Simple Kinetic Model for Extraction of Glucomannan from Porang (*Amorphophallus muelleri* Blume)

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Abstract. Glucomannan can be extracted from the corms of porang (*Amorphophallus muelleri* Blume) by several processing methods. The wet process includes water extraction simultaneous with enzymatic hydrolysis for degrading starch in the porang flour. The experiment carried out by heating phosphate buffer solution to the desired temperature and then adding an amount of amylase. The porang flour was then added into the solution and this time was considered as the starting time of extraction and hydrolysis. In this paper only the extraction of the glucomannan was reported. The influence of temperature on the extraction was discussed and two models were used to analyze data. The increase of temperature increased the extraction rate, reduced the extraction time and gived higher final concentration. The results showed that both simple mass transfer model and rate law model demonstrated good agreement between experimental and calculated data. The simple mass transfer model correlated the experimental and calculated data with SSE of 8.53E-07 and 2.18E-06 for temperature 70 ^{o}C and 80 ^{o}C respectively and the rate law model correlated the experimental and calculated data with SSE of 8.06E-07 and 9.3E-06 for temperature 70 ^{o}C and 80 ^{o}C respectively.

Keywords: Extraction, glucomannan, porang flour, simple mass transfer model, rate law model

1. Introduction

The corms of Amorphophallus sp. have high economic value due to its glucomannan content. It is a perennial herb native to South East Asia. Porang (*Amorphophallus muelleri* Blume) is species that cultivated in Jawa, Indonesia. Glucomannan have been used since ancient time as food and medicine in China and Japan. Used in food industry as a gelling agent, thickener, film former and emulsifier, glucomannan in USA have approved by FDA as GRAS (Generally Recognized as Save) and also authorized in Europe by given an E425 agreement number [1]. Glucomnnan is also widely used in pharmaceutical, cosmetics, and fine chemical areas.

Glucomannan is composed of D-glucose and D-mannose monomers with β-1,4 linkages. The ratio of glucose and mannose is around 1:1,6 [2]. It was reported by Katsuraya et al. [2] that branching point was located at the C-3 of the glucosyl unit in the main backbone, with degree of brancing was around 8%. Some acetyl units were attached in the C-6 position in every 9 to 19 sugar residues [2].

Glucomannan have unique properties. Its 1% solution have high viscosity (30.000 cP) which was the highest among 12 polysaccharides tested [3]. This relates to its high water absorbancy, absorbing 100 g of water per g of glucomannan, and it's high molecular weight, $10^5 - 10^6$. The gelling properties are believed to

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its acetyl groups in the chain. Either dry or wet processing methods were used today to extract glucomannan from Amorphophallus sp. corms. The product of dry processing method have low quality and low price and used in food industry. Higher glucomannan quality can be obtained by wet processing method. This method includes ethanol isolation [4], use of aluminum sulphate solution, water extraction [4] and enzymatic processing [1].

An improved methodology for the extraction of glukomanan was conduct by Chua et al. [1] based on the work of Sugiyama [4]. This extraction process was conducted in room temperature and take 3 hours. Extraction in room temperature is usually conducted to avoid the gelatinization of starch, which may entrain to glucomannan extract. To enhance the glucomannan yield and to shorten the extraction time, it is needed to carry out the extraction at higher temperatures. The gelatinization of the starch could be overcome by hydrolising it with amylase so the hydrolysate can be easily separated from the extracted glucomannan. The extraction process and the starch hydrolysis by amylase were conducted simultaneously. In this paper only the extraction of the glucomannan was reported.

2. Objectives

The solid-liquid extraction always involves mass transfer of the extractive substances from the inner particles to the bulk of solution. Kinetic of extraction process is important to facilitate the design of unit operation. The aim of the research was modeling the kinetic of extraction of glucomannan from porang flour using simple mass transfer model and was compared to rate law model.

3. Materials and Methods

3.1. Materials

Porang corms were collected from Madiun, East Jawa Indonesia. Porang flour was obtained by following the method of Chua [1]. The corms were washed, peeled, and sliced into pieces with 3 – 5 mm thickness. The corms slices were then immersed in 1%(w/w) sodium bisulphite for 1 minute. The corm slices were then oven dried at 120 ^{o}C for 40 min and continued at 60 ^{o}C for 24 hr. The dried slices were then ground and sieved (425 μm aperture) to produce porang flour.

3.2. Extraction Process

The extraction pprocess was carried out in a stirred tank with capacity of 3,5 litres that emerged in oil bath. The glucomannan was extracted by the method followed by Chua [1]. Porang flour (20 g) was stirred in 50% etanol (2000 ml) for 90 minutes at room temperature then the aqueous ethanol separated by filtration. Solution of sodium phosphate buffer at pH 6 (3000 mL) was first heating up until the temperatures reach desired values. An amount of alpha amylase enzyme solution (1 mL) then added to the solution. The resultant pellets then were added to the solution too and that time was considered as the starting time of extraction. The stirring condition maintained at 300 rpm. At a certain time interval, 100 ml of samples were taken out. Samples were then centrifuged at 4000 rpm for 5 minutes. A certain amount of volume of supernatant then was added with 96% ethanol so the final concentration of ethanol was 72% to precipitate glucomannan. Precipitated glucomannan then dried and weighed. The concentration of extracted glucomannan in the solution is calculated as weight of dried glucomannan per volume of supernatant.

3.3. Kinetic Model
3.3.1. Simple mass transfer model

In the solid-liquid extraction, the mass transfer of extractive solute from the inner particle of the solid to the bulk of the liquid occurs in two stages. Firs the diffusion of solute in the inner particle and second the convective mass transport at the solid-liquid interphase. In the case of very small particles, the diffusion of solute in the inner particle was assumed very fast that can be negligible. The rate limiting step then is only the rate of solute transfer from the particle surface to the bulk of solution [5].

The rate of the volumetric mass transfer may be written as

$$N_A = k_c.a\,(C_e - C_l) \tag{1}$$

where C_l is the concentration of glucomannan in solution (g/mL), C_e is the concentration of glucomannan in solution in contact with solid surface which is assumed to be the equilibrium concentration (g/mL) and $k_c.a$ is the volumetric mass transfer coefficient (1/min). The equilibrium relation follows the Henry's law.

$$C_e = H \, C_s \tag{2}$$

where H is Henry's constant (g/mL). The glucomannan content in the solid particles is determined by mass balance of glucomannan in the tank.

$$C_s = \frac{C_0 M - C_l V}{M} \tag{3}$$

where C_s is the concentration of glucomannan in particles (g/g), C_0 is the initial concentration glucomannan in particles (g/g), M is the mass of glucomannan particles (g) and V is the volume of solution (mL). Based on the mass balance of glucomannan in the fluid phase, it can be written the concentration of glucomannan as function of time as follows:

$$C_l = \frac{b}{a} - \frac{b}{a} \exp(-at) \tag{4}$$

whrere t is time (min) and with

$$a = k_c.a \; H \frac{V}{M} + k_c.a \tag{5}$$
$$b = k_c.a \, H C_0 \tag{6}$$

3.3.2. Rate law model

Inspite of have no conceptual association with the phenomena, the rate law have been used in modeling batch solid-liquid extraction process [6].The second order kinetic equation for the extraction rate can be written as follows [7]:

$$\frac{dC_t}{dt} = k(C_e - C_l)^2 \tag{7}$$

Where k is rate constant (ml/g.min) and C_e is extraction capacity (g/mL). Separating variables in (7) and integrating the equation gives:

$$C_l = \frac{C_e{}^2 k \, t}{1 + C_e kt} \tag{8}$$

To obtain a linear form, the equation is rearranged and with new definition of h, the equation can be written as

$$\frac{t}{C_t} = \frac{1}{h} + \frac{1}{C_e} t \tag{9}$$

where h, the initial extraction rate, can be define as

$$h = C_e^2 k \tag{10}$$

4. Results and Discussion

4.1. Simple Mass Transfer Model

Such as other rate curves for batch extraction, rapid increase of glucomannan concentration in the beginning of process was found in this experiment. This follows by slow increase as the extraction continued and will reach an equilibrium state.

Evaluation of the value of Henry's law constant, H, was calculated using the concentration of glucomannan at equilibrium state, the condition in which the glucomannan concentration was constant as the time of extraction were extended. As seen in Fig. 1 the time to reach equilibrium state was 60 minutes for temperature of process 70 °C and was 40 minutes for temperature of process 80 °C.

The values of volumetric mass transfer coefficient, $k_c.a$, could not be determined directly from the relation of glucomannan concentration and the extraction time. This parameter was evaluated by nonlinier least square method until minimal errors was achieved between experimental and calculated values. The residual (SSE-Sum of Square of Errors) was then written as follows:

$$SSE = \sum_i^N \left(C_l^{exp} - C_l^{cal} \right)^2 \tag{11}$$

Table I shows the values of calculated Henry's constant, H, volumetric mass transfer coeficient, $k_c.a$, and SSE for analyzing the extraction kinetic using simple mass transfer model. It can be seen that their values dependent on the remperature. Both of H and $k_c.a$ increased with increasing temperature.

Tabel 1: Values of Parameters in Simple Mass Transfer Model with SSE

Temperature (C)	H (g/mL)	kc.a (1/minute)	SSE
70	0.033	0.0190	8.53E-07
80	0.077	0.0217	2.18E-06

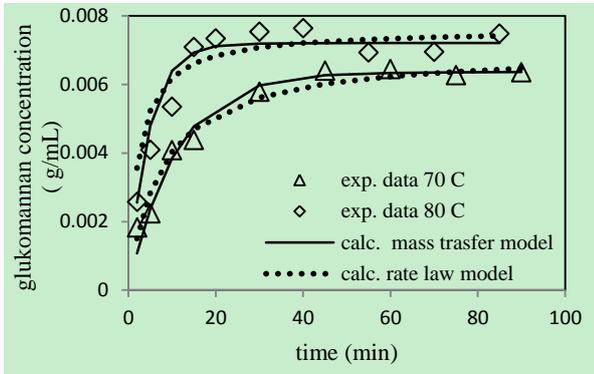

Fig. 1: Concentration of glucomannan extracted from the corms of A. muelleri Blume as function of time with approximation using simple mass transfer model and rate law model
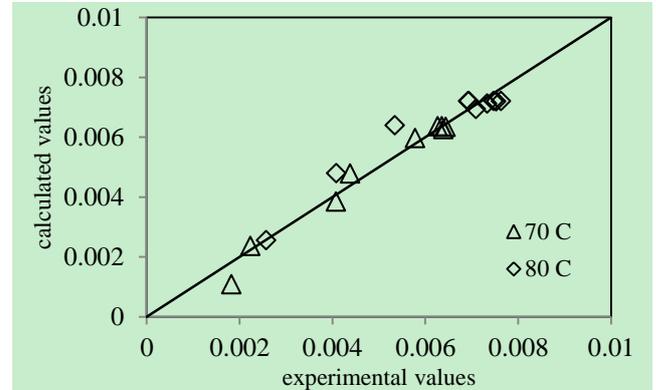

Fig. 2: Correlation between experimetally obtained values of glucomannan concentration vs. calculated concentration using simple mass transfer model

The higher value of H in higher extraction temperature indicated that final concentration increased as shown in Fig. 1. This phenomena may be due to the effect of temperature on solubilization inside of the solid [8]. Value of k_c.a represents the rate of extraction. Higher value means higher rate of extraction and reach equilibrium in a shorter time. Increasing temperature favored the extraction because increased the extraction rate, reduced the extraction time and gived higher final concentration.

Fig. 2 shows the correlation between experimental values of glucomannan concentration extracted form porang flour versus calculated concentration using simple mass transfer model. It can be seen that the calculated values made a good agreement with experimental data. The SSE for this model was of 8.53E-07 and 2.18E-06 for temperature 70 ^{o}C and 80 ^{o}C respectively.

4.2. Rate Law Model

The results of the analyzed data using rate law model are shown in Fig. 3, as a series of plots of t/C_t against t. The parameters in the rate law model were determined from the equation of linier curves using (9) and (10).

Tabel 2: Values of Parameters in Second Order Kinetic Model with SSE

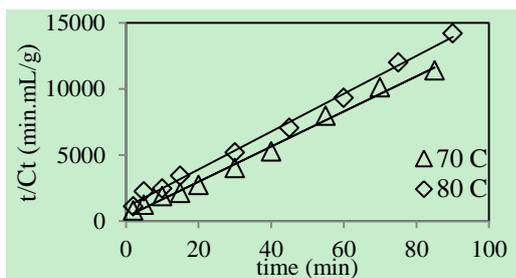| Temperature (C)	h (g/mL.min)	C_e (g/mL)	k (mL/g.min)	SSE
70	0.000953	0.00699	19.5094	8.06E-07
80	0.003330	0.00761	57.5642	9.30E-06

Fig. 3: Second order kinetic model for the extraction of glucomannan from porang flour (ratio of solid/solvent 0,01, 300 rpm)
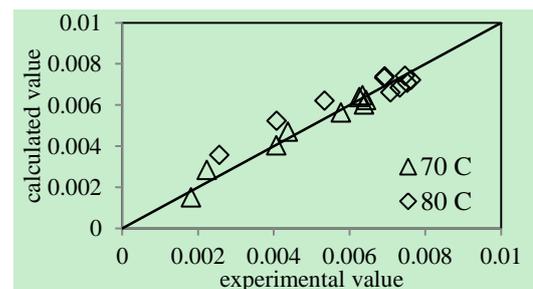

Fig. 4: Correlation between experimetally obtained values of glucomannan concentration vs. calculated concentration using rate law model

The calculated parameters for the rate law model are presented in Table II. The values of all parameters in the rate law model also dependent on temperature. When temperature increased, all the kinetic model parameters increased. This phenomena also reported by other authors [9]-[11]. The initial extraction rate, h, increased 3.5 times as the temperature rised from 70 ^{o}C to 80 ^{o}C. The value of rate constant, k, was found to increase 2.9 times with the same temperature rise. But the increasing of extraction capacity, C_e, was not as greater as the other parameters. At the same temperature rises the values of C_e only increased 1.1 times.

The good agreement between calculated values and experimental data was observed as seen in Fig. 4. The SSE for this model was 8.06E-07 and 9.3E-06 for temperature 70 ^{o}C and 80 ^{o}C respectively.

5. Conclusion

The experimental data on the extraction of glucomannan from porang flour were analyzed by simple mass transfer model and rate law model. Both models demonstrated the kinetic of extraction well. All parameters in both models depend on temperature. The increase of temperature increased the values of all parameters.

6. Acknowledgements

7. References

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