

Demineralization Kinetics of Chitin Isolation from Shrimp Shell Waste

Ahmad Fadli, Drastinawati, Komalasari, Yesi Afriani and Subkhan Maulana

Department of Chemical Engineering, Faculty of Engineering, Riau University
Jl. H.R Subrantas No. 12,5 Km, Pekanbaru 28293, Indonesia

Febli Huda

Department of Mechanical Engineering, Faculty of Engineering, Riau University
Jl. H.R Subrantas No. 12,5 Km, Pekanbaru 28293, Indonesia

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Abstract

Chitin is a biopolymer material which widely used in any field especially for absorbent and dietary drugs. Chitin was isolated by deproteination and demineralization of shrimp shell waste. The aim of this research is determining kinetics of demineralization of chitin isolation. At first, NaOH at concentration 2,5%; shrimp shell; and HCl concentration ranges 0,2 – 1,8 N mixed at room temperature in beaker glass stirred at 50 till 200 rpm. Samples were took off the beaker glass every 5 – 20 minutes for 20 ml. The sample then washed until the pH was neutral. Furthermore, the chitin filtered and destructed by H₂SO₄ and HNO₃ to determining calcium carbonate content by titration of complexometry. The results showed that the kinetic was following pseudo second order equation. The reaction rate increased along with the increasing of HCl concentration. The reaction rate in addition of HCl concentration from 0.2 - 1.8 N and stirring rate of 150 rpm increased from 0.003 to 0.404 min⁻¹. The effect of stirring rate toward reaction rate was undefined by kinetic homogenous reaction. The range of reaction rate in range 0.00167 up to 0.394 min⁻¹

1. Introduction

Sources of chitin are estimated to be as abundant as those for cellulose with a

yearly production of approximately 10^{10} - 10^{12} metric ton [11]. The shrimps production caused 60-70% of total mass become a waste that cause many environmental problems. Shrimp shell usually consist of head, skin, and tail which consists mainly of 30–40% protein, 30–50% calcium carbonate and 15-30% chitin which 80% chitin can be converted into chitosan [7]. Small portion of the waste is used for animal feed, protein hydrolyzate, silage, raw materials of shrimp paste, petis and shrimp crackers that have low selling value, but in some country has been processed into chitin and other derivates for higher selling value.

Chitin and derivates are usually applied in various fields such as textile, photography, agricultures, cosmetics, biotechnology, water treatment, waste treatment, and biomedical industries [3]. Some applications require specific architectures, and the effectiveness of the polymers for these applications was shown to depend on the molecular weight distribution and the degree of deacetylation (DA) [6]. Cost-effective, fast, and easily controlled industrial process for producing chitins of high molecular weight and DA still remains to be developed [8].

According to Percot *et al* [8] the optimum deproteination process obtained with 1 M NaOH within 24 h at temperature close to 70 °C. The optimum demineralization also obtained within 15 min at ambient temperature in an excess of HCl 0.25 M (with a solid-to-liquid ratio of about 1/40 (w/v)). The results showed that content of calcium in shrimp shells is below 0.01% and the DA is almost 95%. Chang and Tsai [1] was reported the kinetics of chitin demineralization reaction could be review by the homogeneous reaction kinetic equation. The kinetics equation of the reaction is obtained by the quasi-order kinetics equation. The optimum results were obtained under HCl 1.7 N, and a ratio of 1: 9 ml/g with a range of k values between 0.0002 - 0.017 min⁻¹.

This study was reported that chitin could be isolated from shrimp shell by deproteination and demineralization. We had successfully obtaining chitin from shrimp shell waste by using NaOH 3.5% and HCl 12 N. The effect of HCl concentration and stirring rate on the result were investigated and reported as well.

2. Experimental

Deproteination has done with 3.5% NaOH solution (Merck, German) which introduced into a conical flask reacted with the powder of shrimp shell solid-to-liquid ratio was 1:10 (w/v) at 65 °C for 2 h and stirred using a magnetic stirrer (Dragon Lab, China) at 150 rpm of a stirring rate. The results of deproteination then quickly filtered and washed with deionized water until neutrality as determined using a pH meter. Furthermore, the precipitate dried in an oven at 100 °C for 4 hours. The deproteinized shell was then soaked in 0.2 solution of HCl at room temperature for 1 hour with stirring rate at 50 rpm. The demineralized samples

were dried and weighed. This was repeated in turns for other HCl concentrations 0.6; 1; 1.4; and 1.8 N. The entire demineralization procedure was then repeated for the stirring rate 50; 150; and 200 rpm.

The concentration of calcium, in the raw as well as demineralized solid materials, was determined using complexometric titration.

3. Result and Discussion

3.1 Reactant Concentration and Stirring Rate Effects on Calcium Conversion

Figure 1 shows calcium conversion at vary concentration and 250 rpm stirring rate, which the highest conversion reached 98%. The demineralization process using HCl with a concentration of 0.2; 0.6; 1; 1.4 obtained the conversion of calcium carbonates by 32%; 93%; 96%; 97%; and 98%, these results showed that the conversion of calcium carbonate increases along with the increasing of HCl concentration. The volume of HCl decreased along with time of reaction, and the conversion is inversely proportional to the addition of HCl. Also with time reaction increased, the conversion did too.

Figure 1 show linearly results between conversion changed with HCl concentration. Synowiecki and Al-Khateeb [10] explained that the rate of reaction is a reduction of reagent concentration the increasing of product concentration in time union.

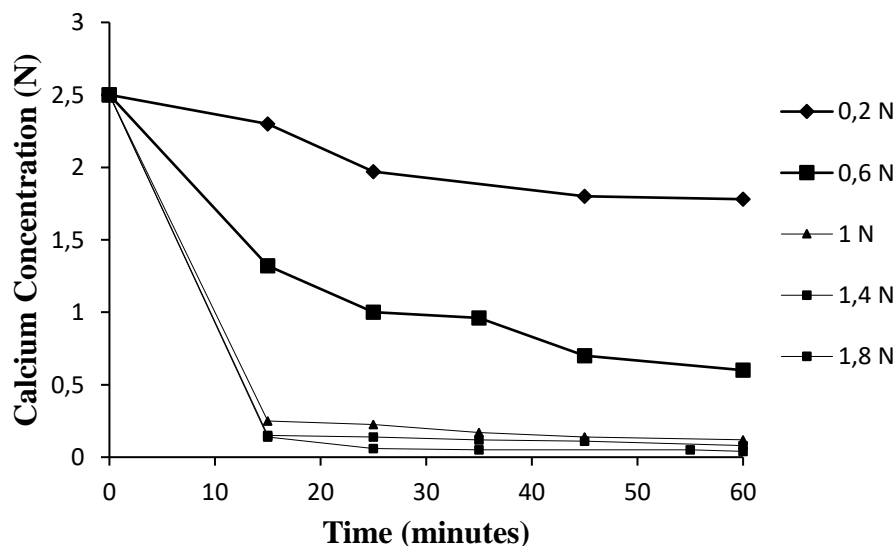


Figure 1. Conversion of CaCO_3 at different HCl concentration

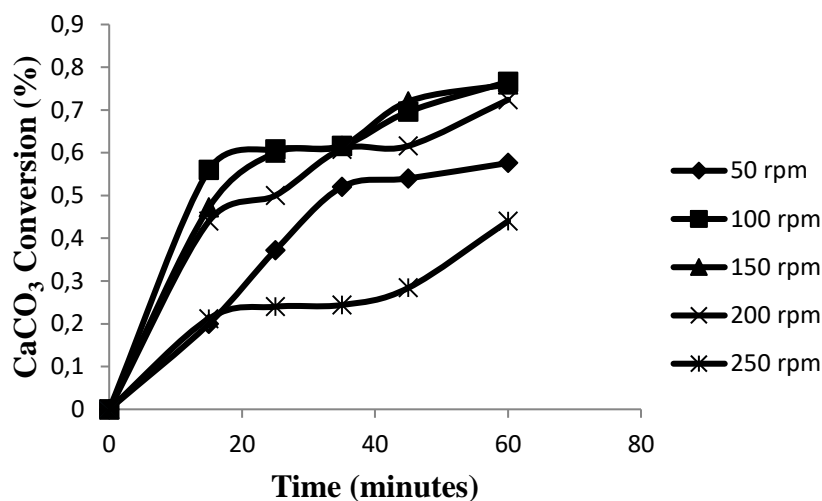


Figure 2. Conversion of CaCO₃ at different stirring rate

The higher HCl concentration the more HCl molecular would have reacted with material such calcium carbonate molecular to produce an aqueous solution (CaCl₂). Time reaction is another important factor to reduce the calcium concentration because the longer time reaction makes the more HCl molecules diffuse into chitin molecules.

Another parameter we used is stirring rate which the results completely was not significant factor for demineralization due to the result obtained. Figure 2 show the conversion increasing along the stirring time, the longer stirring time was held the higher conversion percentage obtained. Based on this study the variance of stirring rate does not significantly affected the demineralization of chitin isolation. However, the stirring rate still given an influence aspect due to the conversion percentage obtained, in the first 15 minutes sampling test, at the stirring rate of 50 and 250 rpm the conversion of calcium carbonates are 94% and 96%.

Non-linear results gained from the effect of stirring rate caused by CO₂ gas formed from the reaction between calcium carbonate and HCl cause solids come up to the reactor walls so that stirring was uneven. So at high speed stirring the solid which powder of deproteination shrimp shell will be more attached. As explained before there were not much effect of stirring rate towards conversion. The data of the result showed in the table below.

Figure 2 shows that stirring rate parameter for 50 to 250 does not have significantly differences. According to Levenspiel [4] theoretical explanation that is reaction rate just have a big impact with both of concentration-dependent term and temperature-dependent term. These experimental results showed righteousness of that theory.

3.1 Determination of Reaction Order (n)

Determining of reaction order used by two methods: differential and integral method [2]. The method used in this research was integral method. The data obtained

from the integral method shows the order of reaction on chitin demineralization in each concentration and agitation rate were more likely to be second-order. Demineralization reaction shows as follow

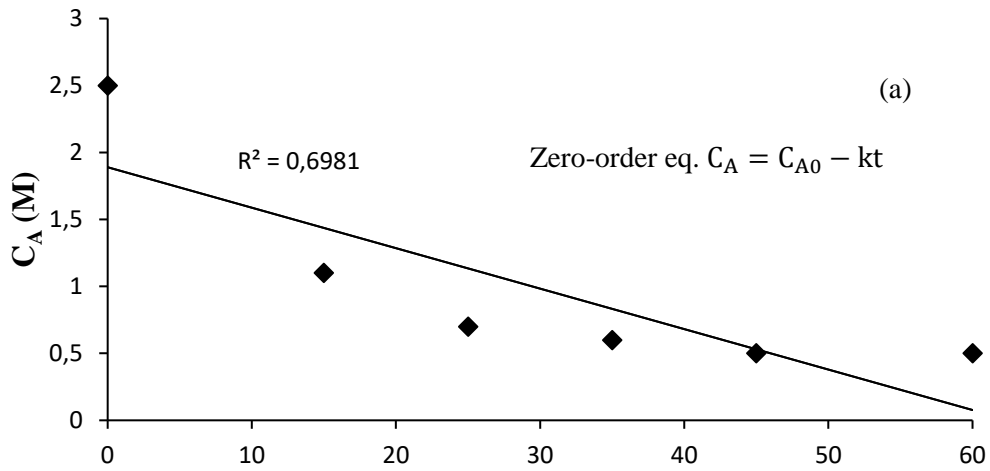
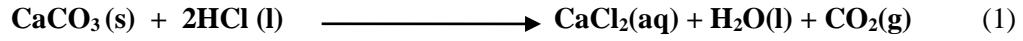


Figure 3. Kinetic-order at 0,6 N HCl and 150 rpm for zero-order

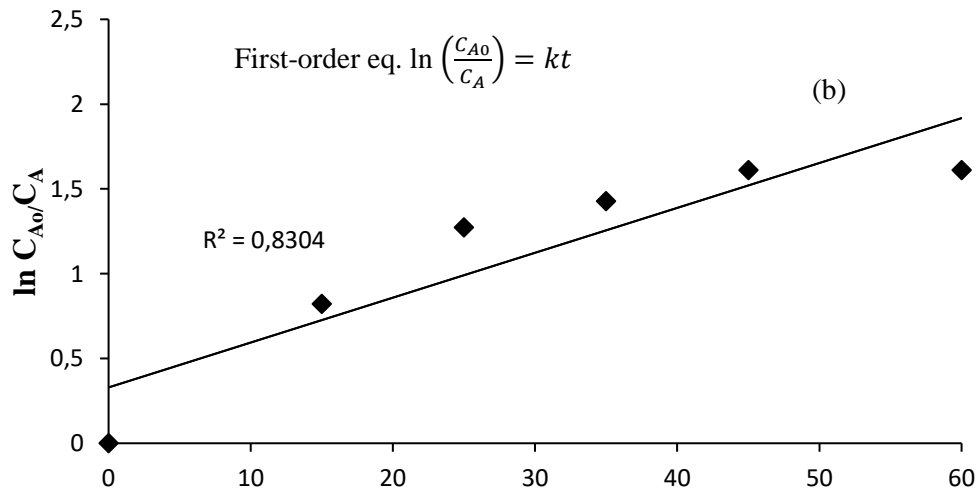


Figure 4. Kinetic-order at 0,6 N HCl and 150 rpm for first-order

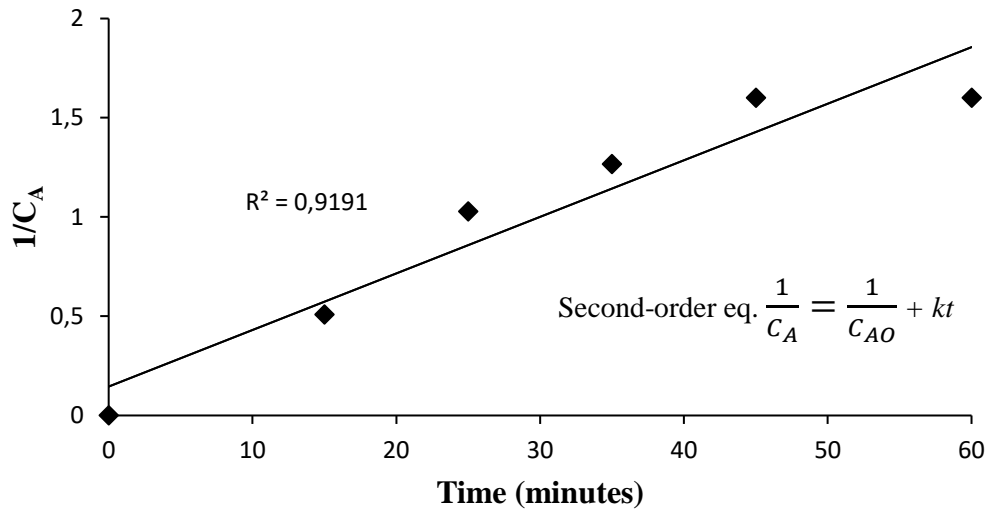


Figure 5. Kinetic-order at 0,6 N HCl and 150 rpm for second-order

$$-r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -kC_A^m C_B^n \quad (3)$$

If the amount of HCl used in excess volume, so it assumed that HCl concentration does not change during the process, thus the rate of demineralization reaction is only influenced by the concentration of calcium carbonate.

$$-r = -\frac{dC_A}{dt} = -kC_A^m \quad (4)$$

Where k' is $k [HCl]^n$ and we want to determine the n (reaction order) value. Demineralization in this study was observed at zero-order, first-order and second order kinetics.

a. The zero-order ($m = 0$) is a reaction that occurs when the magnitude of the reaction rate is not affected by the reactant concentration. The zero-order reaction equation is shown in the following equation:

$$\left(\frac{dC_A}{dt}\right) = -k \quad (5)$$

and after integrating we have

$$C_A = C_{A0} - kt \quad (6)$$

Once integrated and applied to the graph when the process occurs at time (t) versus the magnitude of the CA concentration. Zero-order is shown in Figure 3.

b. The first-order ($m = 1$) is a reaction which rate of reaction directly proportional to the concentration of the reactants.

$$r = -\frac{dC_A}{dt} = k'C_A \quad (7)$$

$$\ln \frac{C_{A0}}{C_A} = kt \quad (8)$$

Once integrated and applied to the graph it was shown by Figure 4.

c. The second order ($m = 2$) is a reaction which speed is proportional to the square of the concentration of one of its reactants or by the product of the concentration of the two reactants. For the second order reaction equation, the equation becomes as follows.

$$r = -\frac{dC_A}{dt} = k' C_A^2 \quad (9)$$

$$\frac{1}{C_A} = -\frac{1}{C_{A0}} + kt \quad (10)$$

Once integrated and applied to the graph it was shown by Figure 5.

Based on the values of percentage error it was indicate small difference of the reaction rate constant (k) between theoretical and data were obtained at second-order kinetics. The highest and lowest percentage error showed respectively by second-order and zero-order with 75.48% and 10.13%. According to Levenspiel [4] the smaller percentage error means smaller deviance of graphical. It also showed second-order kinetics deviance standart were smaller and more relevant to theoretical and experimental results.

3.2 Effect of Reactant Concentration and Stirring rate on Reaction Rate Constant (k)

Reactant concentration is one of the influence factors that can extremely affecting the rate of reactions. The greater concentration of reactant will cause significant conversion increase and faster reaction.

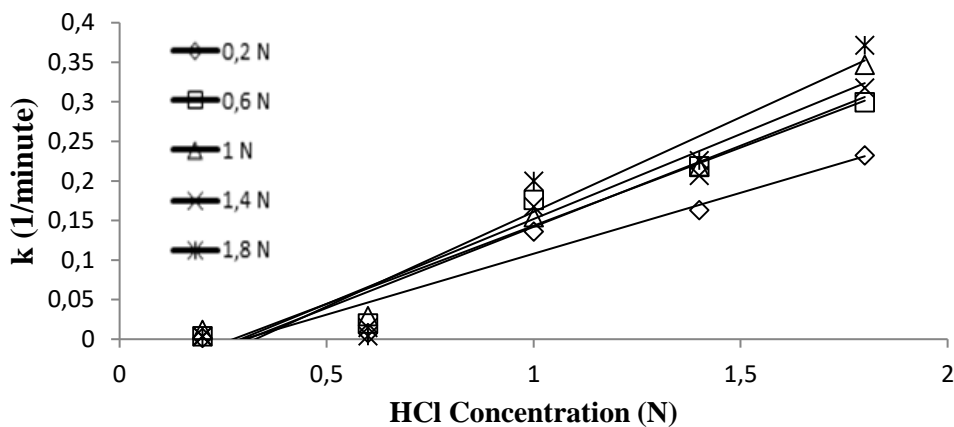


Figure 6. The relationship between HCl concentration and reaction rate constant

The increasing of concentration reactant causes the reaction move to shift at the right side and will increasing the collision frequency thus increasing the rate constant of reactions. *Le Chatelier* principles declared there were changing inside a system that was in the equilibrium condition, it will shift equilibrium in the direction which could restore to initial state. Theoretically a substance can react with other substance if the particles collide with each other, and then the collision will produced energy to begin the reaction. According to Arrhenius formula The way to speed up the collision process is stirring [4].

Figure 6 shows the increasing of k value along the increasing of HCl concentration and stirring rate. The value of k at 0.2; 0.6; 1; 1.4; and 1.8 N at 50 rpm are 0.0016/minute; 0.0077/minute; 0.136/minute; 0.163/minute and 0.23/minute. The lowest k value just only reach 0.0016/minute when the addition of 0.2 N while the highest k value reach number of 0.23/minute obtained when the addition 1.8 N of HCl. Figure above also shows that the effect of stirring rate on reaction rate constant. The addition of 1.8 N HCl at 50; 100; 150; 200; and 250 rpm obtained k values are 0.23/minute; 0.299/minute; 0.22/minute; 0.20/minute; and 0.22/minute. These fluctuating data caused by CO_2 gas formed from the reaction between calcium carbonates and HCl that formed solid to come up into the reactor walls which causing the stirring was uneven.

3.3 FT-IR Analyzing

FT-IR analysis aims to identify the clusters that form a compound so that the known compounds can be known. Figure below show the graphical analyzing of chitin, generally interpretation of chitin spectrum of FT-IR i.e the absorbance band $3649\text{-}3200\text{ cm}^{-1}$ show the vibration of OH; NH asymmetric groups in the 3267 cm^{-1} ; $3125.5\text{-}2891\text{ cm}^{-1}$ shows CH-aliphatic vibration; 1310 cm^{-1} showing CN vibration; 1654 cm^{-1} showing a vibration C = O and the absorption of 1560 cm^{-1} indicating vibration of NH Amide II (Liu *et al*, 2012). FT-IR Analyzed showed a results obtained OH group in the absorption of 3440 cm^{-1} ; the $\alpha\text{-CH}$ vibration in the absorption of 28290 cm^{-1} and also seen uptake at 1300 cm^{-1} as CH-buckling; and C = O vibration as the amide group at 1666 cm^{-1} .

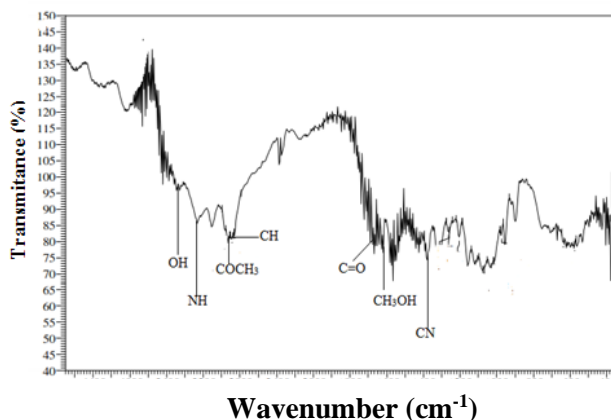


Figure 7. The Result of FT-IR Analyze of Chitin Isolation

Based on functional group analysis showed that the chitin isolation which obtained from shrimp shell waste contained chitin-forming groups and the uptake pattern was close to chitins.

3.4 Comparison with Previous Research

The related research homogenous demineralization kinetics had done by Chang (1997) with raw material type *Solonecera Melantho* or called red shrimp.

Table 2. The Comparison this study with previous research

Information	Chang (1997)	This Study (2017)
Raw Material	Solonecera Melantho	Metapenaeus sp.
Reaction Order	Pseudo first order	Pseudo second order
k	Range 0.00156 - 0.017 min ⁻¹	Range 0.00255 - 0.4 min ⁻¹
Raw material Composition	Protein: 18.01% , Fat: 0.8% , Calcium: 16.1% , Chitin : 17.4%	Protein: 24.03% , Fat: 5.14% , Calcium: 16.6% , Chitin : 18.7%

4. Conclusion

Based on results of this study, it was found a great effects of HCl concentration to calcium conversion. Higher conversion was obtained by added 1.8 N HCl which increase conversion up to 98%. The opposite results were showed from stirring rate as a parameter which nonlinear data obtained caused by most of physical factor. Stirring rate does not significantly affected the conversion yield, for the same time and HCl concentration. The reaction kinetics obtained follow the pseudo-second-order kinetics equation.

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