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ORIGINAL ARTICLES

Removal of Cyanides from Gadung (*Dioscorea hispida Dennst.*) Tuber Chips using Leaching and Steaming Techniques

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ABSTRACT

Gadung (*Dioscorea hispida Dennst.*) has been considered as one of staple foods in Indonesia. However, its high cyanides content has limited its utilisation for commercial food production. This work is aimed to investigate the removal of cyanides content from gadung tuber chips through two consecutive treatments, i.e. leaching and steaming and to propose mathematics model for the leaching process. The results showed that processing water flow rate and leaching time affected the efficiency of cyanides removal in the leaching process. The proposed mathematical model was able to represent the removal of cyanides through leaching process very well. The cyanides content removal was also found to be affected by steaming time. Best processing condition was at leaching using 5.00×10^{-5} $m^3.s^{-1}$ for 3,600 s, followed by steaming for 3,600 s to obtain cyanides content of 29.9 $mg{\cdot}kg^{-1}$. While the yielded gadung tuber chips are considered as safe for consumption, further research on physicochemical characteristic of the gadung tuber flour is necessary for its utilisation consideration.

Key words: cyanogens, dioscoreae, leaching, mathematics model, steaming

Introduction

Gadung (*Dioscorea hispida Dennst.*) is one of unpopular member of tubers which is available in almost all parts of Indonesia's archipelago. This tuber crop is an important source of carbohydrates as an alternative energy source. Moreover, it has been used as staple foods, especially by people in the tropical and sub tropical regions (Liu *et al*., 2006). The resistant starch contained in this food source has been related with a slow digestion in the lower parts of the human gastrointestinal tract, resulting in slow liberation and absorption of glucose. This tuber's digestive property has suggested the utilization of gadung tuber in reducing the risk of obesity, diabetes and other related diseases (Aprianita *et al*., 2009) In addition, as carbohydrate source, gadung tuber does not contain any gluten, which makes gadung tuber becomes an important substance in the reduction in the incidence of celiac disease (CD) or other allergic reactions (Rekha and Padmaja, 2002.). With these benefits in mind, an effort on gadung processing into edible food materials was undertaken.

The major problem related to the limitation of gadung tuber utilization as a food source for human is its high content of hydrogen cyanides in both free and bound forms (Edijala *et al*., 1999.). Liberation of hydrogen cyanides from cyanogenic glycosides occurs via hydrolysis, which may take place during the preparation of the food (Akintonwa *et al*., 1994). Only free cyanides (CN^-) is toxic, and if hydrolysis does not take place the glycoside remains stable and the foods produced from this food material are safe. Consumption of cassava that contains large amounts of cyanogens may cause cyanides poisoning with symptoms of vomiting, nausea, stomach pains, diarrhoea (Akintonwa *et al*., 1994; Lasch and El Shawa, 1981) and other possible acute intoxications (Mlingi *et al*., 1992). In addition, long term impacts due daily consumption of cassava products with unsafe cyanogens level as a staple food may cause chronic cyanides toxicity (Cooke and Maduagwu, 1978.), aggravate goitre (Bourdox *et al*., 1982) and, in severe circumstances, induces paralytic diseases (Tylleskar *et al*., 1992.). Therefore, to prevent serious dietary cyanides exposure, the glucosides and their derivative substances, popularly known as cyanogens, must be removed from the food source before being consumed. Effective processing mode may reduce all cyanogens in cassava products to below the safe level of 10 mg HCN equivalent per kg body weight as set by WHO 1988 (Mlingi *et al*., 1995).

Considering the undesirable health effects of cyanogenic substances, various processing techniques to reduce the toxicity of tubers and roots have been attempted. Some workers (Okpokiri *et al*., 1985; Onwueme, 1978) had reported the HCN levels of their cassava product (20-50 mg/kg) which is already within SON standard (SON, 1985). A modification to the traditional process for fufu flour preparation involves peeling,

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washing and cutting of cassava tubers to increase surface area and reduce boiling time (Chukwuemeka, 2007). The cassava tubers was then boiled for 10 -15 min and soaked in water at room temperature (30 ± 3^{o}C) (1 part of cassava to 3 parts of water) for 24 to 72 h with washing after every 24 h. The tuber chips were finally dried, milled to obtain an average particle size of 0.5 mm and then packaged as fufu flour. This process removed more than half of the initial cyanides content (38.14 mg/kg) to between 10.87-16.2 mg/kg. Another research group reported that submerged boiling of raw cassava tuber in water for 35 min, followed by sun drying resulted in reduction in 81.5% cyanides content of the steamed product (Iwuoha *et al.*, 1997). However, sun-drying of fresh cassava roots with a cyanogenic potential of greater than 100 mg HCN equiv per kg dry wt will not be able to reduce glucoside levels to below 10 mg HCN equiv per kg dry wt (Mlingi *et al*., 1992). Soaking of cassava roots into water removed about 20% of the free cyanides in the fresh root chips after 4 hours, however the bound cyanides remained unchanged.

This paper reports a simple way to remove cyanides from gadung tuber chips by employing leaching and steaming techniques. A mathematics model to represent the leaching process is also proposed here.

Materials and Methods

Materials:

Matured gadung tubers were harvested in June 2010 and were of a uniform medium size and free from mechanical or pathological injuries. Chemical reagents of analytical grade were purchased from Sigma-Aldrich Indonesia and used directly without further purification.

Methods:

Leaching of cyanidess from gadung tuber chips:

Gadung tubers were peeled, washed, cut into 5 cm cubes, and sliced into thin chips (3 mm). One kilo gram of these chips were then charged into a leaching column and arranged as a fixed bed. Fresh water was flown into the leaching column at certain flow rate to hydrolyse the cyanides from the tuber chips and leach them out. Tuber chip samples were taken out at the top, middle and the bottom of the column at every 30 minutes interval for HCN equivalent determination. The analysis of cyanides content in term of HCN equivalent was carried out by alkaline titration method suggested by AOAC (AOAC, 1995). The experiment was terminated when cyanides content in the gadung tuber chips was constant. To ensure the accuracy of the data, each experiment was conducted in triplicate and an average value was taken. The effect of processing water flow rate and time on the leaching efficiency was studied here. Treatment of gadung tuber chips by impregnation in static water of (1/3 weight ratio) for 24, 48 and 72 hours were also performed to compare with treatment of gadung tuber chips with flowing water (Chukwuemeka, 2007).

Modelling of cyanides removal by leaching:

Mathematics modelling is used to represent the cyanides removal by leaching technique. This activity was carried out to estimate the cyanides content in the gadung tuber chips as a function of position and time (C_{CN} = f (z,t)) as illustrated in Fig.1. Some parameters should be defined such as height of bed of gadung tuber chips = L (m), cross sectional area of the leaching column = S (m^2), water flow rate = Q (m^3.s^{-1}), initial cyanides content in the gadung tuber chips= X_{CN0} (mg·kg^{-1}), initial cyanidess content in the processing water = C_{CNo}= 0, density of gadung tuber chips = ρ_b = 729 kg.m^{-3}, and bed porosity = ε = 0.34.

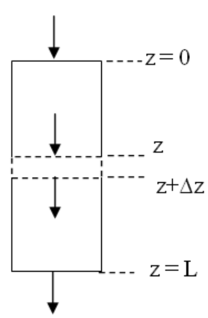

Fig. 1: Volume element of the leaching column.

To simplify the real phenomena, some assumptions were taken:

a. The gadung tuber chips were thin enough so that diffusion rate of cyanides from inner part to the chips surface was relatively fast. Therefore, leaching rate was controlled by mass transfer of cyanides from gadung tuber chips surface to the bulk flow of processing water. This mechanism can be written as:

$$N_{CN} = kca(C_{CN}* - C_{CN}) \tag{1}$$

where C_{CN} = concentration of cyanides in water (g cyanides·g cyanides free water^{-1})
C_{CN}^{*} = concentration of cyanides in water in equilibrium with concentration of cyanides at gadung tuber chips surface (g cyanides·g cyanides free water^{-1})
k_{ca} = volumetric mass transfer coefficient (s^{-1})
N_{CN} = cyanides mass flux (g cyanides·s^{-1}· bed volume^{-1})

b. Mass transfer of cyanides in the axial direction takes place in two different mechanisms, i.e. bulk mass transfer and axial dispersion. Axial dispersion of cyanides in the fluid phase followed Fick's law:

$$N_{CN} = -De\frac{\partial C_{CN}}{\partial z} \tag{2}$$

with De = effective diffusion coefficient (m^2.s^{-1})

c. Correlation between equilibrium concentration of cyanides in the solid phase and fluid phase can be in the form of Henry's like equation:

$$C_{CN}* = H.X_{CN} \tag{3}$$

where H = equilibrium constant

d. Mass balance of cyanides in the processing water (see Figure 1) can be written as:

$$\frac{\partial^2 C_{CN}}{\partial z^2} - \frac{\varepsilon.Q}{S.De} + \frac{k_{ca}}{De}(C_{CN}* - C_{CN}) = \frac{\varepsilon}{De}\frac{\partial C_{CN}}{\partial t} \tag{4.a}$$

If cyanides content in the processing water is very low, the accumulation of cyanides in the processing water is almost zero. This situation leads to the negligence of the right hand side of equation (4.a) and the system becomes under quasy steady state condition. Equation (4.a) can be rewritten as:

$$-\frac{\varepsilon.Q}{S.De} + \frac{k_{ca}}{De}(C_{CN}* - C_{CN}) = \frac{\partial^2 C_{CN}}{\partial z^2} \tag{4.b}$$

e. Mass balance of cyanides in the solid phase of gadung tuber chips forming the equation below:

$$\frac{\partial X_{CN}}{\partial t} = -\frac{k_{ca}}{\rho b}(C_{CN}* - C_{CN}) \tag{5}$$

f. Effective diffusion (*De*) and volumetric mass transfer (k_{ca}) coefficients can be evaluated by finding optimum *De* dan k_{ca} that give minimum value of sum of the square of errors (SSE) between X_{CN} value of experimental (X_{CNexp}) and X_{CN} value from the simulation (X_{CNcalc}).

$$MinSSE = \sum_{1}^{2}(X_{CN\,\exp} - X_{CN\,calc})^2 \tag{6}$$

Steaming of gadung tuber chips:

After cyanides content in the gadung tuber chips was reduced by leaching with flowing fresh water, the tuber chips were then subjected to steaming. Reduction of cyanides content in the tuber chips was investigated at every 15 minutes interval. Effect of steaming on gadung tuber flour crystallinity was studied by scanning electron microscopy (SEM) analysis.

Discussion:

A preliminary experiment was conducted to investigate the efficiency of cyanides removal from gadung tuber chips through impregnation one part weight of tuber chips in three parts weight of static water. The results were as expected, where no significant removals were obtained. While initial cyanides content in the gadung tuber chips was 84.26 mg·kg^{-1}, the cyanides content in the gadung tuber chips after 24, 48 and 72 hours impregnation were 82.40, 81.99 and 80.94 mg·kg^{-1}, respectively. This finding agrees well with that reported on the toxicity investigation of wild yam (*Dioscorea* spp.) tubers of Nepal (Bhandari and Kawabata, 2005).

Fig. 2 shows the profile of cyanides content in the gadung tuber chips at various process water flow rate and time. In any process water flow rate, the cyanides content in gadung tuber chips decreased with increasing leaching time to some extent. Prolong the leaching time did not significantly reduce the cyanides content. This is because the equilibrium concentration of the cyanides between the tuber chips surface and bulk flow of water had been achieved. The cyanides removal became more effective when leaching was conducted at high processing water flow rate. As illustrated in Fig.2, leaching of gadung tuber chips for 10,800 second using lowest processing water flow rate (8.33m^3·s^{-1}) only reduced 28.57% of the cyanides content. As expected, leaching of gadung tuber chips using highest process water flow rate (50.00m^3.s^{-1}) resulted in highest cyanides content reduction, which was 50.55% of the initial content. This phenomenon can be related to solid-fluid mass transfer in a fixed bed system (Seguin *et al*., 1996). The turbulence generated by processing water flow inside the leaching column became more severe as the processing water flow rate was higher. The more turbulence the flow pattern, the better the mass transfer of cyanides from gadung tuber chips into the processing water flow.

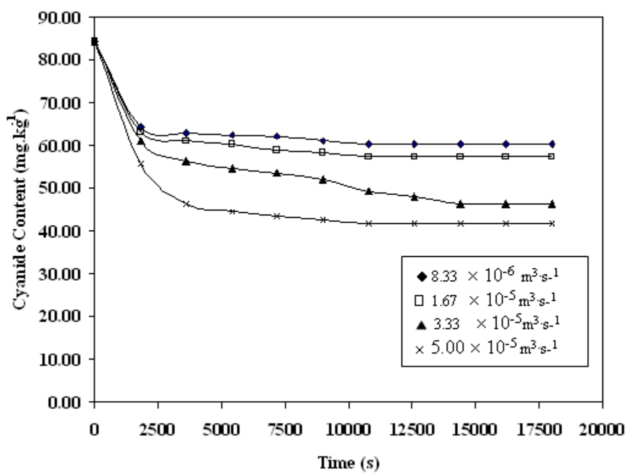

Fig. 2: Profile of cyanides content as a function of time (s).

The comparison of the fraction of cyanogens removal obtained from modelling results and experimental data are presented in Fig. 3. It is visually observed that the model fitted the experimental data very well. The optimum volumetric mass transfer coefficients (k_{ca}) and effective diffusivity coefficients (D_e) as a function of water flow rates are reported in Table I. As expected, the volumetric mass transfer coefficients (k_{ca}) increased with processing water flow rates [19]. The effective diffusivity coefficients (D_e) were found to be constant at about 5.00×10^9 (m^2.s^{-1}). These results obey the correlation proposed by Wilke and Chang (1955) on the diffusivity coefficient of solute in dilute solution, where *De* value is not a function of flow rate. The D_e value is a function of temperature, molecular weight, viscosity, and molar volume of the solvent.

Table 1: The optimum k_{ca} and D_e as a function of processing water flow rates.

Water flow rates (m^3.s^{-1})	$k_{ca \times 10^4}$ (s^{-1})	De $_{\times 10^9}$ (m^2.s^{-1})
8.33	4.70	4.93
16.67	5.40	5.00
33.33	5.70	5.00
50.00	6.20	5.00

Effect of steaming time on the cyanogens content in the gadung tuber chips are presented in Table 2. It is clear in Table 2 that cyanides content in the gadung tuber chips reduced when steamed at a certain period of time. This result proof the statement that thermal treatment can reduce the cyanides content of tubers (Chukwuemeka, 2007). In the beginning of steaming (0-900 s), the cyanides content reduction was very little.

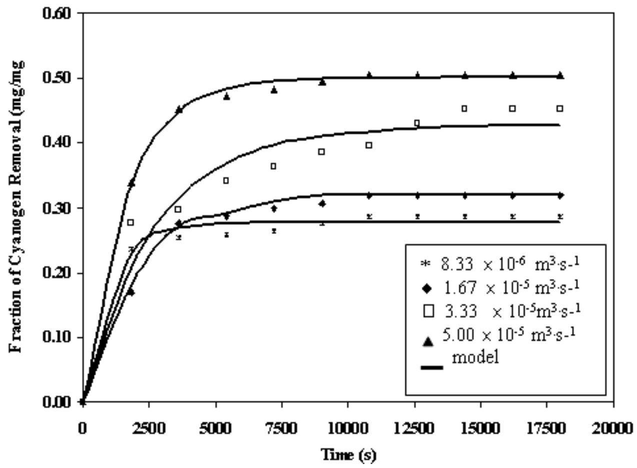

Fig. 3: Comparison of fraction of cyanogens removal obtained from experiment and model calculation.

Table 2: Effect time of steaming on cyanides content.

Time (s)	HCN Content ($mg.kg^{-1}$)	HCN Content reduction (%)	HCN content reduction rate ($mg.kg^{-1}s^{-1}$)
0	46.30	0	0
900	44.41	4.09	3.50E-05
1800	37.22	19.61	13.30E-5
2700	34.50	25.48	5.03E-05
3600	32.68	29.42	3.38E-05
4500	31.78	31.36	1.67E-05
5400	30.87	33.33	1.69E-05
6300	29.96	35.28	1.67E-05
7200	29.96	35.28	0

This is because; the gadung tuber chips underwent temperature increase from room temperature to steam temperature (100^{o}C). The heating followed two heat transfer mechanisms, i.e convective heat transfer from steam to the gadung chips surface followed by conductive heat transfer from gadung chips surface to the inner part of them. This phenomenon showed that at the beginning of the process, the heat was used to increase the temperature and at the same time to thermally remove the cyanogens from the tuber in both surface and inner parts. Microstructure changes on tuber flour obtained by steaming and without steaming are shown in Fig. 5. When maximum temperature (100^{o}C) had been achieved at about 1,800 s, the cyanides removal was very fast, where reduction rate of 13.3×10^{-5} ($mg.kg^{-1}s^{-1}$) took place. Obviously, the cyanides reduction here was much lower and slower than cyanides reduction of cassava reported by previous researchers (Chukwuemeka, 2007; Unung *et al*., 2006). Steaming the cassava mash could reduce the cyanogen content from over 80% to 24%, with similar large reduction in the glucosides, cyanohydrin and HCN content (Unung *et al*., 2006). While about 50-55% of cyanidess content in cassava tuber was removed in just 900 s by steaming (Chukwuemeka, 2007). Steaming of gadung tuber chips in the same period only reduce 4.09% cyanides from them. In fact, the specific heat capacity and thermal conductivity of gadung tuber are higher that those of cassava tuber (Njie *et al*., 1998). The value of the specific heat capacity and thermal conductivity for gadung tuber are 1.766 $kJ \cdot kg^{-1} \cdot {}^oC^{-1}$ and 0.16 $W \cdot m^{-1} \cdot {}^oC^{-1}$, respectively. Whereas the value of the specific heat capacity and thermal conductivity for cassava tuber are 1.638 $kJ \cdot kg^{-1} \cdot {}^oC^{-1}$ and 0.16 $W \cdot m^{-1 \cdot o}C^{-1}$, respectively. This difference can be attributed by harvest date, texture, and initial cyanides content in the tubers. Further addition of steaming period could not increase the tuber chips temperature and even reduce the cyanides reduction rate as shown in Fig. 4. The cyanides content reduction stopped after 5000 s where equilibrium concentration of cyanides in tuber chips had been achieved (29.96 $mg \cdot kg^{-1}$). From technical point of view, the reduction of cyanides content from 3,600 to 4,500 s was not significant (32.68 to 31.78 $mg \cdot kg^{-1}$) or reduced about 31.36-33.33 % from initial cyanides content. In addition, the cyanides reduction rate also decreased from $3.38 \cdot 10^{-5}$ to $1.67 \cdot 10^{-5}$ $mg.kg^{-1}s^{-1}$. While from economical point of view, the longer the steaming time, the more energy used and the higher the processing cost. Therefore, 3,600 s is considered as a reasonably good steaming time.

The cyanogens contents of studied gadung tubers were found to be notably lower than reported cyanogen levels for wild cassava (Nassar and Fichtner, 1978) and reported levels for various food sources (Rezaul and Bradbury, 2002). With average consumption of gadung tuber in Indonesia is about 1.5 kg per day and average body weight of Indonesian people is 60 kg, the content of the gadung tuber chips obtained in this work, 29.96 $mg \cdot kg^{-1}$ dry tuber or equal to 0.749 $mg \cdot kg^{-1}$ body weight. The results indicated that the cyanogens levels found in the gadung tuber chips obtained in this work was satisfactorily below the safety level for cyanides poisoning. The lethal dose range for humans, of HCN taken by mouth, is estimated to be only 0.5 to 3.5 mg·kg^{-1} body weight (Bradbury, 1991). However, the presence of this smaller amount of cyanogens may have some long-term adverse effects on human health. The evidence is now strong that cyanogens ingestion can give rise to chronic neurological disease in humans (Montgomery, 1980).

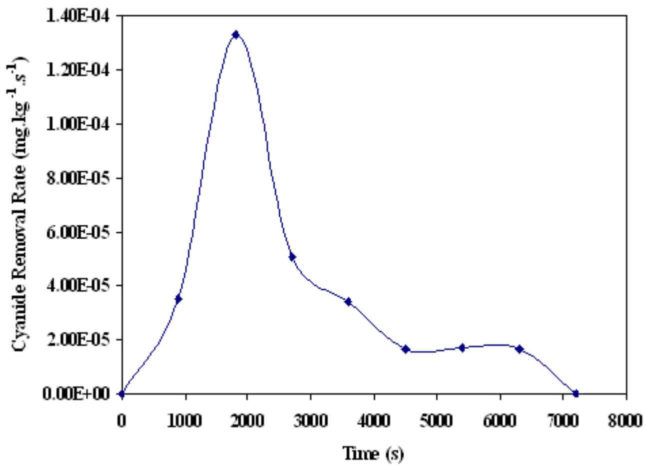

Fig. 4: Cyanides removal rate as a function of time (s).

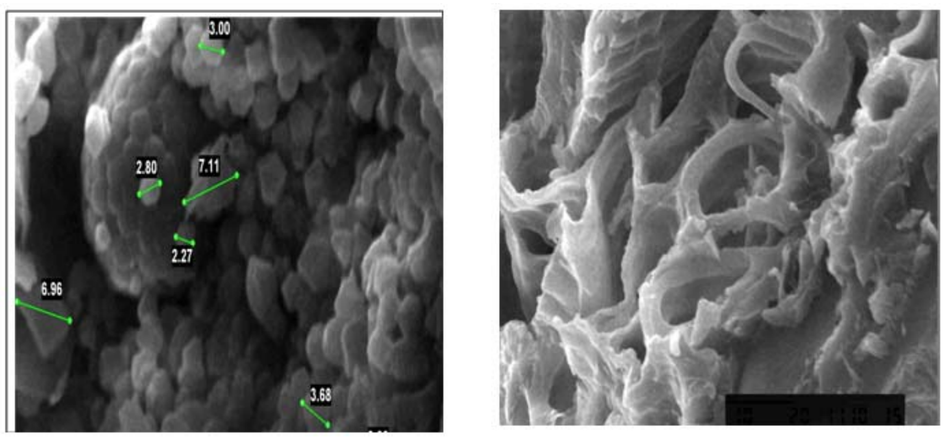

Fig. 5: Microstructue changes of gadung tuber flour processed by steaming (a) and without steaming (b).

Conclusion:

From the experiments carried out in this work, some conclusions can be drawn: processing water flow rate affects the efficiency of cyanides content removal in the leaching process, the proposed mathematical model was able to describe the removal of cyanides through leaching process very well, the cyanides content removal was found to be affected by steaming time, and the yielded gadung tuber chips are safe for consumption.

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