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Effect of pH and Gas Flow Rate on Ozone Mass Transfer of K-Carrageenan Solution in Bubble Column Reactor

Aji Prasetyaningrum*), Dyah Arum Kusumaningtyas, Purbo Suseno, Bakti Jos, and Ratnawati

[1)]Chemical Engineering Department, Faculty of Engineering, Diponegoro University
Jl. Prof. Soedarto SH Tembalang Semarang
Telp. / Fax. (024)7460058 / (024)76480675

*) Corresponding author: aji.prasetyaningrum@che.undip.ac.id

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Abstract

This research was conducted to calculate the mass transfer coefficient value for ozonation reaction of κ-carrageenan solution in the bubble column reactor. Ozone gas was produced using ozone generator type corona discharge. In this study, operating conditions were regulated at ozone gas flow rate 2- 5 L min^{-1}, pH 4-10, and temperature 29 ± 1 ºC. Samples were tested every 5 minutes to determine the dissolved ozone concentration. The results showed that dissolved ozone concentrations increased with increasing ozonation time and ozone gas flow rate. However, a very high gas flow rate can increase turbulence so that the mass transfer coefficient (k_La) value decreased. In alkaline conditions, the formation of free radicals (HO) increases so that the amount of dissolved ozone decreases. The kLa value of ozone gas in κ-carrageenan solution is slightly lower than the kLa value of the ozone gas in the water. The results of this study indicate that (kLa) ozone gas in water is 0.131 / minute while the value (k_La) in κ-carrageenan solution is 0.128 / minute.*

Keywords: *ozone; mass transfer; pH; flowrate*

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INTRODUCTION

Carrageenan is a natural biopolymer typically obtained from the seaweed of red algae (Rhodophyceae). Several studies have demonstrated that low molecular weight carragenan (LMCarr) show a variety of beneficial activities over the carrageenan with relatively high molecular weights (HMCarr) (Campo, 2009). Previously, depolymerization of carrageenan was done by several means which can be divided into three main categories; (1) chemical, (2) biochemical, and (3) physical degradations. The conventional method is operated by using diluted or concentrated acids. Consumption of acid and heat leads to the high cost of production. In addition, the production yield is low, and a wide diversity of oligomers is obtained due to random linkage cleavage. Specific degradation can be achieved by using biochemical technique, i.e., treatment with carrageenanse enzyme. However, additional purification by relatively complex method such as ion exchange chromatography is needed after the digestion (Prasetyaningrum et al., 2017).

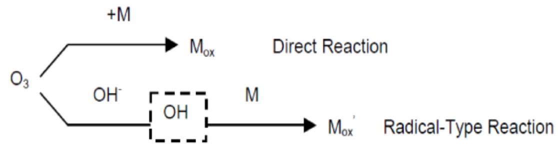

Figure 1. Reaction mechanism of ozone in the aqueous solution (Langlais, 1991)

Ozonation process has attracted many researchers and become an important technique for the water purification and the decomposition of organic compounds. Ozone is an unstable gas contains three oxygen atoms (O_3) and a strong oxidizing agent that can react with organic and inorganic molecules (Khadre et al., 2001, Seydim et al., 2005). Ozone has been applied as chemical reagents for synthesis purposes, purification of drinking water, disinfectants, waste treatment, natural fiber bleaching, etc. Ozone is soluble in many substances. Its value is 14 times higher than oxygen solubility.

Figure 1 shows the reaction of ozone in the aqueous solution. In solution, ozone may react to various compounds (M) through 2 ways: (i) by direct reaction with the molecular ozone and (ii) indirect reaction with the radical species that are formed when ozone decomposes in water.

Ozone can be produced through several processes, such as corona discharge, ultraviolet radiation, electrolysis, and radio chemical source. Corona discharge is more effective than the other processes (Beltran, 2004), so that it applied in most of commercial and industrial processes for ozone production. As it is effective for ozone generation, in this research, the corona discharge was applied for the ozonation process to depolymerize carrageenan. During the generation of ozone, the radical ions and reactive species were produced such as OH*, H_2O_2, O*. These reactive species have been shown to efficiently decompose anorganic and organic compounds (Brink et al., 1991, Lodge et al., 1983). Ozone generation by corona discharge methods requires the following equipment: gas source, dust filters, ozone generators, contacting units, and off-gas destruction.

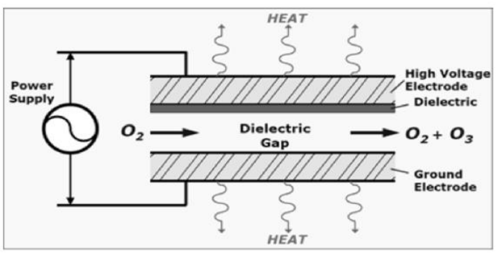

Figure 2. Schematic diagram of ozone generation by corona discharge

Figure 2 represents the ozone generation from corona discharge.

The ozone reactor used in this work consists of two stainless steel electrodes and a glass dielectric. The formation of ozone through an electrical discharge gas process was based on the non-homogeneous corona discharge in air or oxygen. Oxygen was forced between high voltage plates to simulate corona discharge (Langlais, 1991, Gottschalk et al., 2010). The oxygen was broken apart and recombines into ozone.

The generation of ozone involves the intermediate formation of atomic oxygen radicals. The atomic oxygen radicals can react with molecular oxygen to produce ozone. The chemical reactions that occur in the ozone formation system can be described as follows:

$$O_2 + e_{(\text{high energy})} \rightarrow 2O^* + e_{(\text{low energy})} \quad (1)$$

$$2O^* + O_2 \rightarrow O_3 \quad (2)$$

All reactions that can dissociate molecular oxygen into radical oxygen were potential for ozone formation. The effectiveness of the ozonation process is affected by the mass transfer of ozone gas in the reactor. Bubble columns are intensively used as multi-phase reactors in chemical, biochemical and petrochemical industries. They have several advantages in the operation and in the maintenance such as high heat and mass transfer rates, compact and low cost (Degaleesan et al., 2001, Kantarci et al., 2005). Although the construction of bubble columns is simple, but the accurate and successful design and scale-up are required to improve the understanding of multiphase fluid dynamics and its influences. The rate of mass transfer from the gas phase to the liquid phase in bubble column reactor greatly affect the ozonation reaction. The value of the mass transfer rate constant per unit volume is expressed as the mass transfer coefficient (k_La). The mass transfer coefficient of ozone gas in water can be determined by measuring dissolved ozone concentration as a function of time. The value of k_La number was influenced by the reactor design, ozone flow rate, temperature, and pH (Gao et al., 2005; Al-Abduly et al., 2014; Flores-Payan et al., 2015).

Commonly, the modeling of ozone contactors, the mass transfer coefficient (k_La) and other reactor characteristics were estimated from data available in the literature. Nevertheless, in many cases of experimental data were needed in accordance with the type of reactor. The aim of this study is determined the effect of pH and ozone gas flow rate on the ozone mass transfer coefficient (k_La) in the bubble column reactor.

MATERIALS AND METHODS

Materials

In this experiment, all chemicals such as potassium iodide, sulfuric acid, sodium thiosulfate, sodium hydroxide, and sulfuric acid were analytical grade and used without any treatment.

Methods

Ozone was supplied to the system using the ozone generator type dielectric barrier discharge (DBD). The DBD reactor consisted of two high voltage electrodes separated by a layer of glass beads. These components were arranged within a jacketed cell to allow cooling. The cell was then connected to a cooling system to maintain the temperature at desirable levels. Air was used to feed the ozone generator and the flow rate of ozone was adjusted using flowmeter. Ozone gas was distributed at the column bottom through a sparger. Ozone gas flow rate was adjusted at different value: 2; 2.5; 3; 3.5; 4; 4.5 L.min^{-1} and the initial pH at 4; 5; 6; 7; 8; 9; 10. The experiments were carried out at the ambient temperature 29±1◦C.

Sample were taken every 5 minutes, to analyze the dissolved ozone concentrations. After each run, dissolved ozone concentration was determined by the iodometric method (Bader and Hoigne, 1982). The results of the measurement of dissolved ozone concentration were calculated to obtain the mass transfer coefficient (k_La). The schematic of the ozonation process using bubble column reactor shows in Figure 3.

Analysis of dissolved ozone concentration

Determination of dissolved ozone concentration was carried out using the iodometric titration. The principle of this method that iodide ion was oxidized by ozone to form iodine during the ozone gas was bubbling to the KI solution. The liberated iodine was titrated using sodium thiosulfate. The endpoint of the titration was determined by changing the colour of the solution. The dissolved ozone concentration was calculated using the following equation.

$$\frac{\mathrm{Mw}\ O_3 \times V_{Na_2S_3O_3} \times N_{Na_2S_3O_3}}{V_{sampel} \times e_{Na_2S_3O_3}} \qquad (3)$$

Determination of Ozone Mass Transfer Coefficient

Ozone solubility was determined using the equation:

$$\frac{dC_{O_3}}{dt} = k_La\left(C^*_{O_3} - C_{O_3}\right) \qquad (4)$$

$$\ln\left(C^*_{O_3} - C_{O_3}\right) = -k_Lat + C \qquad (5)$$

$C^*_{O_3}$ and C_{O_3} are dissolved ozone concentration in the steady state and dissolved ozone concentration at t minutes ozonation, respectively. The symbol of k_La is the mass transfer coefficient.

RESULTS AND DISCUSSION

Effect of pH

The value of dissolved ozone concentration at different pHs measured from a reaction time of 0 to 60 minutes is shown in Figure 4. Ozonation reactions used a semi-batch system or during the reaction, there was no outflow of liquid. Figure 4 shows that dissolved ozone concentrations increase with increasing ozonation time. However, after 50 minutes of ozonation, there were only slight increament in dissolved ozone concentration and after 60 minutes ozonation, the dissolved ozone concentration was near to constant value.

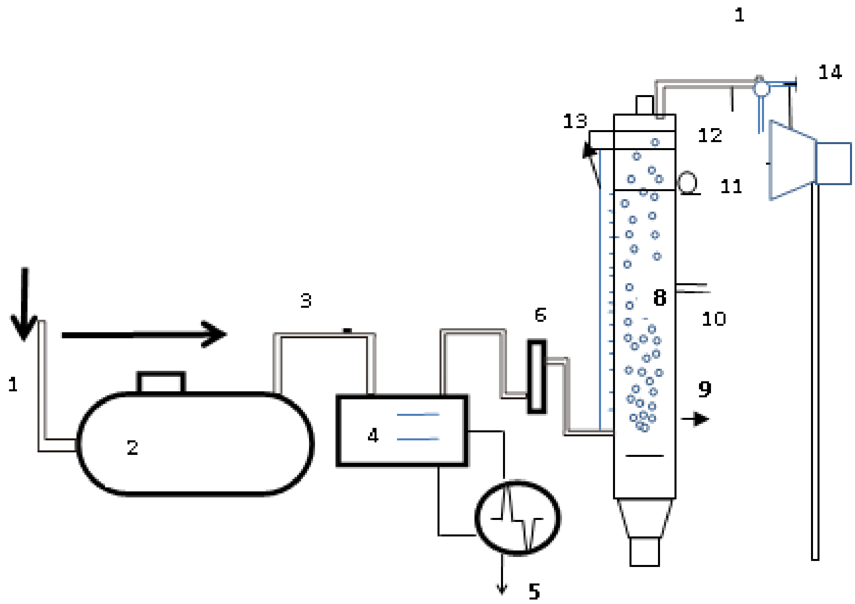

Figure 3. The experimental set up (1) gas flow meter, (2) compressor, (3) valve, (4) ozone generator, (5) high voltage, (6) flow meter, (7) gas sparger, (8) bubble column reactor, (9) output sample, (10) thermoregulator, (11) stopwatch, (12) output gas, (13) scale, (14) camera

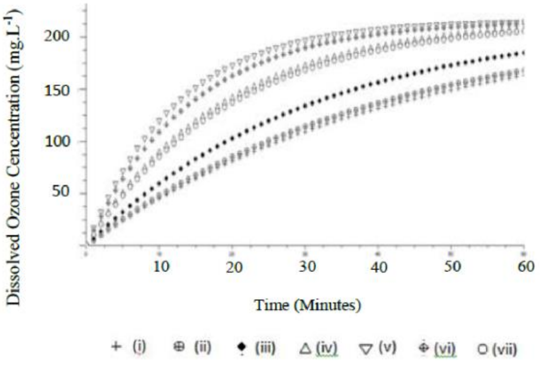

Figure 4. Effect of pH on dissolved ozone concentration with different operating conditions: i) pH 4, (ii) pH 5, (iii) pH 6, (iv) pH 7, (v) pH 8, (vi) pH 9, (vii) pH 10.

Figure 4 also shows the effect of different pHs on dissolved ozone concentration. The operating condition was adjusted at ozone flow rate 4 $L.min^{-1}$ and temperature 29±1 ºC. The total volume of the bubble column reactor was 1500 mL. The ozonation process was carried out at different pHs (4; 5; 6; 7; 8; 9; 10). The results of this study indicate that the increase in pH will increase the dissolved ozone concentration. This research shows, the high ozone concentration when pH is about 7-8. The pH of the water is important and at alkali condition the hydroxide ions initiate ozone decomposition, which involves the following reaction (Beltran, 2014):

$$O_3 + OH^* \rightarrow HO_2^* + O_2 \quad (6)$$

$$O_3 + HO_2^* \rightarrow O_2 + O_2 \quad (7)$$

The increase in pH will cause a decrease in the solubility ratio of ozone in water solution because of the high of pH cause increase of the hydroxide ions (OH-) in water which will initiate ozone decomposition (Wang et al., 1999). pH affects the ozone mass transfer coefficient from the gas phase to the liquid phase. The results of this study indicate that the dissolved ozone concentration decreases with increasing pH value. This is related to OH* ions which accelerate ozone decomposition into OH* radicals (Gao et al., 2005, Lovato et al., 2009).

Effect of Ozone Flow Rate

To determine the effect of ozone flow rate on dissolved ozone concentration, an experiment was conducted with pH 7, temperature 29±1 °C, and flow rate varied between 2-5 $L.min^{-1}$. The volume of KI solution used in the reactor is 1500 mL. Ozonation is carried out for 30 minutes. Figure 5 shows that the dissolved the ozone concentration increase with the increase in ozone gas flow rate. The maximum of dissolved ozone concentration was obtained at the ozone gas flow rate of 4 $L.min^{-1}$. The ozone residence time in the system will be shorter if the ozone gas flow rate is high.

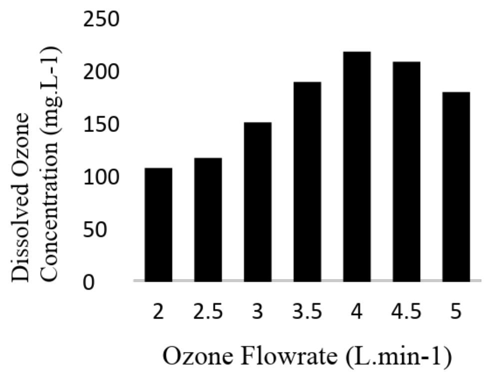

Figure 5. Effect of Gas Flow Rate on Dissolved Ozone Concentration

The short lifetime of oxygen gas which causes the ozone formation process to become imperfect. Oxygen molecules do not have enough time to react to produce ozone (Gottschalk et al., 2010).

Mass Transfer Coefficient in Bubble Column Reactor

Determination of mass transfer coefficients for the ozone-κ-carrageenan solution system, influenced by the concentration of dissolved ozone in water at a different time. In this study, the value of $k_L a$ is calculated using equations (4) and (5). In this study, 1% (b / v) κ-carrageenan concentration was used with the temperature set at 29 ± 1^0C, pH 7 and pressure 1 atm. Mass transfer and chemical reactions occur simultaneously in ozonation of κ-carrageenan solution. Data on the comparison of ozone concentration dissolved in water and in carrageenan solution are presented in Figure 5.

The result indicates that the dissolved ozone concentration in the κ-carrageenan solution is slightly lower compared to the dissolved ozone concentration in water. For 30 minutes ozonation, the average value of dissolved ozone in water was 182.4 mg L^{-1}, while in κ-carrageenan solution, it was 176.4 mg L^{-1}. The value of the dissolved ozone concentration was decreased about 3.28%.

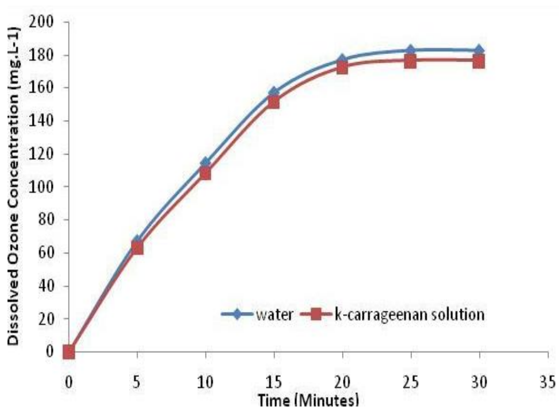

Figure 6. The concentration of ozone dissolved in water and κ-carrageenan solution

The kLa value is estimated by plotting $ln\left(\frac{C^*-C_o}{C^*-C}\right)$ versus ozonation time. The results show that (kLa) ozone gas in water is 0.131/minute while the value (k_La) in κ-carrageenan solution is 0.128/minute. The kLa value of ozone gas in κ-carrageenan solution is slightly lower than the kLa value of the ozone gas in the water. The similar tendency was also found in the research conducted by Kumar et al. (2013) which studied the effect of concentration of contaminants on the value mass transfer coefficient of the oxygen gas and Grima et al., 2009 who studied the kinetic and mass transfer of ozone degradation of organics in liquid/gas-ozone and liquid/solid-ozone systems.

Table 1. Comparison of k_La value with previous research

pH	This research[a)]	Grima. *et al.* (2009)[b)]	Gao *et al.* (2015)[c)]
4	0,036	0,38	0,295
5	0,038	-	0,320
6	0,049		0,260
7	0,058	0,31	0,310
8	0,131	-	-
9	0,043	0,26	-
10	0,035	-	-

a) This research in *bubble column reactor*, gas flowrate Q_g 4 Lmin^{-1}; liquid volume V 1,5 L^1
b) Reactor *aplikon*, gas flowrate Q_g 0,0027 Lmin^{-1}, liquid flowrate C_g 0,3 Lmin^{-1}
c) *Karman contactor*, gas flowrate C_g 0,02 Lmin^{-1}, Volume 10 L

The results of the study showed that for a magnesium hydroxide concentration of 0.2-5% by weight it did not significantly change the kLa value. The kLa value will decrease as the solution concentration increases. The k_La values obtained from this study are compared with the previous studies as presented in Table 1. Comparison of k_La value with previous research presented in Table 1.

In general, the k_La value from this research is smaller than Grima (2009) and Gao et al. (2015). The difference this result caused by the type of reactor, volume of liquid, and the different gas flow rates.

CONCLUSIONS

The results showed that dissolved ozone concentrations increased during 50 minutes of ozonation and subsequently tended to be stable. The dissolved ozone concentration rises as the ozone gas flow rate increases. However, the high flow rate will reduce the dissolved ozone concentration. The maximum of dissolved ozone concentration was obtained at the ozone gas flow rate of 4 L.min^{-1}. The kLa value of ozone gas in κ-carrageenan solution is slightly lower than the kLa value of the ozone gas in the water. The results of this study indicate that (kLa) ozone gas in water is 0.131 / minute while the value (k_La) in κ-carrageenan solution is 0.128 / minute.

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