

Kinetics Study and Product Characteristics of Depolymerization of κ -Carrageenan in the Presence Hydrogen Peroxide

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Abstract: Low molecular weight (LMW) of κ -carrageenan has large applications in pharmaceutical and biomedical function. LMW of κ -carrageenan can be effectively prepared by H_2O_2 oxidation. This study aims to determine the effect of process variables such as reaction time, temperature, solution pH and H_2O_2 concentration on the rate of depolymerization of carrageenan. The functional and morphological properties of LMW of κ -carrageenan was characterized by Fourier transform infrared spectroscopy (FT-IR), SEM and XRD of κ -carrageenan effectively degraded using H_2O_2 and the maximum degradation can be obtained under the reaction condition of 50°C, 1.5% H_2O_2 and pH 10 in 30 minutes reaction times. At these reaction conditions, the degradation rates of κ -carrageenan achieved 76.41% and the kinetic value was 2.46×10^{-4} . The activation energy of plot Arrhenius law of temperature dependence of kinetics rate constant is 41.97 kJ. mol⁻¹. The analysis of functional groups using FT-IR showed that there are no significant changes of structure of degraded κ -carrageenan under H_2O_2 treatment. The results of SEM analysis show that after the degradation process the surface becomes rougher and more porous. The results of the crystallinity test of carrageenan after XRD degradation showed that it became more amorphous.

Keywords: κ -carrageenan, depolymerization, H_2O_2 , kinetics, characterized

1. Introduction

The low molecular weight of sulfated polysaccharides (SPs) has large applications in pharmaceutical and biomedical functions. κ -Carrageenan is a sulfated galactan extracted from *Kappaphycus alvarezii*. The basic structure of κ -carrageenan is ammonium sulfate ester of D-galactose polymer linked in α -1, 3 and β -1, 4 positions [1]. κ -Carrageenans are increasingly used in food industry applications as stabilizing or texturing agents [2] and most recently used in the pharmaceutical industry as an excipient in pill and tablets [1].

The high molecular weight of κ -carrageenan which have markedly limited their application. The renewable resources are increasingly developing with the advance of time, it is worth improving the properties of κ -carrageenan. The attempts have been conducted to broaden the utilization of κ -carrageenan, one of which is through degradation. There have been reported to prepare κ -carrageenan to reduce low molecular weights. Such as variety of techniques, including enzyme-catalyzed [3], hydrolysis acid [4, 5], radiation [6], and ultrasonic process [7]. Among these methods, hydrogen peroxide (H_2O_2) is considered to be high oxidant agent to degradation polysaccharides.

Chang et al. [8] and Qin et al. [9] reported that H_2O_2 can be powerful oxidant to degraded chitosan. Yao et al. [3], it was found that the degradation of gum peach polysaccharides was effective using H_2O_2 . Wu et al. [10] studied that hydrogen peroxide can reduce the molecular weight of curdlan. Li et al. [11], This technique is based on the formation of free radicals, which can attack the glucosidic

linkages of the polysaccharides. The chemical treatment used hydrogen peroxide able to enhance the degradation of κ -carrageenan and created no harmful byproduct [12]. This chemical is therefore considered more environmentally friendly and is preferred especially when a chlorine-free process is desired. However when hydrogen peroxide is used excessively at high temperature will change the structure of polysaccharide [13].

In contrast, so far no researchers have examined and developing results of the degradation of κ -carrageenan using H_2O_2 . So the aims of this work the studied degrading κ -carrageenan and kinetics studied by oxidation using hydrogen peroxide with change the H_2O_2 concentration, pH treatment, and temperature was established. After the oxidation treatment, the product composition, structural function and morphological were examined by FT-IR, SEM, and XRD.

2. Methodology

2.1 Preparation of κ -carrageenan solution

This research uses the commercial raw material of κ -carrageenan extracted from *Kappapicus alvarezii* seaweed. The first 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 chemical was used such as HCl with 37% of purity (E. Merck Cat. No.100317) or NaOH with > 99% purity (E. Merck Cat. No.104698) that are used as pH value regulating chemicals and H_2O_2 food grade with 35% of purity (E. Merck Cat. No.107209).

2.2 Depolymerization by H₂O₂

One hundred milliliters of κ-carrageenan solution was added 5 ml of H₂O₂ solution (0.5%, 1%, 1.5% w/v) and stirred for 30 minutes at a specified temperature (30°C, 40°C, and 50°C). The predetermined pH variations are 3, 7 and 10. After treatment the solution was added to 200 ml polyphenol alcohol to form a gel and remove precipitation.

2.3 Molecular weight determination

For determination of the molecular weight of treated κ-carrageenan, five different concentrations (0.0625 to 1.0 % w/v) of H₂O₂ treated κ-carrageenan solution was prepared. A portion of buffer solution pH 7 was added to adjust polysaccharide concentrations and to keep polysaccharide molecules from intermolecular aggregation [14]. The efflux times of the solutions were measured using an Ubbelohde capillary viscometer (type 531 030c Schott-Gerate, Germany) at a constant temperature at 45.0±0.1 °C. The intrinsic viscosity ([η]) was calculated from the specific viscosity (η_{sp}). The intrinsic viscosity is the average intercept of Huggins and Kraemer equation [15] in Equation (1).

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

In this equation, η_{sp} , [η], 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 [η] and the concentration (c) have the units of mL. g⁻¹ and g. mL⁻¹, respectively. The value of k_H for κ-carrageenan solution is 0.35 [15]. The molecular weight of κ-carrageenan (M) was calculated from the intrinsic viscosity data by Mark Houwink equation (Equation 2).

$$[\eta] = k_{MH}M^a \quad (2)$$

In this equation, k_{MH} and a are constants for a given system.

In this work, the values of k_{MH} and a of κ-carrageenan are 0.00598 and 0.90, respectively. The symbols of M and [η] are expressed in g. gmol⁻¹ and mL. g⁻¹, respectively [16].

2.4 Characterization of product κ - carrageenan Degraded

The products κ-carrageenan degraded were characterized by FT-IR, XRD, and SEM. The functional group properties of κ-carrageenan degraded was determined by FT-IR using a PerkinElmer IR 10.6.1 Spectrophotometer, USA in the range from 400-2000 cm⁻¹ while morphological product was determined by SEM and XRD using a Scanning electron microscope JSM-6510-LA JEOL series, Japan and X-ray diffractometer (XRD-7000, Shimadzu, Japan).

3. Results and Discussion

3.1 Effect of Initial H₂O₂ concentration on degradation of κ-carrageenan

The extent of degradation of κ-carrageenan as concentration of H₂O₂ was varied from 0.5% to 1.5% w/v and the reaction time was varied from 0 to 30 minutes. As shown in Figure 1, the 30 minutes of reaction time, the molecular weight is reduced to 250 kDa, 220.03kDa, and 200.10 kDa with degradation rates of 41.01%, 48.09%, and 52.81% corresponding to original H₂O₂ concentrations of 0.5%, 1%, and 1.5%, respectively. The phenomena of this work can be seen that the higher of concentration of H₂O₂ can increase the degradation rates of κ-carrageenan.

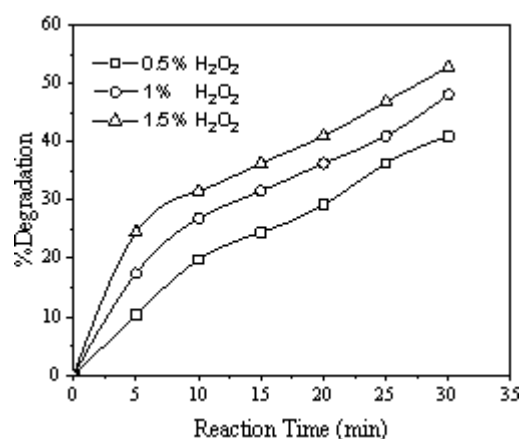
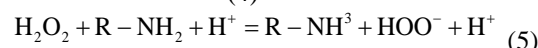
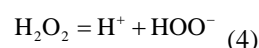
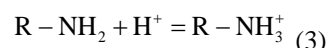


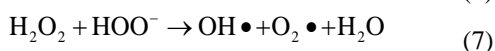
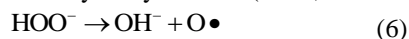
Figure 1: Effect of H₂O₂ concentration on depolymerization of molecular weight of κ-carrageenan. Reaction was kept at 30±1 °C.

(□: 0.5%; ○: 1%; △: 1.5%)

The degradation of κ-carrageenan used chemical treatment can be effective methods for reduce the molecular weight of polysaccharides [11; 17-19]. According to Hou et al. [17] about degradation *Laminaria japonica* fucoidan using the hydrogen peroxide. The research studied that concentration of hydrogen peroxide can be effective to decrease the molecular weight of fucoidan. The change in molecular weights as the H₂O₂ concentration were 16.7 kDa, 7.7 kDa, 4.8 kDa, 3.4 kDa and 2.6 kDa, corresponding to original H₂O₂ concentrations of 0.025 M, 0.05 M, 0.1 M, 0.2 M, and 0.4 M, respectively. The H₂O₂ can be effective agent oxidant because H₂O₂ produce the amount of hydroxyl radicals as oxidant agent which able to attack the linkage of fucoidan [11]. The resulting radicals are powerful oxidants and capable of abstracting hydrogen atoms from the glycosidic bonds of polysaccharide, rearranging the structure of the molecular and breaking glycosidic bonds [20]. Tian et al. [21] studied the mechanism of the depolymerization of polysaccharide by H₂O₂. In the depolymerization system of polysaccharide with H₂O₂ can be showed in Eqs. (3) and (4), and the total reaction is shown in Eqs. (5).



The hydroperoxide anion is very unstable and easily decomposed to high reactive hydroxyl radical (OH^\bullet),



Hydroxyl radical is a very strong oxidant. Hydrogen abstraction has been shown to be the primary chemical activity of HO^\bullet with polysaccharide [22]. It interacts very easily with carbohydrates. Hydroxyl radical removes and incorporates a hydrogen atom to form water. During the procedure, the R-NH_2 interacts preferentially with H^+ to generate R-NH_3^+ , which induces a decrease in $[\text{H}^+]$ and a rise in pH. However, HOO^- is rapidly decomposed to HO^\bullet , which means that H_2O_2 is decomposed continuously as shown in Eqs. (5). Such as radicals react quickly to the formation of water-soluble oxidation products with low molecular weight. When free radical are produced rapidly and sufficiently and spread uniformly, free radicals would have easy access to linkages and break it [19]. In accordance with the mechanism, the addition of H_2O_2 concentration will be able to produce more hydroxyl radicals as well. The number of hydroxyl radicals produced will make molecular weight less than before treatment.

3.2 Effect of pH value on the degradation of κ -carrageenan

The reaction mixture pH value greatly affects the degradation of κ -carrageenan using H_2O_2 . The value pH studied in 4, 7 and 10. The maximum degradation of κ -carrageenan was achieved at pH value 10. It reduced from 423.82 kDa to 180.12 kDa with the extent of degradation was 57.52%, approximately. In the acid liquid medium (pH value 4) the degradation of κ -carrageenan only had little changed. Meanwhile in the pH value 10, the extent of degradation of κ -carrageenan increased from 45.73% to 57.52% as was shown in the Figure 2.

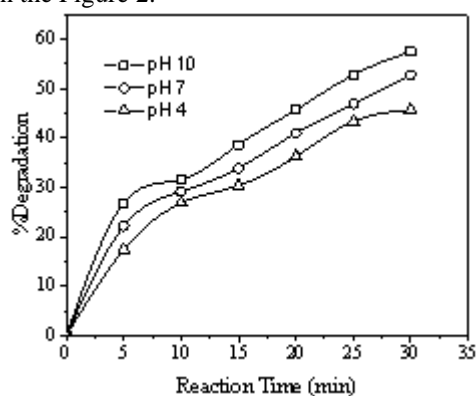
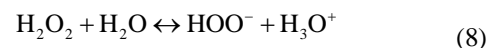


Figure 2: Effect of pH value on degradation of molecular weight of κ -carrageenan. Reaction was kept at 1.5% of H_2O_2 concentration and $30 \pm 1^\circ\text{C}$.

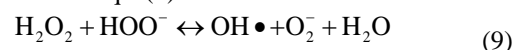
(□: pH 4; ○: pH 7; △: pH 10)

The decomposition of hydrogen peroxide was highly depended on the pH and temperature of the reaction [23]. In this study, pH value able decreased the molecular weight of κ -carrageenan from initial molecular weight 423.82 kDa to 180.12 kDa. The maximum of degradation of κ -carrageenan occurred at the pH value 10 (alkaline medium). According to Wu et al. [24], hydrogen peroxide as chemical treatment to degradation of curdlan able increased the %DE (dextrose

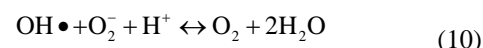
equivalent) in the alkaline condition (shown with the presence of NaOH concentrations). Hou et al. [17] reported that increasing the pH value can increase the degradation rates of fucoidan. The varying of pH value from 3 to 8. At pH 8 the degradation rates of fucoidan achieved 96.7%. Hydrogen peroxide able to produce the hydroxyl radical through the dissociation generates the hydroperoxide anion HOO^- in the alkaline liquid medium, as follows equation below,



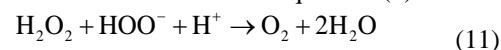
The hydroperoxide anion can react with H_2O_2 , leading to the formation of superoxide and hydroxyl radical in the alkaline medium, shown with Eqs. (2).



Superoxide and hydroxyl radical can combine when the other reagents was presence and produce oxygen and water, as in Eqs. (3)



So that, generally equation of H_2O_2 decomposition in alkaline medium can be summarized in Equation. (4).



The absence of the hydroxyl radical from decomposition hydrogen peroxide in the alkaline medium as oxidizing agent can break the D-galactose β -1, 3 linkages of κ -carrageenan. According the results in this study, pH value 10 had the maximum of the degradation rates of κ -carrageenan caused by presence more of hydroxyl radical.

3.3 Effect of temperature on degradation of κ -carrageenan

In Figure 3, temperature of 30°C , 40°C , and 50°C were selected for testing at 1.5% H_2O_2 concentration at pH 10 and 30 minutes of reaction time were observed for testing the effect of reaction temperature on the degradation rates of degraded κ -carrageenan. The degradation rates in this work are 52.81%, 66.96%, 76.41% for the reaction temperature 30°C , 40°C , and 50°C , respectively. According to the result of this work, enhance the extent of degradation of κ -carrageenan can be influenced by reaction temperature and time reaction. While the reaction temperature is higher, the extent of degradation will be increase.

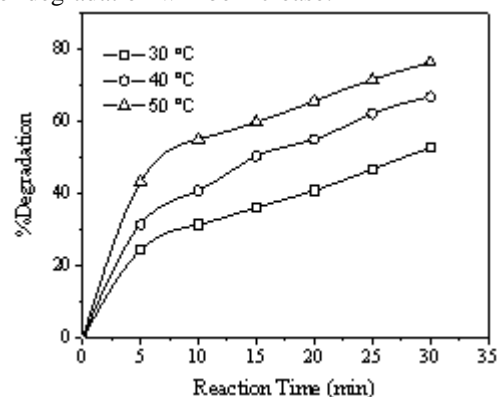


Figure 3: Effect of temperature reaction on the degradation of molecular weight of κ -carrageenan. The reaction was kept at 1.5% of H_2O_2 concentration and pH value 10. (□: 30°C ; ○: 40°C ; △: 50°C)

The temperature of reaction can be factor to enhance the degradation of polysaccharides. The higher temperature of the reaction and the concentration of hydrogen peroxide were the main factors determining the decrease in Molecular weight [17].

While the effective range of reaction temperature is 40°C-90°C [17&21]. The report about depolymerization of chitosan by hydrogen peroxide has studied by Tian et al. [21], that the rise of the temperature increase the initial rate of destruction. It indicate that the reducing of molecular weight was increase. In these work, when chitosan was degraded by 2.0 M H₂O₂ concentration at 60°C for 4h, the molecular weight of chitosan was 11 kDa. While at 70°C, the reducing of molecular weight of chitosan with same condition achieved 9 kDa. The same study has been reported by Hou et al. [17], the fucoidans are degraded by hydrogen peroxide as antioxidant. The range of reaction temperature was 30°C-90°C. At 30°C there is a slow reduction in Mw of fucoidans with an average Mw in the sixth hour above 100 kDa. But the Mw dropped to about 10 kDa after 72h at 30°C. The reduction of fucoidans Mw is mainly for 70°C and 90°C at the first 2 hours. The molecular weight was less than 1 kDa after 4h at 90°C.

3.4 Kinetics of Degradation of κ-carrageenan

The molecular weight of κ-carrageenan decreased with increasing degradation time. The reduction in weight-averaged molecular weight could be described by,

$$\frac{1}{M_t} = \frac{1}{M_o} + \frac{kt}{m} = \frac{1}{M_o} + k't \tag{12}$$

where k (min⁻¹) represents the rate constant, t the reaction time, and m the monomer molecular weight. Kinetics of degradation of κ-carrageenan at varying treatment will be determined and studied. Figure 4a shows the effect of H₂O₂ concentration on the rate constant during degradation of κ-carrageenan. The highest value of kinetic rate constant during degradation of κ-carrageenan by varying of H₂O₂ concentration is 8.74 x 10⁻⁵ min⁻¹ for 1.5% H₂O₂ concentration, respectively. These rate constant are higher than that ultrasonic degradation of κ-carrageenan, 2.69 x 10⁻⁶ min⁻¹, calculated by Ratnawati et al. [25]. Chang et al. [8] also reported about kinetics of degradation of chitosan using H₂O₂ and the value of kinetic rate constant ranged from 4.2 x 10⁻⁴ to 7.1 x 10⁻⁴ min⁻¹ with ranged of H₂O₂ concentration were 0.5%-3.5%. Another report using κ-carrageenan as materials and ozonation as method have studied by Prasetyaningrum et al. [14]. The pH value is an influence on calculating the kinetic value of degradation of κ-carrageenan and the kinetic value at pH 10 achieved 6.32 x 10⁻⁵ and that is lower than this study, 1.05 x 10⁻⁴. In Figure 4b can be seen that pH value influence to increase the kinetics value of degradation of κ-carrageenan.

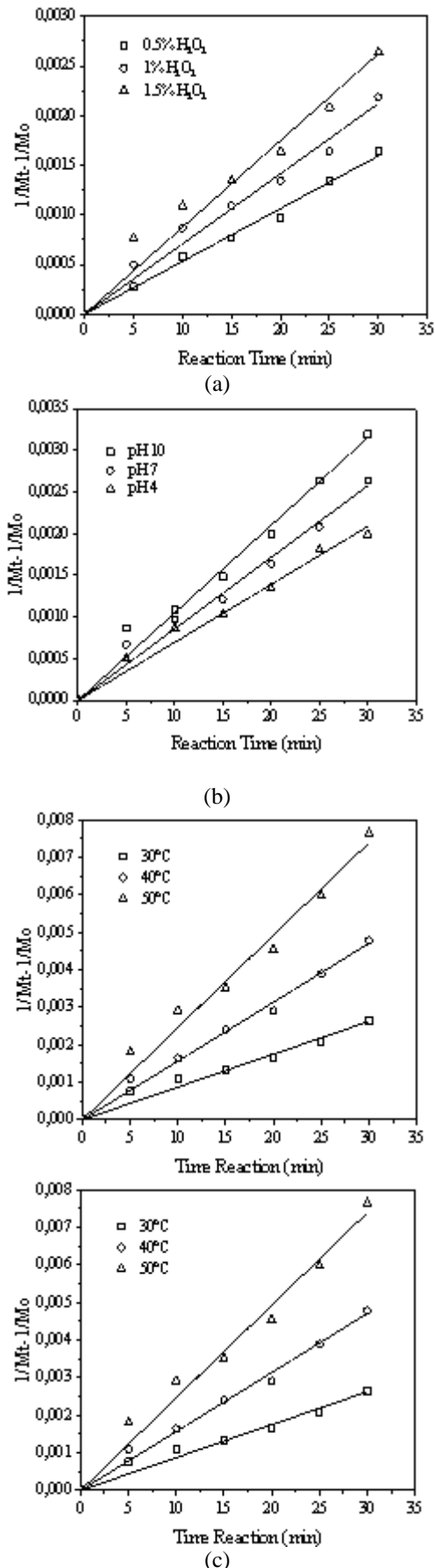


Figure 4: Effect of: a) H₂O₂ concentration; b) pH; c) reaction temperature on kinetic rate constant of degradation of κ-carrageenan

Table 1: Kinetic value of degradation of κ-carrageenan

Treatment	Kinetic constant rate (min ⁻¹)
H ₂ O ₂ concentration	
0.5%	5.32 x 10 ⁻⁵
1.0%	7.08 x 10 ⁻⁵
1.5%	8.74 x 10 ⁻⁵
pH value	
10	1.05 x 10 ⁻⁴
7	8.59 x 10 ⁻⁵
4	6.98 x 10 ⁻⁵
Temperature	
30	8.78 x 10 ⁻⁵
40	1.57 x 10 ⁻⁴
50	2.46 x 10 ⁻⁴

Influence of temperature on the kinetics rate constant of degradation of κ-carrageenan also are determined. Figure 4c shows that temperature can increase the kinetics value of degradation. The kinetics value of influence temperature on the degradation of κ-carrageenan are 8.49x10⁻⁵, 1.13x10⁻⁴, and 1.54x10⁻⁴ min⁻¹ for 30 °C, 40 °C, and 50 °C, respectively. These kinetics value are much higher than that degradation of κ-carrageenan of ultrasound-assisted depolymerization, acid hydrolysis and thermal depolymerization. Ratnawati et al. [25] who degraded κ-carrageenan by ultrasound-assisted found that rate constant increase following the increase of temperature. At temperature 30 °C to 60 °C, the kinetics value were 2.11x10⁻⁸ to 2.63x10⁻⁸ min⁻¹. Determined the kinetics value of degradation of κ-carrageenan using acid hydrolysis at temperature 35 °C, 45 °C, and 55 °C were 1.451x10⁻⁶, 8.352x10⁻⁶, and 2.130x10⁻⁵ min⁻¹. Lai et al. [16] reported kinetic thermal of degradation of κ-carrageenan, resultant *k* values at 75-95 °C were in the range of 1.2x10⁻⁵-7.8 x10⁻⁵ min⁻¹.

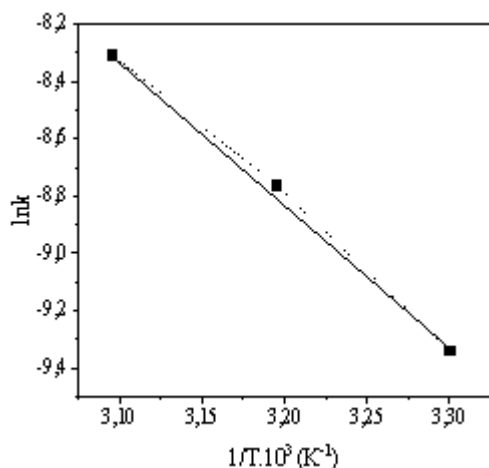


Figure 5: Arrhenius plot of temperature dependence of kinetics rate constant.

The temperature dependence of the *k* value can be given by the Arrhenius law as presented in Equation (13).

$$k = Ae^{-\frac{E_a}{RT}} \tag{13}$$

or

$$\ln k = \ln A - \frac{E_a}{RT} \tag{14}$$

Where A dan *E_a* are pre-exponential factor and activation energy, approximately. Plot of ln *k* versus 1/*T* will result in a

linear line, as presented in Figure 5, with correlation coefficient of 0.99. The value of the intercept and slope can be obtained as A and *E_a*, which are 1537.48 mol. g⁻¹. min⁻¹ and 41.97 kJ. mol⁻¹, respectively.

Most of the reactions degradation have *E_a* value ranging from 40 to 400 kJ. mol⁻¹ [25]. The reported by Lai et al. [16] that the value of activation energy (*E_a*) of the thermal degradation of κ-carrageenan using ranged temperature from 75 °C to 95 °C was 97.2 kJ/mol. The another studied by Holme et al. [26] about kinetics of alginate and chitosan in aqueous solution with temperature treatment from 22.5 to 80 °C at pH close to 5 achieved the activation energies (*E_a*) value were 76±13 kJ/mol and 80±11kJ/mol for chitosan chloride and chitosan glutamate solution.

3.5 Structural and Morphological Properties of κ-Carrageenan degraded

3.5.1 FT-IR Spectra Analysis

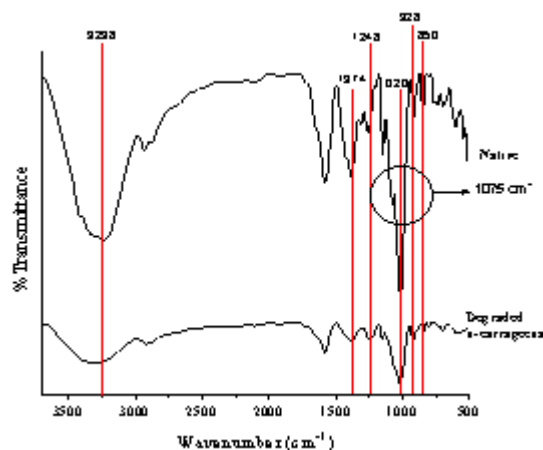


Figure 6: FTIR spectra of native κ-carrageenan and degraded κ-carrageenan by H₂O₂ 1.5%

The structural change of native κ-carrageenan and degraded κ-carrageenan were confirmed by FT-IR spectra as shown in Figure 6. The characteristic absorption peaks of the κ-carrageenan are represented in Table 2 according studied by Murat et al. [27]. In this work, the main characteristic absorption peaks appearing at 1248 cm⁻¹ was attributed to S=O of the sulfate esters and 850 cm⁻¹ was C-O-S of the axial secondary sulfate on C₄ of galactose, respectively. The peak at 928 cm⁻¹ was a characteristic absorption of C-O-C of 3, 6-anhydro-D-galactose. The another peak at 1020 cm⁻¹ and 1374 cm⁻¹ indicated of glycosidic linkage and sulphates, respectively. The peak at 1075 cm⁻¹ also indicated of glycosidic linkage, it can be seen that %transmittance reduced after the treatment. That results indicated that occurring break linkage on the glycosidic linkage. But, the FTIR analysis results show that the functional properties of carrageenan did not change during the oxidation treatment with H₂O₂. This is indicated by the presence of sulfate groups in treated carrageenan at wave numbers 1248, 928 and 850 cm⁻¹. It similar with reported by Kalitnik et al. [28].

Table 2: Absorption peak of κ-carrageenan [27]

Absorption (cm^{-1})	Functional groups
3600-3000	O-H (stretching)
3000-2800	C-H (stretching)
1645-1640	Polymer bound water
1380-1355	Sulphates (stretching)
1380-1370	Methylene group (bending)
1270-1230	O=S=O (asymmetric stretching)
1190	S=O (asymmetric stretching)
1160-1155	C-O-C (asymmetric stretching)
1248	S=O (asymmetric stretching)
1080-1020	Glycosidic linkage
933-928	C-O-C of 3, 6-anhydro-D-galactose
850-840	C4-O-S in galactose

The compared of the native κ -carrageenan to degraded κ -carrageenan by H_2O_2 was described in the Figure 6, there was absorption peak lost at degraded κ -carrageenan by H_2O_2 . It was at 1075 cm^{-1} which combination of C-O and C-OH modes. It signified that degradation process able break the linkages of κ -carrageenan. Also, the %transmittance of the absorption peaks of degraded κ -carrageenan was smoother and lower than native κ -carrageenan. It signified that occurred breaks of the linkages in the κ -carrageenan after degraded used H_2O_2 . As reported by Li et al. [11] the degraded alginate using H_2O_2 after characterized by FT-IR that there were decrease of %transmittance and it indicated that the linkages of alginate was break. As can be seen, the FT-IR spectra of the degraded κ -carrageenan are similar to that of native κ -carrageenan through oxidation hydrogen peroxide treatment, indicating that the main chain structure of degraded κ -carrageenan still remained during degradation process.

3.5.2 SEM

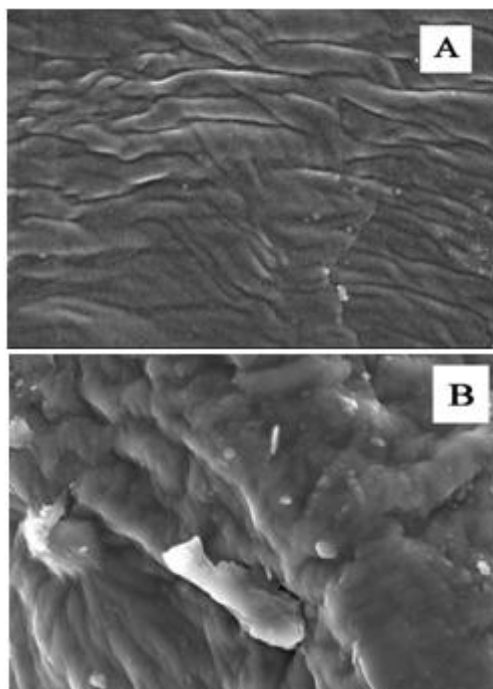


Figure 7: SEM analysis of A) Nativ; B) κ -carrageenan degraded by H_2O_2

The SEM image of native and the product of degraded κ -carrageenan using H_2O_2 was shown in Figure 7. This work shows that the neat degraded κ -carrageenan involved an

irregular morphology with some crack on the surface. That results indicate that the surface morphology of treated κ -carrageenan was relatively more rough and amorphous than the native κ -carrageenan. Shahbazi et al. [29] also reported that the thermal degradation of κ -carrageenan made a rougher and more porous surface than native κ -carrageenan. This is due to the cleavage of the glycosidic linkage of κ -carrageenan during the depolymerization process.

3.5.3 X-ray Diffraction Analysis

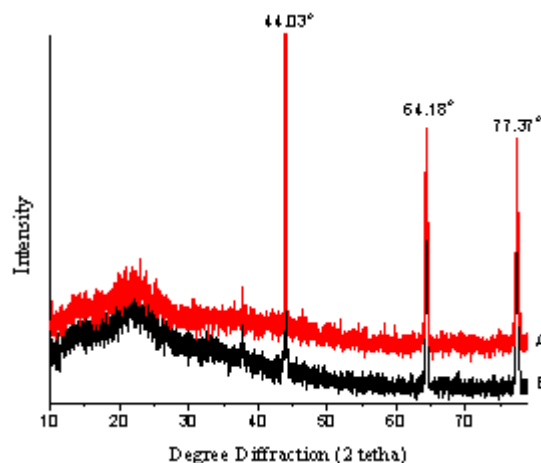


Figure 8: X-ray Diffraction analysis: A) Native; B) κ -carrageenan degraded by H_2O_2

The X-ray diffraction pattern of the native κ -carrageenan and treated κ -carrageenan by H_2O_2 are presented in Figure 8. The results of the XRD analysis of this research shows that there was a decrease in the main peak for degraded κ -carrageenan when compared to native κ -carrageenan. Tian et al. [21] reported that degraded chitosan by H_2O_2 has a lower intensity on the main peak than native chitosan. It indicated that during treatment, κ -carrageenan become the amorphous and the formed of cristalynity was low.

4. Conclusion

κ -carrageenan able be effectively degraded using H_2O_2 and the maximum degradation can be obtained under the reaction condition of 50°C , 1.5% H_2O_2 and pH 10 in 30 minutes reaction times. At these reaction condition, the degradation rates of κ -carrageenan achieved 76.41% and the kinetic value was 2.46×10^{-4} . The activation energy of plot Arrhenius law of temperature dependence of kinetics rate constant is $41.97 \text{ kJ. mol}^{-1}$. The analysis of functional groups using FT-IR, there are no significant changes of structure of degraded κ -carrageenan under H_2O_2 treatment. The result of the X-ray diffraction analysis and SEM analysis indicated that the intensity is lower and it indicated after degradation κ -carrageenan become amorphous and formed of crystalinity was low and the morphological of degraded κ -carrageenan using H_2O_2 was amorphous.

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