} \qquad (4a)$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \qquad (4b)$$

$$pH \geq 8: \quad O_3^{\bullet -} \leftrightarrow O^{\bullet -} + O_2 \qquad (5a)$$

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^- \qquad (5b)$$

$${}^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2 \qquad (6)$$

iii. Finish

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (7)$$

$$H_2O + HO_2^{\bullet} + O_2^{\bullet -} \rightarrow H_2O_2 + O_2 + OH^- \qquad (8)$$

According to Equations (1) and (2), the stage characterizing the start of ozone decomposition may be artificially accelerated by an increase in pH and by compounds that enhance the formation of the hydroxyl radical ${}^{\bullet}OH$. Free radical starters are compounds that induce the formation of the superoxide ion $O_2^{\bullet -}$ from an ozone molecule. Among several compounds, one may mention OH^-, HO_2^-, various metallic cations, formic acid, hydrogen peroxide and ultraviolet light which provides the required energy for the homolithic rupture of an oxygen-oxygen bond (VON GUNTEN, 2003). In the propagation stage, radicals react to produce other radicals. The stage is directly affected by the propagators of radicals, or rather, the compounds which regenerate the radical perhydroxyl from the hydroxyl radical. The finish stage comprises radicals which react among themselves or against other molecules to form another molecule. These reactions produce non-radical species from radical ones. Then, the objective of this paper is to present the effect of a reaction of dissolved ozone in an alkaline water solution with hydrogen peroxide.

Material and method

Figure 1 outlines the experiments on the ozonization of alkaline aqueous solution in a bubble column. The unit is basically formed by an oxygen concentrator, an ozone generator, a reactor or bubble column, a gauge for dissolved ozone and an ozone destructor.

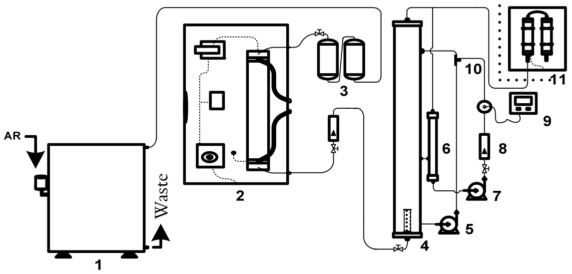

Figure 1. Scheme of the experimental unit: (1) oxygen concentrator; (2) ozone generator; (3) reservoir for concentrated oxygen 90-95%; (4) bubble column; (5) centrifuge pump; (6) degasifier; (7) centrifuge pump to help in the recirculation of the sampled liquid; (8) rotameter to measure discharge of sampled liquid; (9) gauge for dissolved ozone; (10) vacuum tube; (11) ozone destructor installed outside the laboratory.

The bubble column was manufactured from a water-containing PVC tube, internal diameter 6.8 cm; external diameter 7.5 cm; height 202 cm. A gauge for the introduction of oxygen-ozone gas mixture was placed at the column base and a porous diffuser was internally installed to enhance the bubbling of the gas mixture. A gauge was placed at the top of the column for the gas exit leading towards the ozone destructor, outside the laboratory and in an open environment.

The aqueous solution was transported to the bubble column by a Provitec-manufactured AWG-4000 peristaltic pump at a regulating discharge up to 100 L h^{-1}. So that the aqueous solution could be re-circulated, a gauge was installed for the exit of the liquid on the side of the column, at 9 cm from the base, whilst another gauge was also installed 142 cm from the base for the return of the liquid. Re-circulation was provided by a Suprilab-manufactured centrifuge pump, model I5222046.

A sampling site, at 71.5 cm from the base of the column, was installed between the sites used for liquid re-circulation. The aqueous solution was canalized, passed through the de-gasifier and reached the Gecom-manufactured 60 Hz centrifuge pump, model EBC620015. Posterior to the pump, a needle valve to control discharge and a Conaut rotameter, model 400, with a 30 - 300 mL $min.^{-1}$ scale, were installed. The rotameter was employed to verify the discharge of the aqueous solution which then passed through the gauge cell of the dissolved ozone and returned inside the column together with the re-circulation liquid.

Further, 5.0 L of aqueous solution was used in each experiment, coupled to NaOH (PA.-ACS 100% Synth) to correct pH of the solution when required. So that the temperature of the ozonization system could be equalized, the re-circulation of the aqueous solution of the column was bonded to the circulation of the sampled liquid in the gauge cell of the dissolved ozone. Temperature stabilization of the liquid phase at 21°C took some time and was measured by the dissolved ozone gauge. The oxygen-ozone mixture was finally bubbled in the liquid. Ozone generator was switched off after the gas mixture bubbled for 60 min. The other sections of the experimental unit remained on until the dissolved ozone gauge showed the absence of ozone in liquid phase.

Results and discussion

Four assays were performed with ozone concentration in a gas mixture (oxygen and ozone) at a volumetric rate of 1.75 mL $min.^{-1}$ and initial pH of the liquid solution at 8.0. Figures 2 to 5 show the results of the saturation curve of dissolved oxygen in the aqueous solution.

Assays 1 and 2, respectively Figures 2 and 3, kept the same initial rate of ozone concentration in the gas phase at 21 mL at the entrance of the column. However, there was a variation in the liquid (distilled water) re-circulation rate, or rather, 522.5 mL $min.^{-1}$ in assay 1 and 1067.5 mL $min.^{-1}$ in assay 2. Assays 3 and 4, respectively Figures 4 and 5, had the same initial rate at 27 mL for ozone concentration in the gas phase with a change in the liquid (distilled water) re-circulation rate at 522.5 mL $min.^{-1}$ in assay 3 and 1067.5 mL $min.^{-1}$ in assay 4.

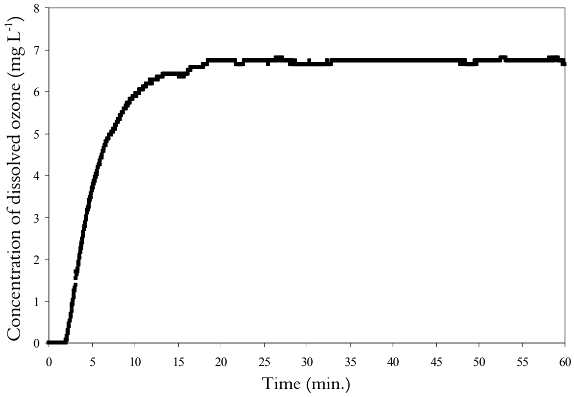

Figure 2. Evolution of the concentration of dissolved ozone during a time period (discharge of liquid re-circulation at 522.5 mL $min.^{-1}$; ozone concentration in gas at 21 mg L^{-1}).

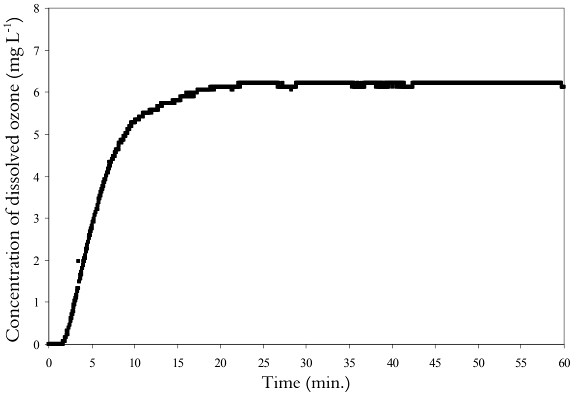

Figure 3. Evolution of the concentration of dissolved ozone during a time period (discharge of liquid re-circulation at 1067.5 mL $min.^{-1}$; ozone concentration in gas at 21 mg L^{-1}).

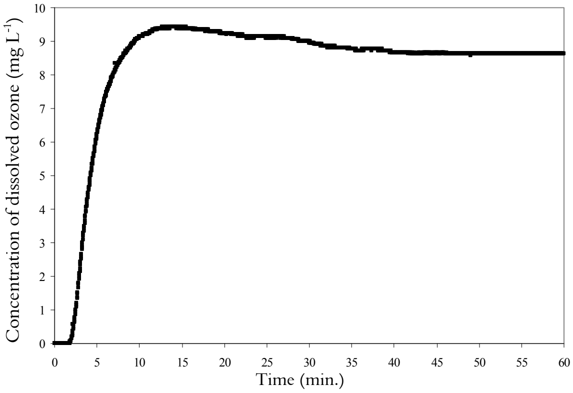

Figure 4. Evolution of the concentration of dissolved ozone during a time period (discharge of liquid re-circulation at 522.5 mL $min.^{-1}$; ozone concentration in gas at 27 mg L^{-1}).

It should be underscored that pH rate of the liquid solution was not taken during the time period but only at the end of each assay, or rather, when the stationary state was reached. Results for final pH of the liquid solutions of assays 1, 2, 3 and 4 were respectively 6.70, 6.75, 6.60 and 6.73.

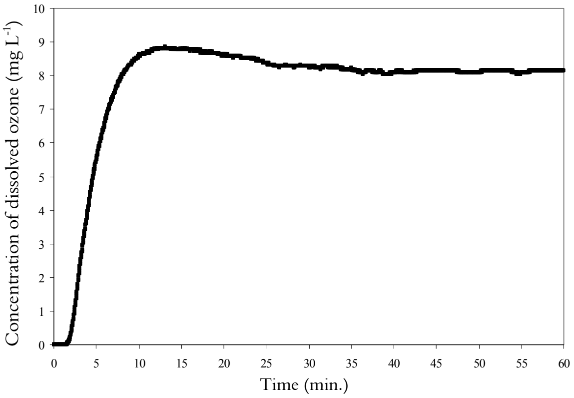

Figure 5. Evolution of the concentration of dissolved ozone during a time period (discharge of liquid re-circulation at 1067.5 mL min.$^{-1}$; ozone concentration in gas at 27 mg L^{-1}).

When the lowest ozone concentration (21 mg L^{-1}) in the gas mixture was used, the lowest quantity of dissolved ozone was also obtained as stationary status was reached. In this case, results of dissolved oxygen concentration in the liquid solution for assays 1, 2, 3 and 4 were respectively 6.73, 6.20, 8.62 and 8.14 mg L^{-1}. Difference between the results of assays 1 and 2 was small, although it was the final rate of the final dissolved ozone concentration. The same situation was reported between assays 3 and 4. Such behavior was foregrounded on the solution´s final pH, which practically kept the same rate, when the assays with the same concentration of ozone in the gaseous state were compared. Thus, liquid re-circulation had only slight affects on the ozonization process within the operational conditions of current research.

Typical curves of dissolved ozone concentration in liquid for a time period during the bubbling of the oxygen-ozone gas mixture were obtained in assays 1 and 2, Figures 2 and 3. This behavior corroborated qualitatively the curves registered by Bin et al. (2001). On the other hand, ozone decomposition occurred during the ozonization of a more concentrated solution, 27 mg L^{-1}, as in assays 3 and 4, which triggered the formation of hydrogen peroxide (H_2O_2) as Equations (7) and (8) showed. According to Lucas et al. (2009), molecular ozone dissolved in a liquid medium was consumed by the hydrogen peroxide produced. Legrini et al. (1993) reported that the interaction of hydrogen peroxide with ozone triggered the formation of reactive radicals, according to

$$O_3 + H_2O_2 \rightarrow O_2 + HO^{\bullet} + HO_2^{\bullet} \qquad (9)$$

The above may explain the peaks of dissolved ozone concentration in the assays 3 and 4 (Figures 4 and 5, respectively). These experiments showed an alkaline solution with pH 8.0 which was ozonized with a gas mixture featuring 27 g m^{-3} ozone and a discharge of 1.75 L min.$^{-1}$. The combined parameters caused the dissolved ozone concentration to reach a higher rate (mean 9.0 mg L^{-1}) in a short time period and thus generated hydrogen peroxide. Since it was an alkaline solution, hydrogen peroxide was formed. The latter reacted immediately with ozone and thus the dissolved ozone concentration in the liquid phase was reduced. Since all reactions are cyclical, they are prone to enter a permanent regime which is disrupted when the dissolved ozone concentration becomes stable. This type of peak in dissolved ozone concentration is not reported in assays 1 and 2 since the equilibrium between the reactions occurred prior to the time when the dissolved ozone concentration reached the stationary status.

Conclusion

A peak in the maximum concentration of dissolved oxygen occurs in the liquid phase prior to the stationary regime in certain operational conditions involving pH (alkaline) and ozone concentration in the gas mixture (with oxygen). The above is due to the self-decomposition of ozone in the liquid phase. Hydrogen peroxide reacts with dissolved molecular ozone and causes a decrease in the concentration of dissolved ozone in the aqueous medium after maximum concentration. On the other hand, changes in re-circulation discharge of the liquid phase only slightly alter the rate of dissolved ozone concentration in the liquid solution when the stationary state is attained.

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Received on November 30, 2010.
Accepted on October 11, 2012.