KINETIC STUDY ON ELIMINATION OF CYANIDE FROM CASSAVA

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ABSTRACT

In this work, a kinetic study and a thermodynamic contribution of the elimination of cyanide from cassava are undertaken. Indeed, the extraction speed constant "k_1" has been determined while considering the extraction of cyanide from cassava like a first order reaction in the main to dimension extraction reactors, because there is a relation between k_1 and the volume of reactor. The time of half extraction determined permits to prove scientifically thereafter that a soaking during 3 days of studied cassava varieties is a good method of cyanide extraction in cassava.
The value of the free enthalpy is relevant to a spontaneous phenomenon.

Key words: cyanide, cassava, kinetic study

RESUME

Dans ce travail, une étude cinétique et une contribution à l'étude thermodynamique de l'élimination de cyanure dans le manioc sont entreprises. En effet, la constante de vitesse de l'extraction « k_1 » a été déterminée en considérant l'extraction du cyanure dans le manioc comme une réaction de premier ordre dans le but de dimensionner un réacteur d'extraction, car il existe une relation entre k_1 et le volume de réacteur. Le temps de demie-extraction déterminé par la suite permet de prouver scientifiquement qu'un trempage pendant 3 jours des variétés de maniocs étudiés est une bonne méthode d'extraction du cyanure dans le manioc.
La valeur de l'enthalpie libre est relative à un phénomène spontané.

Mots-clés : cyanide, cassava, étude cinétique

INTRODUCTION

It is scientifically established and generally recognized that the presence of cyanide in the cassava, which is the basic food for most people in the world is poisonous. This is because after reacting with the sulfide found in human blood, it inhibits formation of the T_4 (thyroxine) hormone, thus depriving the organism of one of its important hormones, which not only supervises the growth and development of the central nervous system as well as metabolism of glucids, lipids and protids but also is a regulator of enzymatic reactions and the body temperature.

The absence of this hormone may lead to diseases such as paraplegy ''KONZO'', goitre, mental stupidity and deafness.

A lot of studies have been performed (1) and data availed on various possibilities of elimination the cyanide from the cassava by soaking in water, exposure to sun light or by cooking.

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None of the above mentioned methods is fast, neither economically profitable nor efficient.

The main purpose is to develop a fast process, stable and sure in order to transform cassava with less of toxic substances in the finished products. Our study aims to evaluate the rate of extraction of the hydrocyanic acid in the cassava in order to dimension reactors.

It should be noted that concerning the medical field, this study contributes to decrease the risks of exposure to cyanide for the regular consumption of cassava, by the optimization of the yield of the transformation. According to the scientific field this work provides interesting physicochemical informations which can be used in the industry.

THEORY

1. Determination of kinetic parameters

It has been established that the elimination phenomenon of cyanide behaves as a first order and the kinetic constant (k_1) which is a measure of kinetic activity of water has been calculated from the classical relation of formal kinetic: $\log\frac{C}{C-x}=\frac{k_1}{2{,}3}t$; $(\log\frac{1}{C-x}=\frac{k_1}{2{,}3}t+\log\frac{1}{C})$ where the slope of $\log\frac{C}{C-x}$ versus time is $\frac{k_1}{2{,}3}$ and where it is clearly demonstrated that the half extraction time is $\tau_{1/2}=\frac{0{,}693}{k_1}$ (2).

In the above mentioned relation C is the initial concentration in cyanide, x its conversion (amount extracted in water) and t is the time expressed in hours.

It should be noted that the concentrations have been measured each time after 7 hours and this during 3 days.

2. K_{true} Determination

Thermodynamic study, has been undertaken, the true equilibrium constant (K_{true}) and the standard free enthalpy ($\Delta G°$) relevant to the process have been determined.

The elimination of cyanide in the cassava by means of water obeys to an equilibrium between two phases (the solid phase and the liquid one) with the equilibrium constant of partition of cyanide between these two phases. The cyanide from glucosic and nonglucosic form is released after enzymatic hydrolysis of the cassava.
The cyanide released in the cassava passes in aqueous solution by diffusion, therefore the elimination of cyanide will be limited by the phenomenon of diffusion and the enzymatic action.

The enzymatic action grows at pH $\leq$ 4, only the diffusion controls the reaction of elimination.

To determine the true equilibrium constant parameters have been defined:

- C_{CNsol} : is the formality of cyanide in the solid phase;
- $C_{CNaq}=x$: is the formality of cyanide in the aqueous phase;
- $X_{CNsolifree}$: is the actual concentration of free cyanide in the solid phase;
- $X_{CNsolbind}$: is the actual concentration of cyanide bound in the solid phase;
- X_{CNaq} : is the actual concentration of cyanide in the aqueous phase.

If:

$$C_{CNsol}=X_{CNsolfree}+X_{CNsolbind} \quad \text{(i)}$$

$$C_{CNaq}=X_{CNaq} \quad \text{(ii)}$$

And that the true equilibrium constant is given by:

$$K_{true}=\frac{X_{CNaq}}{X_{CNsolfree}} \quad (1)$$

The apparent or experimental equilibrium constant can be written:

$$K_{app} = \frac{C_{CNaq}}{C_{CNsol}} \quad (2)$$

By replacing (i) and (ii) in (2), and by considering the reverse of K_{app}, one obtains:

$$\frac{1}{K_{app}} = \frac{1}{K_{true}} + X_{CNsolbind}\frac{1}{C_{CNaq}}$$

$$\frac{C-x}{x} = \frac{1}{K_{true}} + X_{CNsolbind}\frac{1}{C_{CNaq}}$$

$$\frac{C}{x} - \frac{x}{x} = \frac{1}{K_{true}} + X_{CNsolbind}\frac{1}{C_{CN\,aq}}$$

$$\frac{C}{x} = 1 + \frac{1}{K_{true}} + X_{CNsolbind}\frac{1}{x}$$

The plot of $\frac{C}{x}$ versus $\frac{1}{x}$ gives a line whose the original ordinate is $(\frac{1}{K_{true}} + 1)$ allowing thus to determine the true equilibrium constant. And then $K_{true} = \frac{1}{Original\ ordinate - 1}$

3. Determination of standard free enthalpy ($\Delta G°$)

The standard free enthalpy relevant to the process is given by:

$$\Delta G° = -RT \ln K_{true}$$

The temperature of measure was of 27°C or (300,0±0,5) K, R = 8,314 $\frac{J}{K.mol}$.

EXPERIMENTAL SECTION

Two varieties of cassava namely ''Sadisa'' and ''Mvuama'' which were at the 6th day after harvest in BAS-CONGO have been used.

The cyanhydric acid is gotten by steam distillation and introverted in an erlenmeyer containing NaOH 0,75 M.

The enzymatic action has been inhibited before distillation while fixing the pH to a value lower or equal to 4. Cyanide is measured out by argentimetric method of BRUDZYNSKI. (3,4).

Standard deviation has been used to established precision of our measures.

The experimental data obtained were treated with ORIGIN 6.1. computer programme.

RESULTS AND DISCUSSIONS

In tables 1, 2 and 3, the concentration values of the cassava varieties studied are given.

Table I: Cyanide concentrations in the fresh cassava, type SADISA in milligram of cyanide per kilogramme of cassava (mg/kg).

Number of the test	Soaking Time (Hours)	Volume of $AgNO_3$ in ml: 1st test	2nd test	3rd test	Average	Concentration of CN in mg/kg
1	07	0,5	0,6	0,6	0,56±0,06	145,712±0,050
2	14	0,7	0,6	0,7	0,66±0,06	171,732±0,050
3	21	0,8	0,9	0,9	0,86±0,06	223,772±0,050
4	28	0,9	10	0,9	0,93±0,06	241,986±0,050
5	35	1,2	1,2	1,3	1,23±0,06	320,046±0,050
6	42	1,4	1,4	1,5	1,43±0,06	372,086±0,050
7	49	1,5	1,4	1,5	1,47±0,06	382,494±0,050
8	56	1,5	1,4	1,5	1,47±0,06	382,494±0,050
9	63	1,5	1,6	1,5	1,53±0,06	398,106±0,050
10	70	1,5	1,5	1,6	1,53±0,06	398,106±0,050

Table II: Cyanide concentrations in the dried cassava, type SADISA in milligram of cyanide per kilogramme of cassava (mg/kg)

Number of the test	Soaking Time (Hours)	Volume of $AgNO_3$ in ml: 1st test	2nd test	3rd test	Average	Concentration of CN in mg/kg
1	07	0,3	0,2	0,3	0,26±0,06	67,652±0,050
2	14	0,3	0,3	0,4	0,33±0,06	85,866±0,050
3	21	0,4	0,4	0,3	0,36±0,06	93,672±0,050
4	28	0,4	0,4	0,5	0,43±0,06	111,886±0,050
5	35	0,6	0,5	0,5	0,53±0,06	137,906±0,050
6	42	0,5	0,6	0,6	0,56±0,06	145,712±0,050
7	49	0,6	0,6	0,7	0,63±0,06	163,926±0,050
8	56	0,7	0,7	0,8	0,73±0,06	189,946±0,050
9	63	0,7	0,8	0,7	0,73±0,06	189,946±0,050
10	70	0,8	0,8	0,7	0,73±0,06	189,946±0,050

Table III: Cyanide concentrations in the dried cassava, type MVUAMA in milligram of cyanide per kilogramme of cassava (mg/kg).

Number of the test	Soaking Time (Hours)	Volume of $AgNO_3$ in ml: 1st test	2nd test	3rd test	Average	Concentration of CN in mg/kg
1	07	0,1	0,1	0,2	0,13±0,06	33,826±0,050
2	14	0,1	0,2	0,2	0,16±0,06	41,632±0,050
3	21	0,2	0,3	0,3	0,26±0,06	67,652±0,050
4	28	0,3	0,4	0,3	0,33±0,06	85,866±0,050
5	35	0,3	0,4	0,4	0,36±0,06	93,672±0,050
6	42	0,5	0,5	0,6	0,53±0,06	137,906±0,050
7	49	0,6	0,5	0,6	0,56±0,06	145,712±0,050
8	56	0,6	0,6	0,7	0,63±0,06	163,926±0,050
9	63	0,6	0,7	0,6	0,63±0,06	163,926±0,050
10	70	0,6	0,6	0,7	0,63±0,06	163,926±0,050

According to the above-mentioned results in the tables it can be seen the concentration of cyanide increases with the soaking time and becomes constant after 63 hours for fresh

Sadisa. The dry Mvuama and Sadisa however require 56 hours. What demonstrates that the fresh variety contains more cyanide than in the dry varieties.

Sadisa and Mvuama dry varieties have been shortly dried at 60°C, by means of the stove and they have therefore low concentrations in cyanide compared to fresh Sadisa (5).

Generally the normal concentration of cyanide ranges between 15 and 400 mg/kg of fresh weight and the residues of cyanide can become very important in dried tubers from 30 to 100 mg/kg (5).

The fundamental classification of the cassava varieties is based on the cyanhydric acid concentration they contain (1):
Soft variety contains 50 mg HCN/kg of fresh matter and intermediate variety ranges from 50 mg to 100 mg HCN/kg of fresh matter while Bitter variety has more than 100 mg HCN/kg of it.

Results in this paper show the use of bitter variety furthermore. Figure 4 represents the plots of cyanide concentration versus soaking time for the varieties studied.

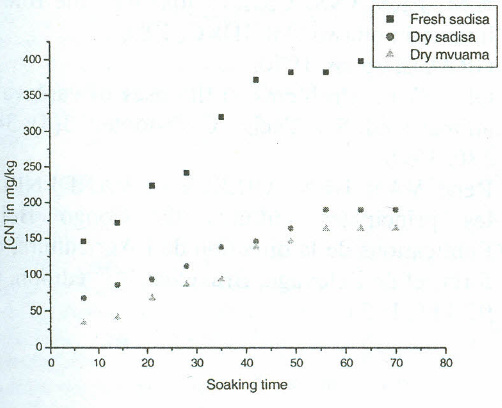

Figure 1: Curves giving the variation of cyanide concentration in varieties of cassava studied according to the soaking time.

It can be seen in this figure that the cyanide concentration is around 398,106 mg/kg for fresh Sadisa while for dry Sadisa and dry Mvuama the cyanide concentration values are respectively 189,946 mg/kg and 163,926 mg/kg.

Extraction speed constants and time of half extraction are calculated and results are presented in following tables:

Table IV: Determination of extraction speed constant "k_1" for (a) Fresh SADISA, (b) Dry SADISA and (c) Dry MVUAMA

a.

Time (hour)	C	X	C − x	$\frac{1}{C-x}$	$\log\frac{1}{C-x}$
7	398,106	145,712	252,394	0,00396	-2,402
14	398,106	171,732	226,374	0,00442	-2,355
21	398,106	223,772	174,334	0,00574	-2,241
28	398,106	241,986	156,120	0,00641	-2,194
k			0,024242±0,003105 h^{-1}		

b.

Time (hour)	C	x	C − x	$\frac{1}{C-x}$	$\log\frac{1}{C-x}$
7	189,946	67,652	122,294	0,0080	-2,087
14	189,946	85,866	104,080	0,0096	-2,017
21	189,946	93,672	96,274	0,0104	-1,984
28	189,946	111,886	78,060	0,0128	-1,892
k			0,020309±0,002507 h^{-1}		

c.

Time (hour)	C	x	C − x	$\frac{1}{C-x}$	$\log\frac{1}{C-x}$
7	163,926	33,826	130,100	0,0076	-2,114
14	163,926	41,632	122,294	0,0082	-2,087
21	163,926	67,652	96,274	0,0104	-1,984
28	163,926	85,866	78,060	0,0128	-1,892
k			0,025277±0,003933 h^{-1}		

Table V: Speed constants and times of half extraction for the studied varieties.

Samples	Speed constant k_1 ($hour^{-1}$)	Time of half extraction $\tau_{1/2}$ (hour)
SADISA(fresh)	0,024242±0,003105	28,587 h
SADISA(dry)	0,020309±0,002507	34,123 h
MVUAMA(dry)	0,025277±0,003933	27,416 h

In this table it can be seen that after at least three days, all the concentration in free cyanide is eliminated for all the species (samples). It can also be seen in this table the kinetic activity of water (k_1) depends on the species of cassava ($k_1(Dry\ mvuama) \succ k_1(Fresh\ sadisa) \succ k_1(Dry\ sadisa)$) and for the same species it depends on the physical structure
($k_1(Fresh\ sadisa) \succ k_1(Dry\ mvuama)$).

The true equilibrium constants of extraction and standard free enthalpy (ΔG°) deduced are presented in the table below:

Table VI:

Variety	K_{truc}	$\Delta G^0 (\frac{J}{mol})$
Sadisa (fresh)	1,011±0,001	- 27,286±0,005
Sadisa (dry)	1,067±0,003	- 161,751±0,001
Mvuama (dry)	1,003±0,001	- 7,471±0,001

The extraction standard free enthalpies of Gibbs for studded varieties are negative, which translate the spontaneousness.

CONCLUSION

To the light of the results gotten in this work, It has been possible to show that the almost total elimination of cyanide to cold weather is done after 3 days, as expressed by extraction half times, with the help of the classic kinetic formalism, while treating the process of cyanide extraction in cassava like a first-order reaction.

The kinetic constants of extraction show that the elimination of cyanide is faster with mvuama variety than sadisa's one.

The negative value of the standard free enthalpy attests that the process is spontaneous.

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