Research Article

Kinetics of Oxidative Depolymerization of κ-carrageenan by Ozone

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Abstract

Depolymerization kinetics of κ-carrageenan by ozone treatment has been studied at various pHs and times. The purified κ-carrageenan with the initial molecular weight of 271 kDa was dispersed in water to form (1 % w/v) solution. Ozone with 80±2 ppm concentration and constant flow rate of 3 L.min^{-1} was bubbled into the κ-carrageenan solution. The experiments were conducted at pH of 3, 7, and 10 at different times (5, 10, 15, and 20 minutes) of ozonation. The viscosity of the solution was measured using Ubbelohde capillary viscometer, which was then used to find the number-average molecular weight by Mark-Houwink equation. The number-average molecular weight data was treated using zero, first, and the second-order reaction kinetics model, to obtain the kinetics of κ-carrageenan depolymerization. The depolymerization is assumed to occur by random scission. The results show that the kinetics rate constant of κ-carrageenan depolymerization is higher at lower pHs. The second-order model is more suitable for describing the kinetics of depolymerization of κ-carrageenan by ozonation process. The rate constants for the second-order kinetics model are 5.45×10^{-4} min^{-1}, 1.27×10^{-4} min^{-1}, and 7.21×10^{-5} min^{-1} for pH 3, 7, and 10, respectively. The actual values of reaction order under acid and alkali conditions are ranging from 1.88 to 1.90. Copyright © 2017 BCREC Group. All rights reserved.

Keywords: Depolymerization; Kinetics; κ-carrageenan; Ozone

1. Introduction

κ-Carrageenan is a substantial gelling polysaccharide extracted from several species of red seaweed (*Rhodophyceae*). Structurally, it consists of repeating disaccharide units of alternating (1/3)-*a*-D-galactose-4 sulfate and (1/4)-*β*-3, 6-anhydro-D-galactose residues [1-3]. The structure is depicted in Figure 1.

The size or degree of polymerization of κ-carrageenan plays a critical role in determining their application. The high-molecular-weight (HMW) κ-carrageenan has limited applications as it is insoluble in water and it forms a viscous solution. By changing HMW κ-carrageenan into low molecular weight (LMW), κ-carrageenan increases the bioavailability and its potential
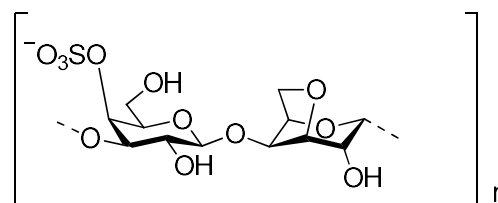
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Figure 1. Basic structure of κ-carrageenan [3]

applications for biomedical applications [4-21].

LMW carrageenans have been produced by thermal depolymerization [20], acid hydrolysis [6,16,21-25] and enzymatic hydrolysis [12,13, 15,26,27]. There were several different techniques, such as microwave-assisted depolymerization [28], sonication [29-31], irradiation [17,32], and oxidation using H_2O_2 [21,33]. Acidic hydrolysis has been considered as a common and fast method to produce a series of carrageenan oligomers, but the use of chemicals causes a potential increase in the level of environmental pollution. The enzymatic method is not preferable because of relatively expensive and complex process [27].

Due to the high oxidation potential, ozone may be an alternative approach to achieving degradation of organic and inorganic compounds [34-53]. Ozone can react either indirectly (decomposition via a chain-reaction mechanism resulting in the production of hydroxyl free radicals) or directly (via selective reactions with substances in the water matrix). This combined effect makes ozone highly effective when compared to other chemicals. Therefore, the efficacy of an ozonation process is usually based on the effects of both reaction mechanisms, and these largely depend on the pH, type and content of natural organic matter, and alkalinity [34]. Ozone reacts with organic compounds through various complex reactions forming reactive species. The primary nitrogen atom in amino acid, C–H bond in alkanes, S–H bond in sulfhydryl are vulnerable sites to be attacked by ozone [34,39,45].

There have been many studies on ozone depolymerization of polysaccharides, such as guar gum [44], cellulose materials [45], starch [38,40], gelatin [43], and chitosan [37,42,46]. The kinetics of depolymerization of a macromolecule by ozone treatment have also been reported. Chen *et al*. [47] studied the kinetics and pathways of oxidative degradation of N-Nitrosopyrrolidine by ozone/UV process, while Dai *et al*. [48] investigated the kinetics of degradation of phenoxy acetic acid (PPA) in aqueous solution by ozonation at different initial pH, the concentration of PPA and ozone dosage. Kinetic study of aflatoxins degradation in the presence of ozone with different ozone concentration and temperature have been reported by Agriopoulou *et al*. [49]. The degradation of aflatoxins was described by a first order kinetic equation. Lignin [50] and guar gum [44] were also degraded by ozone with first-order reaction pathway. On the other hand, several researchers utilized the pseudo-first-order model to describe the kinetics of depolymerization of N-Nitrosopyrrolidine [47], phenoxy acetic acid [48], textile dyes [51], wine distilleries wastewaters [52], and sulfamethoxazole [53].

The reports on the study of kinetics depolymerization of κ-carrageenan by ozone treatment were not available in the literature at the moment. Therefore, the aim of this work is to study the effect of pH on the depolymerization kinetics of κ-carrageenan solution using ozonation process.

2. Materials and Methods

2.1. Materials

The raw material used in this work was commercial κ-carrageenan derived from seaweed *Kappaphycus alvarezii*, produced by CV. Karagen Indonesia, Semarang, Indonesia. For preparation, the κ-carrageenan was dissolved in distilled water at 70 °C and stirred for 15 minutes. Purified κ-carrageenan was obtained by filtration and ethanol precipitation. The pH of the κ-carrageenan solution was adjusted by adding HCl with 37 % of purity (E. Merck Cat. No. 100317) or NaOH with > 99 % purity (E. Merck Cat. No. 104698). All chemical reagents were of analytical grade and directly used without further purification.

2.2. Ozone treatment

Purified κ-carrageenan was completely dissolved in distilled water to form 1 % (w/v) solution. The experiments were carried out in a glass reactor equipped with an ozone bubble diffuser. Ozone gas with a concentration of 80±2 ppm was produced by an ozone generator (Dipo Technology Indonesia). In this research, ozone was generated by passing air between two electrodes with a high potential difference (approximately 30 kV). Ozone was bubbled into the solution with a constant flow rate of 3 L.min^{-1}. The experiments were conducted at pH of 3, 7, and 10. The pH of the κ-carrageenan solution was adjusted with hydrochloric acid or sodium hydroxide solution and measured with a pH meter (Hanna Instruments HI 98107). The ozone treatment was conducted at temperature 29±1 °C and different times, i.e. 0 (control), 5, 10, 15, and 20 minutes. Ozone-treated κ-carrageenan was llected, rinsed with distilled water, and filtered with Buchner funnel. The residue was dried at 60 °C for 24 h in a forced air oven for further analysis. Schematic experimental of ozone treatment of κ-carrageenan is depicted in Figure 2.

2.3. Molecular weight determination

For determination of molecular weight of ozone-treated κ-carrageenan, 5 different concentrations (0.016 to 1.0 % w/v) of ozone-treated κ-carrageenan solution were prepared. A portion of buffer solution of pH 7 was added to adjust polysaccharide concentrations and to keep polysaccharide molecules from intermolecular aggregation. The efflux times of the solutions were measured using an Ubbelohde capillary viscometer (type 531 030c Schott-Gerate, Germany) in a constant temperature at 45.0±0.1 °C. The intrinsic viscosity ($[\eta]$) was calculated from the specific viscosity (η_{sp}). The intrinsic viscosity is the average intercept of Huggins and Kraemer equation [54] in Equation (1).

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \qquad (1)$$

In this equation, η_{sp}, ($[\eta]$), k_H, and c are specific and intrinsic viscosity, Huggins constant, and the concentration of the solution, respectively. The specific viscosity (η_{sp}) and the Huggins constant (k_H) are dimensionless, while the intrinsic viscosity ($[\eta]$) and the concentration (c) have the units of mL.g^{-1} and g.mL^{-1}, respectively. The value of k_H for the κ-carrageenan solution is 0.35 [54].

The molecular weight of κ-carrageenan (M) was calculated from the intrinsic viscosity data by Mark Houwink equation (Equation 2).
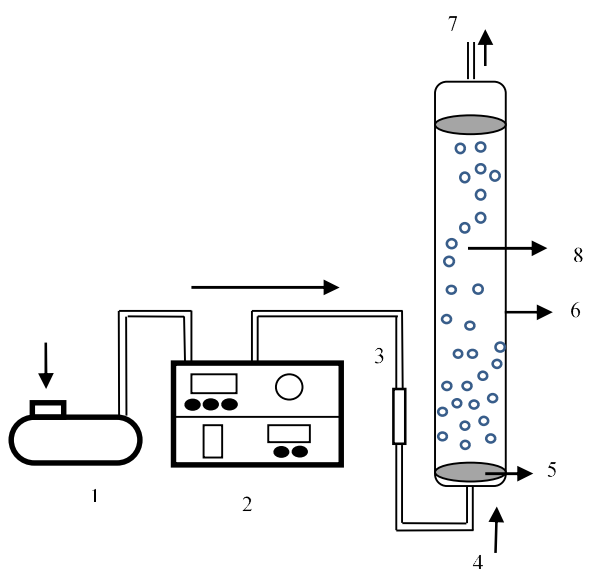

Figure 2. Schematic experimental of ozone treatment system : 1) compressor; 2) ozone generator; 3) flow meter; 4) ozone gas input; 5) sparger; 6) bubble column reactor; 7) ozone gas output; 8) κ-carrageenan solution

$$[\eta] = k_{MH} M^{\alpha} \qquad (2)$$

In this equation, k_{MH} and α are constants for a given system. In this work, the values of k_{MH} and α for κ-carrageenan are 0.00598 and 0.90, respectively. The symbols of M and $[\eta]$ are expressed in g.gmol^{-1} and mL.g^{-1}, respectively [20].

2.4. Mathematical treatment for kinetics model

The dissociation of polymer molecules into smaller units is known as depolymerization. The simplest possible depolymerization occurs when a polymer formed by random polymerization undergoes depolymerization is by random bond breaking. In a random scission, all bonds of a polymer chain are equally susceptible to break with the rate proportional to the remaining unbroken bonds following Equations (3).

$$-\frac{d(N_0 p)}{dt} = k N_0 p \qquad (3)$$

In this equation, N_0 denotes initial number monomers in the reaction mixture, p is the fraction of monomers bonded in polymers, and k is the reaction rate constant. The fraction of monomers bonded in polymers, p, can be related to the number-average molecular weight of polymer [55] as Equation (4).

$$p = 1 - \frac{m}{M_t} \qquad (4)$$

The depolymerization behavior of carrageenan under ozone treatment is expressed according to the zero, first and second order reaction kinetics model [56]. Combination and integration from $t = 0$ to $t = t$ of Eqs. (3) and (4) leads to Eqs. (5), (6), and (7) for zero order (k_z), first order (k_f), and second order (k_s) reaction, respectively.

$$\frac{1}{M_t} = \frac{k_z}{m} t + \frac{1}{M_0} \qquad (5)$$

$$\ln\left(1 - \frac{m}{M_t}\right) - \ln\left(1 - \frac{m}{M_0}\right) = -k_f t \qquad (6)$$

$$\frac{1}{\left(1 - \left(\frac{m}{M_t}\right)\right)} = k_s t + \frac{1}{\left(1 - \left(\frac{m}{M_0}\right)\right)} \qquad (7)$$

In these equations, M_t and M_0 (D$_a$) are the number-average molecular weight of polymer at time t and at time 0, respectively, and m (D$_a$) is the average molecular weight of

disaccharide unit (192 Da), based on the assumption that chain breakage occurs primarily at the 3,6-anhydrogalactose linkage [20,22].

3. Results and Discussion

3.1. Kinetics depolymerization of к-carrageenan by ozone treatment

Three kinetics models (Equations (5), (6) and (7)) are employed in this work to describe the kinetics of ozone treatment for depolymerization of к-carrageenan. Plot of $(1/M_t)$ versus t, $\ln(1-m/M_t)-\ln(1-m/M_0)$ versus t, and $1/(1-m/M_t)$ versus t at various pHs are depicted in Figure 3.

The percent of average absolute deviation (% AAD) of the model was also calculated. It is defined as Equation (8).

$$\% AAD = \left[\frac{Y_{\exp} - Y_{calc}}{Y_{\exp}} \right] x 100\% \qquad (8)$$

In this equation, Y is the left-hand side of Equation (5)-(7). Subscript exp and $calc$ refer to experimental and calculated values, respectively. The depolymerization rate constants (k), correlation coefficient (R^2), and %AAD for the models at various pHs are listed in Table 1.

The correlation coefficient of the second order reaction is slightly larger than that of the zero and first-order reaction. It indicates that second order model is more suitable for describing the kinetics of depolymerization of к-carrageenan by ozonation process. Arias *et al.* [57] reported kinetics data on the reactions of ozone with lignin and cellulose in aqueous solution at pH 2 and 4 and temperature range of 20-40 °C. The results gave the same trends, in which the ozonation of both lignin and cellulose at low temperature were also described by a second order kinetics scheme.

The kinetics equation of second order reaction is similar to pseudo-first order model [47,48,51-53]. In this work, the rate constant for second order model (k_s) at pH 10 is 7.21×10^{-5} min^{-1}. Ratnawati *et al.* [29] who degraded к-carrageenan by ultrasound method found that the kinetics rate constant for pseudo-first order model at 30 °C and pH 10 was 1.74×10^{-6} min^{-1}. The rate constant of ozone treatment is 41.4 fold of that of ultrasonic treatment. Lai *et al.* [20] reported that the kinetics rate constants of к-carrageenan at 75-95 °C during 25 hours of thermal depolymerization were in the ranges of 2.0×10^{-7} to 1.3×10^{-6} s^{-1} or 1.2×10^{-5} to 7.8×10^{-5} min^{-1}. The apparent value of kinetics rate constants of depolymerization by ozone treatment is 0.9-6.0 fold of thermal depolymerization.

3.2. Effect of pH on kinetics of depolymerization of к-carrageenan by ozone treatment

Table 1 shows that the rate constant value of second-order reaction (k_s) for pH 7 and pH 3 are 1.27×10^{-4} min^{-1} and 5.45×10^{-4} min^{-1}, respectively. The rate constant value of depolymerization of к-carrageenan by ozone treatment at
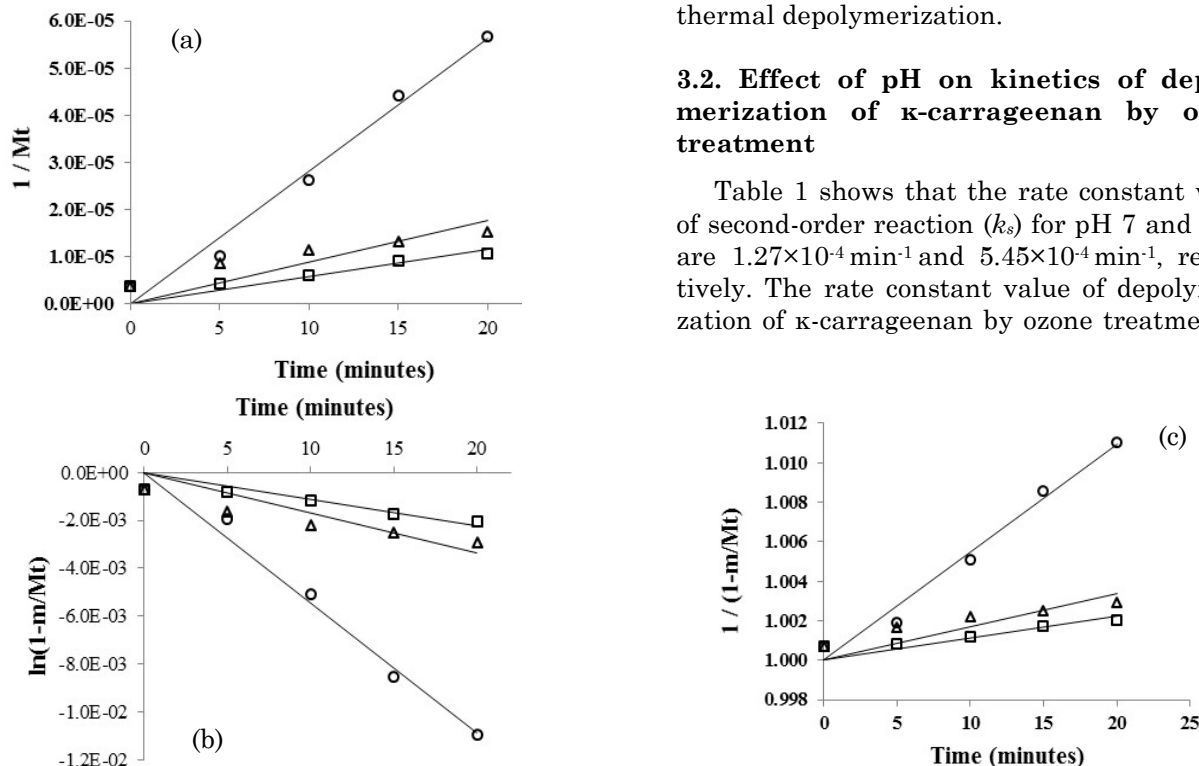

Figure 3. Time dependencies of (a) $1/M_t$ according to zero-order model, (b) $\ln(1-m/M_t)$ according to first-order model, and (c) $1/(1-m/M_t)$ according to second-order model for к-carrageenan at pH 3 (○), pH 7 (Δ), and pH 10 (□)

lower pH is slightly larger than that at higher pH. The apparent rate constant at pH 3 is 4.3 fold of that at pH 7. Abad *et al.* [58] reported that the highest rate constants of reactions of κ-carrageenan were achieved at pH 2. For cellulose oxidation by ozone in aqueous solution, it was found that the rate constant was 3 to 4 order of magnitude at lower pH [57].

At an acidic pH, it is possible that hydrolysis reaction may have occurred resulting in the fragmentation of κ-carrageenan [58,22-24]. Singh and Jacobson [22] reported the kinetics constant of the first-order rate of hydrolysis of κ-carrageenan at pH 2 was 7.8×10^{-7} min^{-1}. For this research, the first-order rate kinetics constant of ozone treatment at pH 3 is 5.42×10^{-4} min^{-1} and 694 fold of that of non-ozonation treatment at pH 2. The results show that the combinations of ozone treatment and low pH gives the significant effect of increasing the rate constant value of κ-carrageenan depolymerization.

3.3. Determination of reaction order of depolymerization of κ-carrageenan by ozone treatment

The results of this work show that κ-carrageenan depolymerization by ozone treatment tends to follow the second order model. The mathematical modeling is needed to determine the actual value of the reaction order. The residual of the model and experimental was minimized using Solver of Microsoft Excel 2007 to determine the actual value of reaction order. The values of second order kinetics rate constants used in this calculation are 5.45×10^{-4}

min^{-1}, 1.27×10^{-4} min^{-1}, and 7.21×10^{-5} min^{-1} for pH 3, 7, and 10, respectively. The apparent reaction order and the % AAD at various pHs are listed in Table 2.

As presented in Table 2 that the values of reaction order of depolymerization of κ-carrageenan by ozone treatment at different pHs are 1.88-1.90, so it could be concluded that reaction is a non elementary reaction. The range of the overall % AAD at pH 3, 7, and 10 are 10.21, 10.00, and 8.16 %, respectively. It indicates that second order reaction is more suitable for describing ozone depolymerization of κ-carrageenan.

4. Conclusions

The kinetics oxidative depolymerization of κ-carrageenan by ozone has been investigated. The highest rate constants of reactions of κ-carrageenan with ozonation treatment are achieved at lower pH. For the similar conditions, the apparent value of rate constants of κ-carrageenan depolymerization by ozone treatment is higher than depolymerization by ultrasound methods and almost equal to thermal depolymerization. The actual values of reaction order (*n*) are 1.88, 1.89, and 1.90 for pH 3, 7, and 10, respectively. For all pHs, the ozonation of κ-carrageenan tends to follow the second order reaction model.

Acknowledgement

Table 1. Kinetic rate constants at different initial pH for depolymerization of κ-carrageenan using

pH	Zero-order reaction			First-order reaction			Second-order reaction		
	k_z (min^{-1})	R^2	%AAD	k_f (min^{-1})	R^2	%AAD	k_s (min^{-1})	R^2	%AAD
3	4.94×10^{-4}	0.97	11.67	5.42×10^{-4}	0.98	11.62	5.45×10^{-4}	0.98	11.62
7	1.22×10^{-4}	0.93	9.43	1.07×10^{-4}	0.96	9.08	1.27×10^{-4}	0.97	7.98
10	6.32×10^{-5}	0.94	8.33	6.32×10^{-5}	0.94	8.17	7.21×10^{-5}	0.96	8.26
Over all		0.95	9.81		0.96	9.62		0.97	9.29

Table 2. The apparent of reaction order depolymerization of κ-carrageenan by ozone treatment

pH	Initial k_s (min^{-1})	*n*	% AAD
3	5.45×10^{-4}	1.88	10.21
7	1.27×10^{-4}	1.89	10.00
10	7.21×10^{-5}	1.90	8.16

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