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To cite this article: E Purwanto *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **703** 012041

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The kinetics oxidative degradation of chitosan in formic acid with the presence of hydrogen peroxide

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Abstract. The chitosan degradation in formic acid solution with the presence of hydrogen peroxide was investigated in this work. Temperature and reaction time had a significant effect on reducing the molecular weight of chitosan, and it is clear that it decreased the molecular weight faster at the first 15 minutes of reaction time. Therefore, the molar concentration of chitosan in the solution increased with temperature and reaction time. The reaction order was determined from the molar changes of chitosan on reaction time and found followed -0.1 reaction order to the molar concentration of chitosan. The Arrhenius equation was used to study the correspondence influence of reaction temperature on the degradation reaction rate constant. The results suggest that the values of degradation rate constant increased with higher reaction temperature. The value of activation energy was determined under the experimental operating conditions examined to be 99.8 kJ/mol. The FT-IR spectra demonstrated that there was no change in the chemical structure of chitosan before and after the degradation reaction.

1. Introduction

Chitosan is generally accepted as a product derivative of chitin that ordinarily acquired from crustacean shell through partial deacetylation reaction using base or enzyme [1]. Chitosan has a different structure compared to chitin concerning some acetyl groups present in chitin which have been replaced by atoms H. Hence, chitosan will have a varying degree of deacetylation (DD) with a chemical name as (1→4)-2-amino-2-deoxy-β-D-glucan.

As amino-polysaccharides, chitosan is extensively utilised for some purposes with great features regarding biocompatible, antibacterial, biodegradable, nontoxic, and environmentally friendly. Accordingly, chitosan is utilised in numerous applications, for example, in foods, biomaterials, medicine, cosmetics, and pharmaceutical products [2-6]. However, low solubility in water is the characteristic of original chitosan derived from the shell of shrimps as it has high molecular weight. These properties make the original chitosan have a limited utilisation in particular for medical applications. Therefore, it is necessary to obtain a chitosan product through the degradation process that accomplishes its higher solubility and preserves its biological properties. Oligomer chitosan with high solubility in solvents can be achieved through degradation reactions via several techniques. The degradation can be carried out by a chemical method using acids [7-10], high impact energy [11-13], and enzymatic [14-15].



Recently, acetic acid has been widely implemented in oxidative degradation using hydrogen peroxide as an oxygen carrier. However, there is little attention to the exploitation of formic acid as an acid solvent in the chitosan degradation with the utilisation of hydrogen peroxide. Formic acid may show better performance than acetic acid as a solvent when combined with hydrogen peroxide. The utilisation of hydrogen peroxide and synergised with formic acid has been widely employed, as shown in another type of oxidation reaction called epoxidation reaction [16-17]. Hence, this work aims to study the influence of reaction temperature and time on chitosan degradation and determine the kinetics of chitosan degradation in the formic acid solution with the presence of H₂O₂.

2. Materials and methods

2.1. Materials

The feedstock of chitosan with an average molecular weight of approximately 3300 kDa and a degree of deacetylation of 96.31% was used in this research. This chitosan was obtained from Xi' An Lukee Bio-Tech Co. Ltd. Hydrogen peroxide, formic acid, acetic acid, sodium hydroxide, and ethanol absolute were supplied by Chem-supply as laboratory reagent grade.

2.2. Feedstock preparation of chitosan solution

The starting of chitosan solutions was prepared in a glass reactor with dissolving chitosan to obtain 10 g/L chitosan in 1% formic acid solution. A calculated amount of formic acid solution was dissolved in the water to obtain 800 mL 1% formic acid solution. Following this, 8 grams chitosan dissolved in this acid solution and stirred with low rotation speed overnight to ensure chitosan has been soluble thoroughly.

2.3. Experimental setup and procedure

The chitosan degradation was carried out in a 1-L glass reactor equipped with a magnetic stirrer, condenser and thermocouple. The reactor was located on a heating plate and connected with temperature control, whose temperature could be maintained $\pm 1^\circ\text{C}$. The reaction temperature was set by adjusting the temperature controller connected to the heating plate, and a calculated amount of hydrogen peroxide was added when the desired reaction temperature was reached with a final concentration 1% (w/v) in the mixture. The degradation reactions were run at several isothermal conditions and samples were taken at certain reaction times. After the degradation reaction, the samples were collected and cooled to terminate the reaction. It was then neutralised with 2 M NaOH solution to pH 8-9. The neutralised solution was then filtered off to separate solid phase (low molecular weight of chitosan) and liquid phase (oligomer chitosan soluble in the water). After that, the solid phase was washed with water until the remaining washing water was neutral. Next, the remaining impurities in the solid phase was removed using ethanol. Finally, the solid was vacuumed and then dried at 60°C to remove the water content. The solid product was analysed to determine its molecular weight using the viscometric method, and FT-IR was performed to monitor the formation and disappearance of functional groups of original and low molecular weight of chitosan.

2.4. Analytical methods

The viscosity-average molecular weight of chitosan (M_v) was measured using an Ubbelohde viscometer with a capillary diameter of 0.36 mm at 30°C. The several dilute solutions of chitosan in 1% acetic acid solution (C) were measured its flowing time (t_s) and the solvent acetic acid (t_0) in duplicate for each. The specific viscosity of the dilute chitosan solutions (η_{sp}) was calculated from relative viscosity (η_r) according to the following equation (1):

$$\eta_r = \frac{t_s}{t_0}, \quad \eta_{sp} = \eta_r - 1 \quad (1)$$

Huggins equation (2) was performed to determine the intrinsic viscosity (η) from the known value of specific viscosity (η_{sp}):

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \quad (2)$$

by plotting $\frac{\eta_{sp}}{C}$ vs C , the intercept at $C = 0$ was obtained as the intrinsic viscosity (η) [8]. The M_v value was determined through the Marck-Houwink equation (3):

$$[\eta] = K.M_v^a \quad (3)$$

The value of K and a for chitosan in 1% acetic acid solution are 0.0474 mL/g and 0.723, respectively [18]. Those values of K and a are constant and defined as the Mark-Houwink constants.

2.5. Kinetics model

Kinetic model of chitosan degradation has been developed according to the rate of chemical reaction definition. The degradation rate is expressed as the number of moles of cutting off the glycosidic linkage in the chitosan chain to yield the two pieces [19] according to the following equation (4):

$$R = \frac{d[M]}{dt} = kM^n \quad (4)$$

M is known as the molar concentration of chitosan (mol/L). The properties k and n represent the reaction rate constant and reaction order, respectively. In this case, the reaction order (n) typically has a negative value as with the increasing of chitosan solution concentration, the degradation rate will decrease. The molar concentration of chitosan can be calculated through equation (5):

$$M = \frac{C}{M_n} \quad (5)$$

Then, the solution of the differential equation (4) is described in equation (6):

$$M_t^{1-n} - M_0^{1-n} = (1-n)kt \quad (6)$$

where M_t is chitosan concentration at a certain reaction time (t) and M_0 is the initial concentration of chitosan. It is obvious that the value of C as the solution concentration remains constant (g/L), but the molar concentration (molarity in mol/L) each time increases with the reducing number of molecular weight through the degradation process. The M_n value is the number-average molecular weight can be calculated from the M_v value through equation (7) below:

$$M_v = \left[(1+a)\Gamma(1+a) \right]^{\frac{1}{a}} M_n \quad (7)$$

where $\Gamma(1+a) = \int_0^{\infty} e^{-t} t^a dt$ and the value of M_v is obtained from equation (3) above.

3. Results and discussions

3.1. The influence of reaction temperature and time on the molecular weight of chitosan

The reaction temperatures of degradation were varied at 40, 50 and 60°C for 120 min reaction time to study the influence of reaction temperature on the chitosan degradation. The corresponding of viscosity-average molecular weight (M_v) was plotted on a logarithmic scale in correlation with reaction time t at the different reaction temperatures, as depicted in figure 1. The results indicated that the M_v value decreased with the addition reaction time. The reaction temperature similarly demonstrated a substantial effect on chitosan degradation indicated by a significant reducing the molecular weight of chitosan. The corresponding rate of decrease for M_v value of chitosan in percentage was 98.26, 99.40, and 99.83% respectively for 120 reaction time from the initial M_v value of chitosan of 3300 kDa. The M_v value of

chitosan dropped to 57.4, 19.8, 5.6 kDa for 120 min, respectively. Interestingly, the most significant reduction of M_v value was achieved at the first 15 minutes of reaction time with the corresponding rate of decline in percentage for M_v value was 94.33, 96.58, 98.47% respectively.

Figure 2 shows the correlation between the molar concentration of chitosan (M_t) vs reaction time (t) and the result indicated that the molar concentration of chitosan increased with the rise of reaction time. This finding implies that a random scission of glycosidic linkage occurred and results in a lower number-average molecular weight of chitosan. Therefore, it will increase the molar concentration of chitosan with additional reaction time.

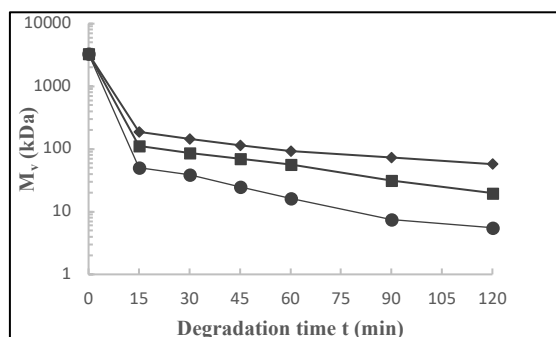


Figure 1. The influence of reaction temperature on the viscosity-average molecular weight of chitosan (M_v) for different temperatures: (◆) 40°C; (■) 50°C; (●) 60°C.

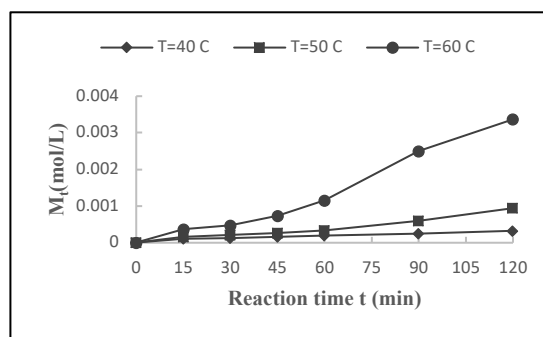


Figure 2. The molar concentration of chitosan vs time.

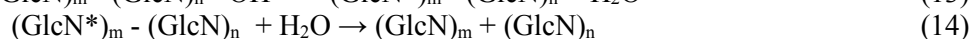
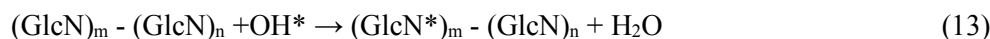
These results confirm a previous finding stated that reaction temperature plays an essential role for chitosan degradation [20]. The experimental results conclude that hydrogen peroxide in the formic acid solution may accelerate chitosan degradation during the degradation reaction. The reaction mechanism of chitosan degradation is mainly under the attack of powerful oxidant, namely, hydroxyl radical [21]. The reaction step is illustrated as follows, R-NH₂ first produces R-NH₃⁺ in acid solution and decomposition of H₂O₂ also occurred as shown in equation (8) and (9) then summarised as a total reaction in equation (10). The reaction mechanism of chitosan degradation with hydrogen peroxide in the acid solution is as follows [21]:



The hydroxyl radical (HO*) is easily produced from the decomposition of hydroperoxide anion as it is not stable, and the reactions in equation (11) and (12) take place.



Eventually, the hydroxyl radical (OH*) attacks the glycosidic linkage in chitosan to produce oligomer chitosan according to the reactions in equation (13) and (14).



3.2. Kinetics degradation of chitosan

Some different rate models have been suggested regarding polymer degradation [19, 22, 23]. However, in this paper, the reaction rate was modelled as a function of molar concentration with a negative order n according to equation (4) [19]. Utilising equation (6) as the solution of the differential equation (4), the reaction order (n) can be determined by performing trial and error of the n value on plotting $[M_t^{1-n} - M_0^{1-n}]$ vs t . The n value of -0.1 showed the best fit of the curve with the kinetic model. The

finding of this study indicated that chitosan degradation followed -0.1 reaction order corresponding to the chitosan concentration.

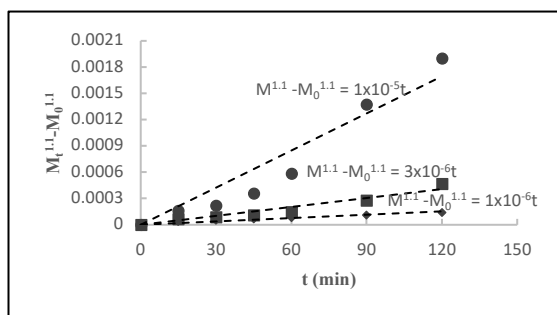


Figure 3. The changes of the molar concentration of chitosan fitted with -0.1 reaction order for different temperatures: (♦) 40°C; (■) 50°C; (●) 60°C.

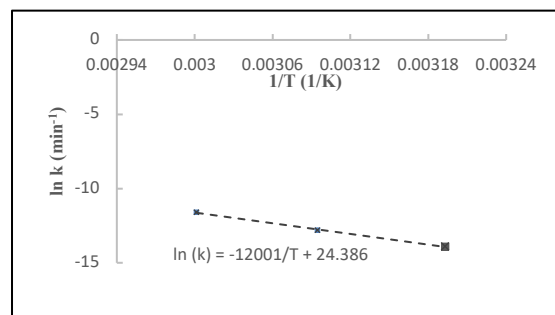


Figure 4. Plot Arrhenius to determine the rate constant

The changing for the molar concentration of chitosan was modelled according to -0.1 reaction order indicated a good fit with a coefficient of correlation $R^2 \geq 0.921$ (figure 3). The value of rate constants (k) for different temperatures: 9.1×10^{-7} (40°C), 2.7×10^{-6} (50°C), 9.1×10^{-6} (60°C) (mol/L) $^{1.1}$ /min. These rate constants are higher than compared to using sonolysis method with additional of Fe(III)/H₂O₂ in acetic acid solution with the value of k is in the range $1.538 - 4.923 \times 10^{-9}$ mol $^{1.7}$ L $^{-1.7}$.min $^{-1}$ for additional H₂O₂ between 0.0 – 1.2 mL [23]. They also reported that the reaction order was -0.7 using the same model used in this paper. This results showed that the chitosan degradation rate increased with reaction temperature indicated by the higher value of k as the temperature increase (figure 4). From the plot between $\ln(k)$ and $1/T$, the value of activation energy (E_a) was obtained to be 99.8 kJ/mol. This activation energy value is considerably higher than that for degradation using electrochemical with electrode Ti/Sb-SnO₂ ($E_a = 43.61$ kJ/mol) and close to the value stated for acetic acid and H₂O₂ ($E_a = 88.5$ kJ/mol) [20, 24].

3.3. FT-IR spectra of degradation products

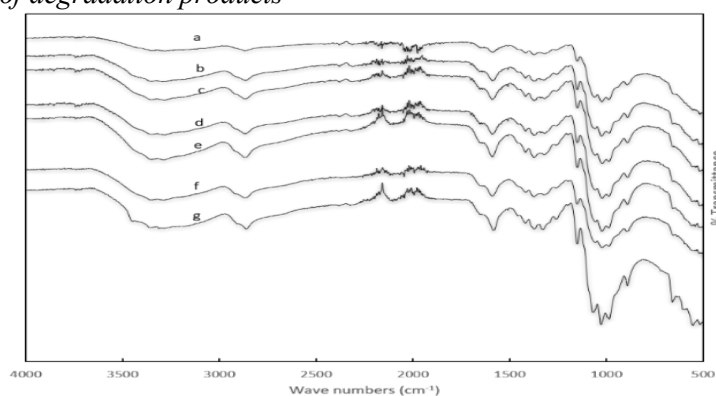


Figure 5. FT-IR spectra of chitosan for degradation at 60°C with reaction time 0 min (a), 15 min (b), 30 min (c), 45 min (d), 60 min (e), 90 min (f), 120 min (g).

The FT-IR spectra of chitosans for different reaction times at a reaction temperature of 60°C is described in figure 5. The peak which appeared at around 3368 cm $^{-1}$ was referred to as the stretching vibration of N-H and O-H [25]. The peaks at 1648 cm $^{-1}$ and 1324 cm $^{-1}$ were assigned as amide I and amide III, respectively [26]. The peaks, as indicated at about 1597, 1156 and 1079 cm $^{-1}$ were amide II, C-O-C, and C-O, respectively [25]. The β -D-(1 \rightarrow 4) glycosidic bond shown at the peak in the range 1158-895 cm $^{-1}$ [27]. The results of FT-IR spectra confirmed that there is no formation of a carboxylic group during the degradation reaction as there was no peak appeared at 1735 cm $^{-1}$ attributed to the

carboxylic group [28]. The results suggest that the chemical structure of initial chitosan and depolymerised chitosan remained the same and there was no significant difference with the increasing of the reaction time of degradation. Hence, it can be concluded that with the utilisation of H₂O₂ in 1% formic acid, there is a primary reaction occurred with the cutting off the β-glycosidic linkage, and no side reaction occurred with the formation of the carboxylic group during the chitosan degradation.

4. Conclusions

Oxidative degradation of chitosan in formic acid solution utilising hydrogen peroxide as an oxidising agent had been done and resulted in lower molecular weight of chitosan. The reaction time and temperature have a significant effect on the degradation reaction and the faster decrease occurring at the first 15 minutes. The degradation followed -0.1 reaction order to the molar concentration of chitosan and the activation energy is 99.8 kJ/mol. The chemical structure of chitosan remained identical during the degradation reaction and indicated only primary reaction occurring with the cutting off the β-glycosidic linkage to produce lower molecular weight of chitosan.

Acknowledgments

Mr Edy Purwanto would like to thank the Indonesia Endowment Fund for Education (LPDP), Ministry of Finance; collaborated with the Directorate General of Higher Education (DIKTI), Ministry of Research, Technology and Higher Education, the Republic of Indonesia for financial support.

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