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ORIGINAL PAPER

Kinetic study of chitosan degradation by an electrochemical process

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Abstract The kinetics of chitosan degradation by an electrochemical process was studied in this work. The order of degradation reaction was determined according to the dependence of degradation rate constant on initial chitosan concentration. For electrochemical degradation of chitosan, the apparent rate constant varied inversely with initial chitosan concentration, suggesting that the degradation reaction was zeroth-order in chitosan concentration. The influence of experimental conditions on the degradation rate constant was also investigated in detail. The degradation rate constant increased with current density, acetic acid concentration, and temperature. The influence of temperature on the degradation rate was modeled using the Arrhenius equation and the activation energy was determined to be 14.16 kJ/mol under the experimental conditions examined. The variation of sodium acetate concentrations had a negligible influence on degradation rate of chitosan.

Keywords Chitosan · Electrochemical · Degradation · Kinetics

Introduction

Chitosan is a copolymer of 1-4 linked *β*-D-glucosamine and *β*-D-*N*-acetylglucosamine. Chitosan and its derivatives have a special set of interesting properties: nontoxicity, biocompatibility, controllable biodegradability, and nonantigenicity. These properties make chitosan an attractive biopolymer for applications in wide

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areas such as biotechnology, pharmaceuticals, wastewater treatment, cosmetics, agriculture, food science, and textiles [1–3]. However, the applications of chitosan are limited by its high molecular weight and poor solubility. When chitosan is degraded, its solubility and some special biological, chemical and physical functions can be improved [4, 5].

Many methods have been applied to degrade chitosan such as acid hydrolysis [6], oxidative degradation [7, 8], enzymatic method [9], ultrasonic degradation [10], gamma radiation [11], ultraviolet degradation [12, 13], microfluidization [14], and microwave irradiation [15]. We recently communicated a novel, electrochemically based approach in which chitosan was treated by electrolysis using $Ti/TiO_2–RuO_2$ electrode without additions of chemical and biochemical reagents [16]. The results showed that the molar mass of chitosan dramatically decreased with the increase of electrolysis time and current density, and the chemical structure of degraded chitosan was not obviously modified. The main part of this previous short communication [16] focused on demonstration of the feasibility of degradation of chitosan by an electrochemical process, while this work mainly aims to investigate two fundamental aspects which have not yet been investigated in detail: (1) the kinetic behavior of electrochemical degradation of chitosan; (2) the influence of experimental conditions including chitosan concentration, current density, reaction temperature, acetic acid concentration and sodium acetate concentration on the degradation rate constant.

Experimental

Materials

Chitosan, with degree of deacetylation (DD) of 89.8% and viscosity average molecular weight (M_v) of 327 kDa, was purchased from Jinke Biochemical Co. (Zhejiang, China). All other chemicals were of analytical grade. Distilled water was used. $Ti/TiO_2–RuO_2$ electrode (5 cm × 7 cm) was prepared by thermal deposition of TiO_2 and RuO_2 (Ti/Ru molar ratio = 7:3) on Ti plate [17].

Analytical methods

Viscosity of dilute chitosan solutions in 0.1 mol/L sodium acetate–0.2 mol/L acetic acid was measured at 30.0 ± 0.1 °C using a glass capillary Ubbelohde viscometer with a capillary diameter of 0.58 mm. The dilute solutions had relative viscosities, η_{rel}, from about 1.2 to 2.0 to assure good accuracy and linearity of extrapolation to zero concentration. Flow times were measured in triplicate, for each sample, and their average values were used for the calculations. The limiting viscosity number ("intrinsic viscosity"), $[\eta]$, was obtained by double extrapolation to zero concentration of Huggins' and Kraemer equations, respectively

$$\frac{\eta_{\text{sp}}}{C} = [\eta] + k' \cdot [\eta]^2 \cdot C \tag{1}$$

$$\frac{\ln \eta_{\text{rel}}}{C} = [\eta] + k'' \cdot [\eta]^2 \cdot C \tag{2}$$

where η_{rel} and η_{sp} are the (dimensionless) relative and specific viscosities, k' and k'' are the Huggins' and Kraemer's coefficients, respectively, and C is the solution concentration.

The M_{v} of chitosan was calculated using the Marke–Houwink–Sakurada relationship (3):

$$[\eta] = K \cdot M_{\mathrm{v}}^{a} \tag{3}$$

where a and K are constants for the buffer solution and chitosan system.

These constants were calculated using the two following equations, proposed by Kasaai [18] as a model to calculate a and K for chitosan in any solvent–temperature system using viscometric constant data previously reported by several research groups:

$$a = 0.6202 + \left(\frac{0.699x}{0.4806 + x}\right) \tag{4}$$

$$\log K \cdot 10^{-5} = -5.7676a + 5.9232 + 0.003(T - 20) \tag{5}$$

where $x = [\mathrm{DA}/(\mathrm{pH} \cdot \mu)]$, with DA, degree of acetylation of chitosan (DA = 1 − DD), pH of chitosan solution in a solvent with ionic strength of μ, T, temperature of chitosan solution [18].

The potentiometry method was used to determine the DD of original chitosan and its degraded products [19]. Dried chitosan of 0.2 g was accurately weighed and dissolved in 20 mL of 0.1 mol/L hydrochloric acid standard solution, and stirred for 2 h at 25 ± 0.1 °C. The mixture was diluted with 20 mL double distilled water, and then was titrated with 0.1 mol/L caustic soda standard solution. The degree of deacetylation (DD) was calculated as follows:

$$w = \frac{0.016(c_1V_1 - c_2V_2)}{G(1 - W)} \times 100\% \tag{6}$$

where c_1 is the concentration of HCl (mol/L); c_2, the concentration of NaOH (mol/L); V_1, the volume of HCl (mL); V_2, the volume of NaOH (mL); G, the sample weight (g); W, the water percentage of sample (%) and 0.016 is the weight of NH_2 equal to 1 mL of 1 mol/L HCl (g). Then:

$$\mathrm{DD} = \frac{w}{9.94\%} \times 100\% \tag{7}$$

where 9.94% is the theoretical NH_2 percentage of chitosan.

Electrolysis of chitosan

Chitosan and sodium acetate were completely dissolved in acetic acid solution firstly. The electrolysis of 250 mL chitosan solution was performed in a reactor (diameter 7 cm × height 12 cm) with Ti/TiO_2–RuO_2 as anode, stainless steel as cathode (5 cm × 7 cm) and the spacing of 20 mm between two electrodes. A DC potentiostat was used as the power supply for the electrolysis. During the electrochemical treatment the solution was stirred constantly and the temperature was controlled continuously with a thermostat. After degradation, the resulting solution was neutralized with 2 mol/L NaOH solution to pH 8–9, added ethanol (twice volume of the solution), filtered off, washed thoroughly with ethanol, and the products were collected after drying overnight in a vacuum at 60 °C.

Theoretical model

In this study, the electrochemical degradation of chitosan might be zero-, first-, or second-order degradation reaction. In order to investigate the kinetic behavior, *n*th-order kinetic equation was used to describe the electrochemical degradation of chitosan.

The *n*th-order kinetic is given by [20]:

$$\frac{\mathrm{d}L}{\mathrm{d}t} = -kL^n \tag{8}$$

where L is the total number of degradable linkages, t is the reaction time, k is the rate constant, and n is the order of reaction.

When $n = 1$, the degradation reaction is first-order process and its kinetic is given by

$$\frac{\mathrm{d}L}{\mathrm{d}t} = -kL \tag{9}$$

L can be substituted to $N(M/m - 1)$ where N is the total number of polymer chains, M is the average molecular weight, and m is the molecular weight of the repeating unit. Assuming that $M/m \gg 1$, Eq. 9 can be obtained as follows:

$$\frac{1}{M_t} = \frac{1}{M_0} + \frac{kt}{m} \tag{10}$$

where M_0 and M_t are average molecular weight of polymer at time zero and time t, respectively.

When $n \neq 1$, the following result is obtained by integrating Eq. 8 and making appropriate substitutions:

$$\left[\left(1 - \frac{m}{M}\right)^{1-n} - \left(1 - \frac{m}{M_0}\right)^{1-n}\right] = \frac{k(n-1)}{N_0^{1-n}}t \tag{11}$$

Thus, for zeroth order, $n = 0$

$$\frac{1}{M_t} = \frac{1}{M_0} + \left(\frac{k}{mN_0}\right)t \tag{12}$$

And, for second order, $n = 2$

$$\frac{1}{M_t} \cong \frac{1}{M_0} + \left(\frac{kN_0}{m}\right)t \tag{13}$$

Here, the approximation made for the second-order case is similar to that made for the first-order analysis and is valid as long as the degradation is not carried out to the extent that only very small polymer molecules remain.

In previous studies, the inverse relation between molecular weight and reaction time was traditionally considered as evidence for first-order kinetics [20–22]. However, Eqs. 10, 12, and 13 reveal that, regardless of the order of the reaction, the same functional dependence of molecular weight on reaction time is predicted for zero-, first-, and second-order degradation reaction. Therefore, this linear relationship between $1/M_v$ and t is not enough evidence to determine the true reaction order [20].

Instead, the true reaction order can be determined by examining the effect of initial polymer concentration (c_0) on the apparent rate constant, S (slope of $1/M$ vs. reaction time plot). According to Eqs. 10, 12, and 13, the equation of S can be derived as follows [20]:

$$S = \frac{kN_0^{n-1}}{m} \tag{14}$$

Substituting

$$c_0 = \frac{N_0 V}{N_{av} m} \tag{15}$$

where N_{av} is the Avogadro number and V is the sample volume, then

$$S \propto c_0^{n-1} \tag{16}$$

Thus, for a zeroth-order reaction ($n = 0$), S is proportional to ($1/c_0$); for a first-order reaction ($n = 1$), S is independent of c_0; for a second-order reaction ($n = 2$), S is proportional to c_0. It is, therefore, critical that the relationship between S and c_0 is checked before any conclusions on reaction kinetics are made.

Results and discussions

Determination of reaction order

In order to determine the reaction order of electrochemical degradation of chitosan, we first plotted $1/M_v$ as a function of reaction time at different chitosan concentrations under conditions of 0.2 mol/L acetic acid, 0.3 mol/L sodium acetate, 120 mA/cm^2, and 60 °C (Fig. 1). As shown in Fig. 1, the inverse M_v changed linearly with reaction time. In previous studies, this linear relationship between $1/M_v$ and t was traditionally considered as evidence for first-order kinetics [20–22]. Our above theoretical analysis reveals that this linear relationship is expected regardless of the reaction order and the true order can be determined according to the dependence of degradation rate constant on initial polymer concentration.

For determining the relationship of S and c_0, the S value was obtained from the slope of the straight line in Fig. 1 and then the plot of S as a function of c_0 was shown in Fig. 2. As can be seen from Fig. 2, S is proportional to ($1/c_0$) in the range of 0.25–0.45% (w/v) chitosan concentrations. According to the above theoretical analysis, this relationship of S and c_0 confirms that the electrochemical degradation is zeroth-order in chitosan concentration. A possible explanation of the observed

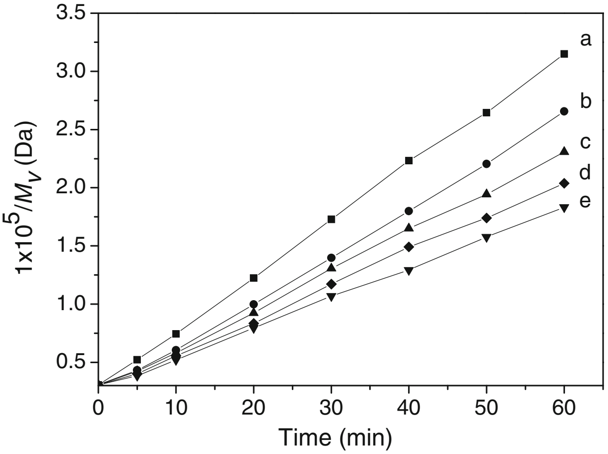

Fig. 1 $1/M_v$ of chitosan versus treatment time at different initial chitosan concentrations of 0.25% (w/v) (*a*), 0.3% (w/v) (*b*), 0.35% (w/v) (*c*), 0.4% (w/v) (*d*), and 0.45% (w/v) (*e*)

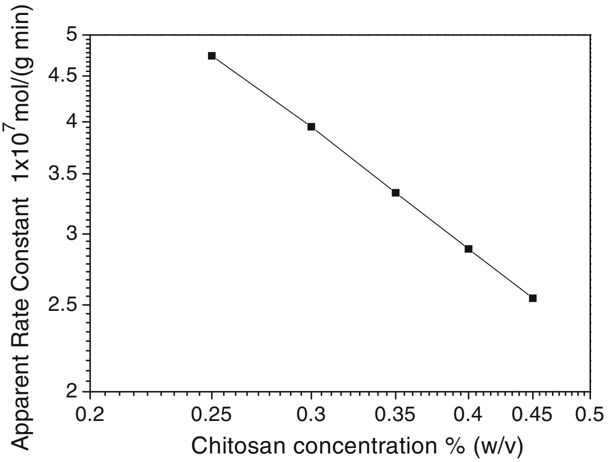

Fig. 2 Apparent rate constant as a function of initial chitosan concentration

zeroth-order degradation reaction presents as follows. In this study, there are sufficient chitosan molecules for the electrochemical degradation at 0.25–0.45% (w/v) chitosan concentrations. Thus, the increase of chitosan concentration did not increase the number of degraded bonds of chitosan molecules, implying that the electrochemical degradation is zeroth-order in chitosan concentration under the experimental conditions examined. Similar kinetic behavior was observed for enzymatic catalysis of simple substrates at high substrate/enzyme ratios and was termed "substrate saturation" [20, 23].

Effect of current density on degradation rate constant

Current density is an important factor affecting the electrolysis kinetics. Thus, the electrolysis experiments at different current densities of 40, 80, 120 and 160 mA/cm^2 were conducted under conditions of 0.3% (w/v) chitosan, 0.2 mol/L acetic acid, 0.3 mol/L sodium acetate and 60 °C. The variation of $1/M_v$ of chitosan with reaction time at different current densities is shown in Fig. 3. The S for each experiment was calculated from the slopes of best fit lines in Fig. 3 and then summarized in Table 1. As shown in Table 1, significant differences between the S values obtained at different current densities. When the current densities varied from 40 to 160 mA/cm^2, the S increased from 1.13×10^{-7} to 7.47×10^{-7} mol/(g min), demonstrating that the increase in current density would result in an increase in S values. A similar effect of current density on an electrochemical degradation was also observed in other studies [24–26].

Effect of temperature on degradation rate constant

Like other electrochemical reactions, temperature could have a significant effect on the rate of degradation. Therefore, the electrolysis experiments at different reaction temperatures of 30, 40, 50 and 60 °C were conducted under conditions of 0.3% (w/v) chitosan, 0.2 mol/L acetic acid, 0.3 mol/L sodium acetate and 120 mA/cm^2. The variation of $1/M_v$ of chitosan with treatment time at different reaction temperatures is shown in Fig. 4. The S for each experiment was calculated from the slopes of best fit lines in Fig. 4 and then summarized in Table 2. As shown in Table 2, when the reaction temperatures were varied from 30 to 60 °C, the S increased from 2.39×10^{-7} to 3.95×10^{-7} mol/(g min). It indicated that the increase of reaction temperature had a positive effect on degradation rate of

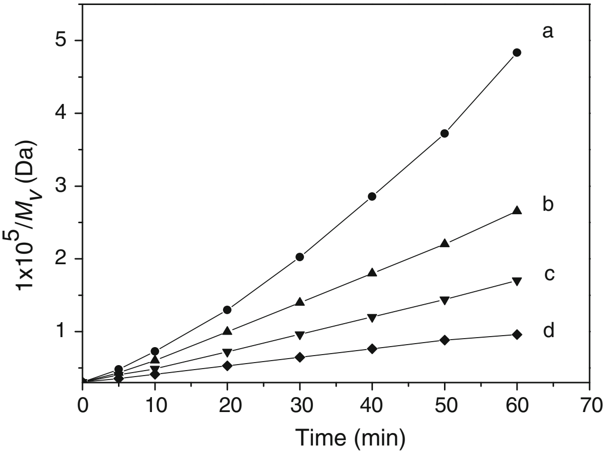

Fig. 3 $1/M_v$ of chitosan versus treatment time at different current densities of 160 mA/cm^2 (*a*), 120 mA/cm^2 (*b*), 80 mA/cm^2 (*c*), and 40 mA/cm^2 (*d*)

Table 1 Apparent rate constants (S) for electrochemical degradation of chitosan at different current densities

Current density (mA/cm^2)	S (mol/(g.min))
40	1.13×10^{-7}
80	2.34×10^{-7}
120	3.95×10^{-7}
160	7.47×10^{-7}

Experimental conditions: 0.3% (w/v) chitosan, 0.2 mol/L acetic acid, 0.3 mol/L sodium acetate, and 60 °C

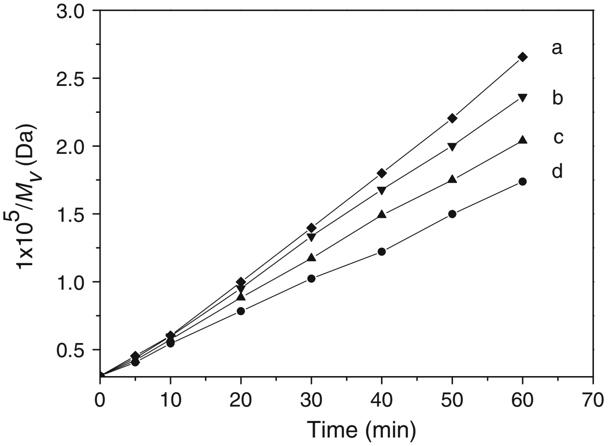

Fig. 4 $1/M_v$ of chitosan versus treatment time at different reaction temperatures of 60 °C (*a*), 50 °C (*b*), 40 °C (*c*), and 30 °C (*d*)

Table 2 Apparent rate constants (S) for electrochemical degradation of chitosan at different reaction temperatures[a]

Reaction temperature (°C)	S (mol/(g min))
30	2.39×10^{-7}
40	2.89×10^{-7}
50	3.43×10^{-7}
60	3.95×10^{-7}

[a] Experimental conditions: 0.3% (w/v) chitosan, 0.2 mol/L acetic acid, 0.3 mol/L sodium acetate, and 120 mA/cm^2

chitosan. Hence, the electrochemical degradation of chitosan was accelerated synchronously with temperature increase.

The influence of temperature on the rate of degradation was modeled using the Arrhenius equation [21, 26]:

$$\ln S = \ln A - \frac{E_a}{RT} \tag{17}$$

where A is the frequency factor, R is the universal gas constant, 8.314 J/(K mol), and T is the temperature in Kelvin. The apparent rate constant for the electrolysis of 0.3% (w/v) chitosan in 0.2 mol/L acetic acid–0.3 mol/L sodium acetate solution at

120 mA/cm^2 was plotted in the Arrhenius plot (Fig. 5). From the data shown in Fig. 5, the activation energy (E_a) for the degradation reaction was determined to be 14.16 kJ/mol which is significantly lower than that for H_2O_2 degradation ($E_a = 88.5$ kJ/mol) or nitrous acid hydrolysis of chitosan ($E_a = 87.1$ kJ/mol) [21, 27].

Effect of sodium acetate concentration on degradation rate constant

The addition of an electrolyte in solution during electrolysis can influence the treatment, since it modifies the conductivity of the solution and facilitates the passage of the electrical current. Thus, the investigation of influence of sodium acetate (used as supporting electrolyte) concentration on the degradation rate constant of chitosan was carried out by electrolysis of 0.3% (w/v) chitosan under conditions of 0.2 mol/L acetic acid and 60 °C. The sodium acetate concentrations varied from 0.1 to 0.6 mol/L and the current density of 120 mA/cm^2 was held constant during the electrochemical treatment. As shown in Fig. 6, when the sodium acetate concentrations varied from 0.1 to 0.2 mol/L, the S increased from 3.56×10^{-7} to 3.89×10^{-7} mol/(g min). Whereas, when the sodium acetate concentrations varied from 0.2 to 0.6 mol/L, the S was statistically the same. Therefore, the variation of sodium acetate (supporting electrolyte) concentrations had a negligible influence on degradation rate of chitosan under constant current density. A similar effect of supporting electrolyte concentration on an electrochemical degradation was also observed in other studies [26, 28, 29]. Moreover, it can be seen Fig. 6 that the voltage decreased from 17.8 to 7.2 V as the sodium acetate concentrations varied from 0.05 to 0.6 mol/L, indicating that increasing sodium acetate concentration decreased the voltage during the electrochemical treatment.

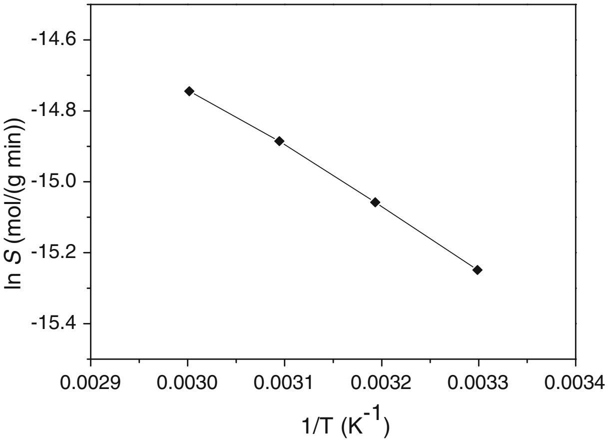

Fig. 5 Arrhenius plot of the degradation of 0.3% (w/v) chitosan in 0.2 mol/L acetic acid–0.3 mol/L sodium acetate solution at 120 mA/cm^2

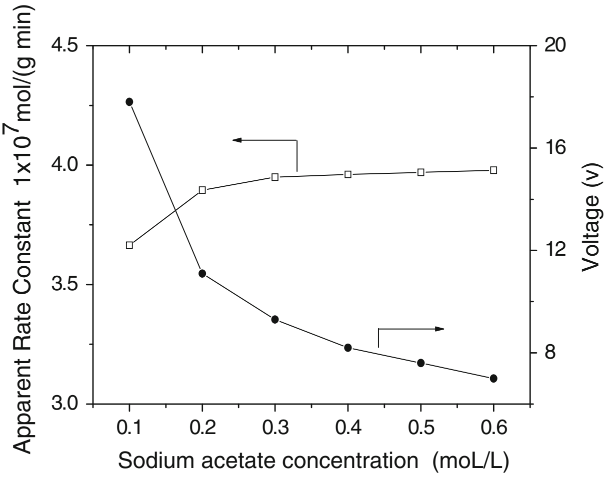

Fig. 6 Effect of sodium acetate concentration on apparent rate constant and voltage under conditions of 0.3% (w/v) chitosan, 0.2 mol/L acetic acid, 60 °C, 120 mA/cm^2

Effect of acetic acid concentration on degradation rate constant

Investigation of the effect of acetic acid concentration on the degradation rate constant of chitosan was carried out by electrolysis of 0.3% (w/v) chitosan under conditions of 0.3 mol/L sodium acetate, 120 mA/cm^2 and 60 °C. The acetic acid concentrations varied from 0.05 to 0.6 mol/L during the electrochemical treatment. As shown in Fig. 7, when the acetic acid concentrations varied from 0.05 to 0.6 mol/L, the S increased from 2.54×10^{-7} to 5.84×10^{-7} mol/(g min). It indicated that higher acetic acid concentration resulted in a better degradation of

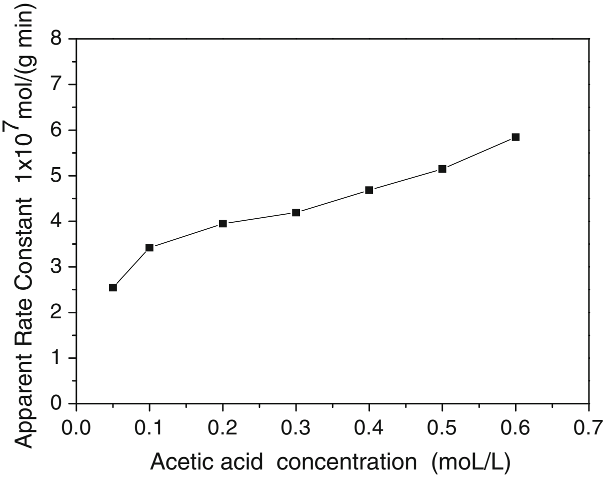

Fig. 7 Effect of acetic acid concentration on apparent rate constant under conditions of 0.3% (w/v) chitosan, 0.3 mol/L sodium acetate, 60 °C, 120 mA/cm^2

chitosan. A similar effect of acid concentration on an electrochemical degradation was also observed in other studies [25, 30, 31]. Moreover, these *S* values for the electrochemical degradation of chitosan varied from 1.13×10^{-7} to 7.47×10^{-7} mol/(g min) under the experimental conditions examined. They are less than those for H_2O_2 degradation of chitosan (2.60×10^{-6}–4.40×10^{-6} mol/(g min)) calculated from the data of Chang et al. [21] and those for nitrous acid hydrolysis of chitosan (4.18×10^{-4}–4.04×10^{-5} mol/(g min)) calculated from the data of Allan et al. [27], but higher than those for ultrasonic degradation of chitosan ($\sim 0.58 \times 10^{-7}$ mol/(g min)) calculated from the data of Chen et al. [32].

Conclusions

In this work, the degradation rate constant was inverse dependent of initial chitosan concentrations in the range of 0.25–0.45% (w/v) which confirmed that the electrochemical degradation is zeroth-order in chitosan concentration. During the electrochemical treatment, the experimental conditions (current density, reaction temperature and acetic acid concentration) affected the degradation rate of chitosan. The degradation rate constant increased with current density, acetic acid concentration and temperature. The influence of temperature on the rate of degradation was modeled using the Arrhenius equation and the activation energy was determined to be 14.16 kJ/mol under the experimental conditions examined. The variation of sodium acetate concentrations had a negligible influence on degradation rate of chitosan.

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