



APPLICATION OF SECOND ORDER KINETIC MODEL ON THE EXTRACTION OF GLUCOMANNAN FROM PORANG (*Amorphophallus muelleri* Blume): THE INFLUENCE OF STIRRING SPEED AND SOLID MASS/VOLUME RATIO

Fadilah^{1,2}, Rochmadi², Siti Syamsiah² and Djagal Wiseso Marseno³

¹Chemical Engineering Department, Sebelas Maret University, Jl. Ir. Sutami Surakarta, Indonesia

²Chemical Engineering Department, Gadjah Mada University, Jl. Grafika Yogyakarta, Indonesia

³Faculty of Agricultural Technology, Gadjah Mada University, Jl. Bulaksumur Yogyakarta, Indonesia

ABSTRACT

The extraction of glucomannan from Porang flour was conducted simultaneously with starch hydrolysis using amylase. Only the extraction process is reported in this paper. The kinetic of the extraction was analyzed using second order kinetic model. The influence of two operating parameters, i.e stirring speed and solid mass/volume ratio, were studied. The value of kinetic parameters, i.e the initial extraction rate, h , extraction capacity, C_e , and the extraction rate constant, k , increased as stirring speed increased, i.e. 4.95 times, 2.5 times, and 1.4 times, respectively, as the stirring speed increased from 300 rpm to 600 rpm. The increase of solid mass/volume ratio from 2.67 to 10.7 g/L results in an increase in h (8.86 times) and C_e (3.26 times) but not in k , which decreased (by 0.833 times).

Keywords: Margins extraction, second order model, glucomannan

INTRODUCTION

Glucomannan is polysaccharide with a very high molecular weight (about 200,000 to 2,000,000 Daltons). The solutions of this natural polymer have highest viscosity among others [1]. This copolymer comprises of D-glucose and D-mannose in a ratio of 1:1.6. The linear chain is linked by β -1,4 glycosidic bonds with some short branches at the C-3 of the glucosyl unit and acetyl groups attached at the C-6 in every 9 to 19 of sugar residues [2].

Glucomannan is widely used in food industry for thickening, gelling, texturing and water binding [3]. In spite of its use for foods and medicine since long time ago in China and Japan, glucomannan is considered as generally recognized as safe (GRAS) ingredient by FDA in US in 1994 and achieved an E number (E425) as a food additive in Europe in 1998. Recently glucomannan has been studied for its application in the field of pharmaceutical, bio-technical and fine chemical industry. The reason for this is because of its good film forming, good biocompatibility and biodegradable activity [4].

The main source of glucomannan is Konjac tuber, a species of *Amorphophallus sp.* A species of *Amorphophallus* that is native to Indonesia named Porang (*Amorphophallus muelleri* Blume) also have a high glucomannan tuber.

Konjac flour, containing 60-70 % glucomannan is produced by grinding the dried slices of Konjac tubers. Starch in konjac tuber is considered as impurity since its presence can reduce its viscosity and increase its turbidity [5]. Starch may be removed through dry and wet processes. In dry processing method, removal of starch is done by wind blowing, whereas wet method involves gum precipitation in alcohol, which could be done at room temperature [6] and high temperature [5, 7]. One of the drawbacks of high temperature processing is the formation

of gelatinous starch. This may be overcome by hydrolyzing the starch with amylase such that the hydrolysate can be easily separated from the extracted glucomannan.

In this research, the extraction of glucomannan was carried out simultaneously with starch hydrolysis by amylase. This paper reports the extraction of glucomannan. The extraction involves mass transfer of glucomannan from the inside of particles to the bulk of solution. It is important to get a good understanding of the phenomena of extraction process. For this reason the kinetics of extraction of glucomannan was studied by analysing the influence of stirring speed and solid mass/volume ratio on the extraction process.

LITERATURE REVIEW

Previous researches observed that extraction process of glucomannan follows second order kinetics [8, 9, 10, 11, 12], which could be described as the following equation:

$$\frac{dq}{dt} = k(C_e - C_t)^2 \quad (1)$$

Where, C_e is the concentration glucomannan at saturation condition, C_t is the concentration of glucomannan at any time, k is rate constant (ml/g.min) and C_e is extraction capacity (g/mL). Separating variables of equation (1) and integrating it with application of boundary condition $C_t=0$ at $t=0$ and $C_t=C_t$ at $t=t$ gives:

$$C_t = \frac{C_e^2 k t}{1 + C_e k t} \quad (2)$$

Equation (2) can be rearranged to the following relations



$$C_t = \frac{h}{h + k C_t} \quad (3)$$

To obtain a linear form, the equation is further rearranged as follows:

$$\frac{1}{C_t} = \frac{1}{h} + \frac{k}{h} C_t \quad (4)$$

Where, h is the initial extraction rate defined as

$$h = C_e k \quad (5)$$

MATERIALS AND METHODS

Porang tubers used in this research was obtained from Madiun, East Jawa, Indonesia. The procedure to obtained porang flour followed the previously reported method [13]. The medium for carrying the extraction process was buffer solution containing potassium dihydrogen phosphate and dipotassium hydrogen phosphate at pH 6. Alpha amylase from Sigma (A 3403 *Bacillus licheniformis*) was used for hydrolysing starch. Ethanol 96% used for precipitating glucomannan extract.

First the porang flour was washed with 50% ethanol for 90 minutes then the pellets was separated by filtration. Meanwhile, the phosphate buffer solution was placed in a stirred jacketed tank with cooking oil as heating medium. The solution was first heated until desired temperature (70 °C). An amount of amylase was added to the solution and the stirring speed was adjusted. The washed pellets that previously prepared was then introduced into the solution. This was the starting time for simultaneous of extraction of glucomannan and hydrolysis of starch in porang flour. Samples were taken at a certain time interval than they were centrifuged and precipitated by adding 96% ethanol. Dried glucomannan were weight to calculate the concentration of extracted glucomannan.

The influence of stirring speed was studied while keeping the other variables constant. The experiments were carried out at stirring speed of 300, 400, 500 and 600 rpm at constant solid mass/volume ratio (10.7 g/L) and certain amount of amylase (10,000 U). To study the influence of solid mass/volume ratio, the experiments were conducted at stirring speed of 400 rpm, with the amount of enzyme was 10,000 U, and solid mass/volume ratio were 2.67, 8.02, and 10.7 g/L.

RESULTS AND DISCUSSIONS

Figure-1 shows the increasing of glucomannan concentration in the solvent at various stirring speed. As can be seen, the glucomannan concentration increases rapidly in the beginning and gets slow afterwards. The fast increases of glucomannan concentration in the solvent at the beginning is caused by quick passing the readily accessible glucomannan into the solution. Since the glucomannan concentration is very low in the solvent, a very large concentration gradient is formed, leading a very fast extraction rate. As the process continues, the glucomannan concentration in the solvent increases,

causing a slower mass transfer rate, since the gradient concentration decreases.

The process goes on until it reaches a final concentration which is constant although the extraction time is extended. This is known as equilibrium state and the constant concentration is known as equilibrium concentration. It is seen that the final concentration varied with the stirring speed. Higher stirring speed produces higher final concentration.

The experimental results were then analyzed using second order rate law model by plotting t/C_t against t as shown at Figure-2. It can be seen that the experimental data make a straight line according to equation (4). The extraction capacity, C_e , was calculated from its slope and the initial extraction rate, h , was calculated from its intercept. The extraction rate constant, k , was calculated according to equation. (5). Table-1 presents the calculated h , C_e , k , and the coefficient of determination, R^2 . As presented in Table-1, R^2 is very high, indicating that this model is able to describe the process.

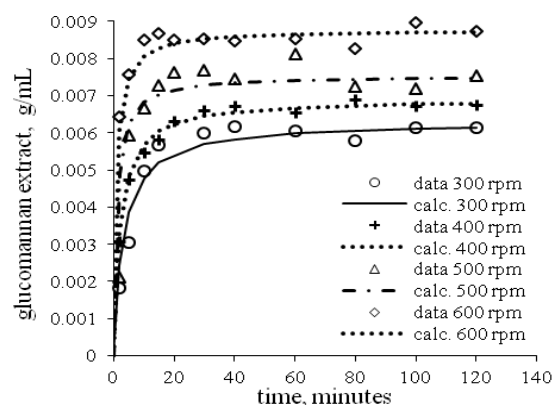


Figure-1. Concentration of glucomannan as function of time for various stirring speed.

The value of h , C_e , and k rise as stirring speed increases. Higher speed of stirring may cause higher turbulence which means higher mass transfer rate of solutes from particles to solvent.

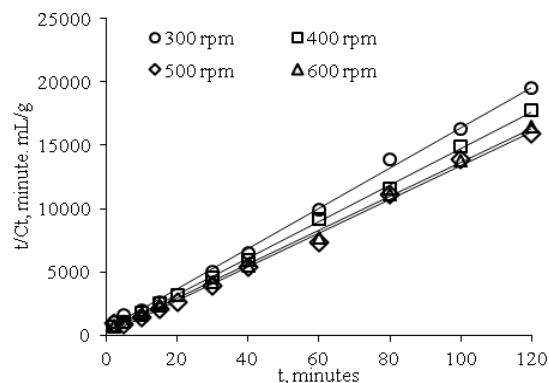


Figure-2. Second-order kinetics of extraction of glucomannan at various stirring speed.



Table-1. Values of parameter in second order kinetic model of solid liquid extraction of Porang flour at different stirring speed at solid mass/volume ratio 10.7.

Stirring speed, rpm	h , g/mL.min	C_e , g/mL	k , mL/g.min	R^2
300	0.00198	0.00629	50.013	0.997
400	0.00318	0.00692	66.551	0.999
500	0.00704	0.00754	123.802	0.995
600	0.00982	0.00877	127.477	0.998

When the stirring speed increases from 300 rpm to 600 rpm, the initial extraction rate, h , increased by 4.95 times, the extraction rate constant, k , were found to increase 2.5 times and the values of the extraction capacity, C_e , were found to increase 1.4 times.

The evolution of the glucomannan concentration in solvent for different ratio of porang mass-solvent volume is shown in Figure-3. The figure follows the same pattern as found in Figure-1. The extraction process begins with very fast mass transfer then is followed by a slowly one. It can be seen from Figure-3 that the final concentration vary with solid mass/volume ratio.

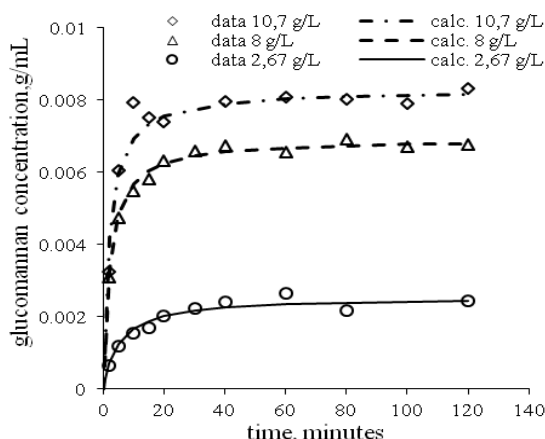


Figure-3. Concentration of glucomannan as function of time at different solid mass/volume ratio.

Plotting t/C_t against t were used to evaluate the process parameter i.e. h , C_e and k as can be seen in Figure-4. A straight line curve were formed and its coefficient of determination is very high (Table-2). This indicates that the experimental results have a good agreement with the second order model.

Influence of solid mass/volume ratio on the process parameter can be seen on Table-2. It can be seen that if the solid mass/volume ratio increase, the initial extraction rate, h , and the extraction capacity, C_e increased, while the extraction rate constant, k decreased. The same results were reported by Qu [12]. Increasing the solid

mass/volume ratio by four fold (2.67 – 10.70 g/L) caused the value of h increased by 8.86 times and the value of C_e increased by 3.26 times, while the value of k were found to decrease 0.833 times.

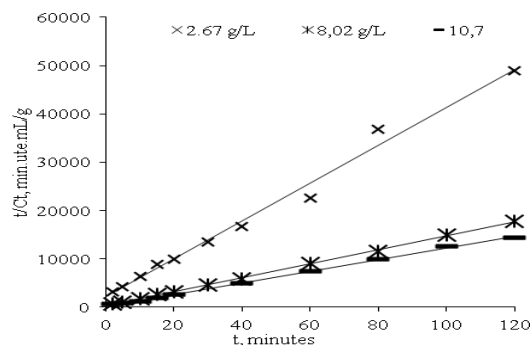


Figure-4. Second-order kinetics of extraction of glucomannan at various solid mass/volume ratio.

Table-2. Values of parameter in second order kinetic model of solid liquid extraction of Porang flour at various solid mass/volume ratio at stirring speed 400 rpm.

Solid mass /volume ratio, (g/L)	h , g/mL.min	C_e , g/mL	k , mL/g.min	R^2
2.67	0,00047	0,00254	73,792	0.988
8,02	0,00318	0,00691	66,550	0.999
10,70	0,00422	0,00828	61,517	0.998

The fitness of the second order model with the experimental results confirms that the extraction process of glucomannan from Porang flour by buffer solution behave in two successive stages as was described before. Figure-5 also verifies this conclusion.

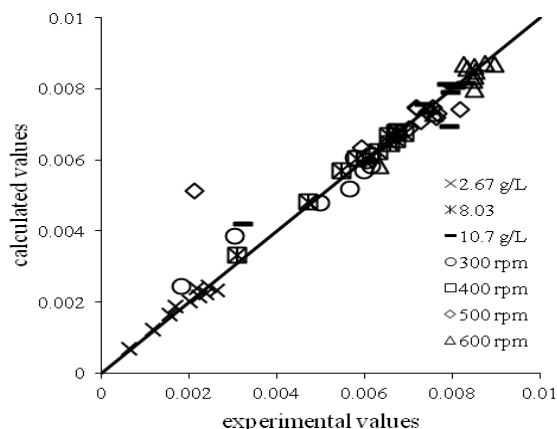


Figure-5. Correlation between experimentally obtained values of glucomannan concentration compared with calculated concentration.



CONCLUSIONS

The extraction of glucomannan from Porang flour by buffer solution was studied and the kinetic of the extraction was evaluate based on the second order model. The results showed that the proposed model gives a very high goodness of fit with the obtained experimental data. The value of kinetic parameters, i.e the initial extraction rate, h , extraction capacity, C_e , and the extraction rate constant, k , increased as stirring speed increased. The value of initial extraction rate, h , and extraction capacity, C_e , increased as solid mass/volume ratio increased but the extraction rate constant, k decreased.

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REFERENCES

- [1] Yaseen, E.I., Herald, T.J., Aramouni, F.M., and Alawi, S. 2005. Rheological properties of selected gum solutions. *Food Research International*. 8: 111-119.
- [2] Katsuraya, K., Okuyama, K., Hatanaka, K., Oshima, R. Sato, T., and Matsuzaki, K. 2003. Constitution of konjac glucomannan: chemical analysis and ^{13}C nmr spectroscopy. *Carbohydrates Polymers*. 53: 183-189.
- [3] Takigami, S. 2000. Konjan Mannan in *Handbook of Hydrocolloids*, edited by Phillips, G.O., and Williams, Woodhead Publishing Limited.
- [4] Zhang, Y., Xie, B.J., and Gan, X. 2005. Advance in the applications of konjac glucamannan and its derivatives. *Carbohydrate Polymers*. 60: 27-31.
- [5] Xu, W., Wanf, S., Ye, T., Jin. W., Liu, J., Lei, J., Li, B., and Wang, C. 2014. A simple and feasible approach to purify konjac glucomannan from konjac flour – Temperature effect, *Food Chemistry*. 158: 171-178.
- [6] Chua, M., Chan, K., Hocking, T.J., Williams, P.A., Perry, C.J. and Baldwin, T.C. 2012. Methodologies for the extraction and analysis of konjac glucomannan from corms of *Amorphophallus konjac* k. Koch. *Carbohydrate Polymers*. 87: 2202-2210.
- [7] Tatirat, O. and Charoenrein, S. 2011. Pysisicochemical Properties of Konjac Glucomannan Extracted From Konjac Flour by a Simple Centrifugation Process. *LWT-Food Science and Technology*. 44: 2059-2063.
- [8] Harouna-Omaru, H.A., Faudet, H, Porte, C. and Ho, Y.S. 2007. Comparison of kinetic models for the aqueous solid-liquid extraction of tilia sapwood in a continuous stirred tank reactor. *Chemical Engineering Communications*. 194: 537-552.
- [9] Linares, A. R., Hase, S. L., Vergara, M. L. and Resnik, S. L. 2010. Modeling yerba mate aqueous extraction kinetics: Influence of temperature. *Journal of Food Engineering*. 97: 471-477.
- [10] Rakotondramasy-Rabesiaka, L., Havet, J.L., Porte, C., and Faudet, H. 2007. Solid-liquid extraction of protopine from *Fumaria officinalis* L. – Analysis determination, kinetic reaction and model building. *Separation and Purification Technology*, 54, 253-261.
- [11] Sayyar, S., Abidin, Z.Z., Yunus, R., and Muhammad, A. 2009. Extraction of oil from jatropha seeds-optimization and kinetics. *American Journal of Applied Sciences*. 6(7):1390-1395.
- [12] Qu, W. Pan, Z., and Ma, H. 2010. Extraction modeling and activities in antioxidants from poemgranate marc. *Journal of Food Engineering*. 99:16-23.
- [13] Fadilah, Rochmadi, Siti Syamsiah, and Haryadi, 2013. Investigation of mannanase activity in commercial α -amylase: preliminary research on purification of glucomannan from porang (*Amorphophallus muelleri* Blume). *Proceeding of Regional Symposium on Chemical Engineering 2013*. Bohol, Phillippines.