Effects of Solvent/Solid Ratio and Temperature on the Kinetics of Vitamin C Extraction from *Musa Acuminata*

Khairul Anwar Mohamad Said[1], Ibrahim Yakub [2] and Nurul Ain Mohamed Alipah [3]
[1,2,3]*Department of Chemical Engineering, Universiti Malaysia Sarawak,*
Kota Samarahan, Malaysia.
[1]*Email: mskanwar@feng.unimas.my*
[2]*yibrahim@feng.unimas.my*
[3]*Email: 3mhdplh@yahoo.com*

RETRACTED

Abstract

This work studied on the kinetics of Vitamin C extraction from banana peel at different solvent/solid concentration and temperature. Musa Acuminata was ground into smaller sizes and were contacted with methanol as a solvent in an ultrasonic bath. To study the effect of solvent/solid ratio, [illegible], 5.0 and 10.0 ml/g ratio were used for the extraction at fixed temperature. Then, the temperature was varied with the heating element available in the ultrasonic bath at 30, 45 and 60 °C to study the effect of temperature on the extraction kinetics. It was found that high solvent/solid ratio (10 ml/g) provides more solute-solvent contact and prevents the extracted Vitamin C from coming to contact with the air. Besides, higher temperature (60 °C) contributes sufficient kinetic energy for Vitamin C distribution in the solvent which is important to prevent degradation with air. The best fitted kinetic model for Vitamin C extraction from Musa Acuminata is Ana et al. (2007) with equilibrium concentration of 0.05 g/L and 0.40 g/L.hr extraction rate

Keywords: *kinetic model, vitamin C, solid/solvent ratio, temperature*

1. Introduction

Bananas and plantains are great source of calories, carbohydrate, potassium, starch, provitamin A and other carotenoids. Due to the contents of phytochemicals compounds, bananas exhibit biological properties such as antioxidants, antimicrobial, anti-ulcerogenic, anti-inflammatory, anti-proliferative and anticancer activities [illegible]. More importantly, banana is an antioxidant-rich fruit because in common, a bright colored fruit indicates the presence of antioxidants.

Antioxidants are chemicals that resist or neutralize oxidation in cells. Every dietary source of antioxidants comes from secondary plant metabolites. It scavenge free radicals by inhibiting reaction within cells brought about by dioxygen or peroxide molecules, also called reactive nitrogen species. Flavonoids or [illegible]flavonoids are secondary plant metabolites and the majority of its function was antioxidants which commonly found in food and beverages [2].

In general, ascorbic acid or Vitamin C is a natural antioxidant that primarily exists in fruits and vegetables which is available in its reduced form as L-ascorbic acid and its oxidized form as L dehydroascorbic acid [3]. Vitamin C or ascorbic acid is an antioxidant that is soluble in water, unstable, easily oxidized acid and can be deteriorated by oxygen, alkali and high temperature.

For the last few years, the consumer demand of nature-derived products gave a rising impact on various areas like food industry, nutraceuticals, cosmetics, flavors/fragrances, and also the pharmaceutical industry [4]. Many new extraction technologies like ultrasonic-assisted extraction,

Manuscript History:
Received 12 August, 2015, Revised 17 September, 2015, Accepted 21 September, 2015, Published 30 September, 2015

e-ISSN 2289-7771

accelerated solvent extraction, microwave-assisted extraction, supercritical fluid extraction, subcritical water extraction and enzyme-assisted extraction are used to help increase extractions. These new techniques have been developed and they are faster, have better extractions and less solvent usage. To meet the high consumer demand, many processes requires optimization, process development for various new products [5].

The most common technique used to take extracts with high antioxidants activity is direct extraction using solvents [6][7][8]. However, there are some disadvantages when using those techniques such as long extraction time and high solvent consumption. For those reason, the application of ultrasound assisted extraction (UAE) offers a lot of benefits including the less usage of solvents, low temperature, time saving and low water consumption for extraction [9]. Ultrasonic wave accelerate cell disintegration due to intense sonication causes enzymes or proteins to be released from cells. The cell membrane must be destructed in order to extract it. The mechanical effects of ultrasound give faster, greater and more complete penetration of solvent into cellular materials and imp[illegible] mass transfer. Some of the studies used ultrasonic-assisted extraction method including extracti[illegible]henols from rice bran [10], extraction of pomegranate (*Punica granatum L.*) seed oil [11] an[illegible]actio[illegible]f Epimedin C from fresh leaves of *Epimedium* [12].

In this study, the kinetic of Vitamin C extraction from banana peel[illegible]as e[illegible]luate[illegible]sing linearized Ana et al. (2007) method because it fitted the model so well. The [illegible]d us[illegible] in this extraction resembles that of hydrodistillation but using ultrasonic wave to pr[illegible]de he[illegible]nuously.

2. Materials and methods

Banana of the species *Musa Acuminata* was obt[illegible]ed loc[illegible]y. The peel was shredded into small pieces, cleaned and freeze-dried for an hour. The w[illegible] of b[illegible]na peel are consistent around 5mm whereas the length are varied. All banana peel [illegible]as clea[illegible]n municipal tap water. A total of 10 g banana peel was placed in a 250 ml beaker tha[illegible]bmerged in an Elmasonic S900H ultrasonic bath (Elma Schmidbauer GmbH, Germany) at a co[illegible]nt[illegible]r of 2000 W and ultrasonic frequency at 37 kHz. The solvent used was 60% metha[illegible]whic[illegible]as added into the beaker at different solvent/solid proportion (4.5, 5.0 and 10.0 ml/g)[illegible]e t[illegible]perat[illegible]e was also varied at 30, 45 and 60 °C to study the effect of temperature on extraction [illegible]ic wave. Each parameter configuration are repeated three times where the final val[illegible]re ba[illegible]n average. In an interval of 15 minutes, a sample was taken from the solvent to determi[illegible]Vitamin[illegible] content using titration method.

Titration method in [illegible]s st[illegible]was conducted using starch solution, iodine solution and vitamin C standard. Starch indi[illegible]or solution[illegible].5%) was prepared by mixing 0.25 g of soluble starch (corn flour) with 50 ml of nea[illegible]ili[illegible] water in a 100 ml conical flask. It was stirred to let it dissolve and cooled before usage. Iodine[illegible]tion[illegible]0.005 mol/liter was prepared by adding 2 g of potassium iodide and 1.3 g of iodine i[illegible]100[illegible]aker. A few ml of distilled water was added and swirl for a few minutes until iodi[illegible]s d[illegible]lved. Iodine solution was transferred to a 1 liter volumetric flask and the solution was filled [illegible]e liter mark with distilled water. 1ml of sample was taken and was diluted in 250ml conica[illegible]k with 200ml of distilled water. 50ml aliquot of the solution was taken for titration and mixed with [illegible] ml starch solution and diluted again with 200ml of distilled water. The sample was again titrated with 0.005 mol/liter iodine solution. The endpoint of the titration is identified as the first permanent trace of a dark blue-black colour due to the starchiodine complex. The titration was repeated three times with same amount of aliquots of sample solution until concordant results were obtained. The average of iodine used was calculated.

3. Results and discussion

Figure 1 shows the effect of sonication time with different solvent/solid ratio at 30 °C on the extraction yield of Vitamin C from banana peel. The methanol concentration used throughout this

e-ISSN 2289-7771

experiment was kept constant at 60%. Initially, the yield can be seen to increase at the first 15 mins especially when the solvent/solid ratio used was 4.5 ml/g where the amount of extracted vitamin C reach 0.222 mg/g. This amount can be translated to a rate of 0.015 mg/g per minute. However after that, the extraction of the banana peel using this solvent/solid ratio yielded less Vitamin C compared to the other solvent/solid ratio which continued to increase until the 30th minute end up at 0.137 mg/g followed by slight increment to 0.153 mg/g. This shows that Vitamin C experienced degradation earlier when 45 ml of solvent was used compared to when using higher volume of solvent. In 1988, Mason and Lorimer found that this phenomenon happens because oxidation rate of vitamin C are further increase with ultrasound [13]. Although this studied almost 30 years old, several other researcher has also verified the impact of ultrasound towards antioxidants especially at lower temperature [14][15].

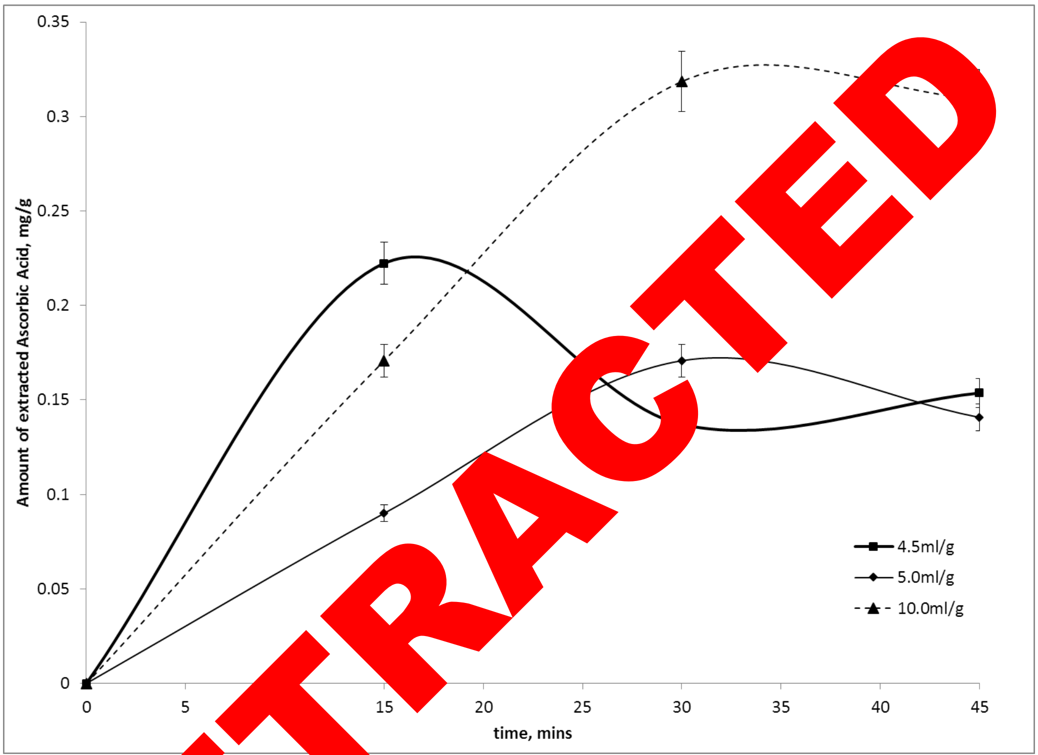

Figure 1. Extraction yield of Vitamin C from banana peel at solvent-to-solid ratio; 4.5ml/g, 5ml/g, 10ml/g, extraction temperature of 30 °C; and methanol concentration of 60%.

Figure 2 shows the effect of sonication time on the extraction yield of Vitamin C from banana peel with different solvent/solid ratio at 45 °C. Similar pattern can be seen for all three systems where the yield increased at the first 15 mins (0.087 mg/g, 0.219 mg/g and 0.305 mg/g for 4.5 ml/g, 5.0 ml/g and 10.0 ml/g respectively.) with extraction in 10.0 ml/g solid/solvent ratio experienced the steepest increase in yield at rate of 0.020 mg/g per minutes, followed by extraction in 5.0 ml/g solid/solvent ratio. This shows that increasing the temperature to 45 °C only improved the extraction of Vitamin C in high solid-to-solvent ratio while reducing the performance of the low solvent concentration. Based on Figure 1 until 3, the trend show that there are two stages of extraction; the rapid phase until 30th minute while slow phase are refer to the plateau trend line. Rapid diffusion phase refer to the initial stage of process involve diffusion from the surface of particles including damaged cell walls. On the other hand, slow diffusion phase indicate the diffusion from inside the particles [16]. Figure 2 show that 10 ml/g solvent/solid ratio experienced sudden reduction of yield from 0.420 mg/g high to 0.267 mg/g low. This

e-ISSN 2289-7771

sudden decrease might cause by insufficient kinetic energy to diffuse the dissolved solute within particles of banana peels.

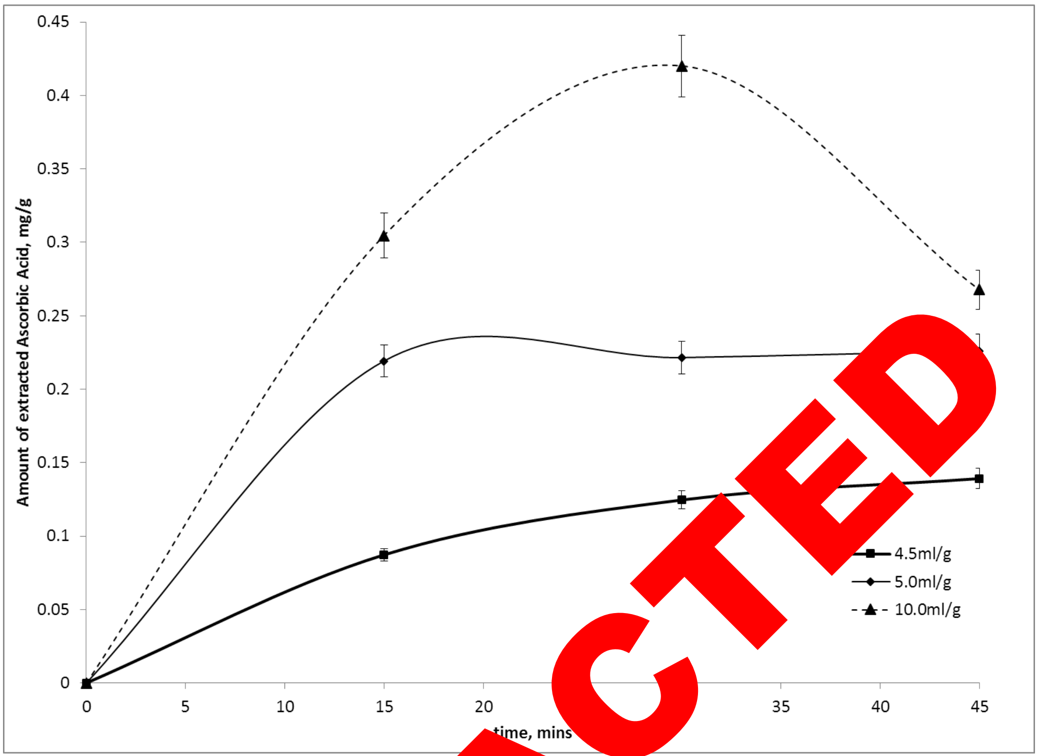

Figure 2. Extraction yield of Vitamin C from banana peel at solvent-to-solid ratio; 4.5ml/g, 5ml/g, 10ml/g; extraction temperature of 45 °C; and methanol concentration of 60%.

Figure 3 shows the effect of extraction time at a higher temperature that is 60 °C. The extraction became preferable at 10.0 ml/g solvent/solid ratio where the yield increases until around the 30th minutes at 0.428 mg/g and did not experience severe Vitamin C reduction. Nevertheless, solvent/solid ratio of 4.5 ml/g and 5.0 ml/g only managed to reach as high as 0.120 mg/g and 0.150 mg/g respectively after a duration of 30 minutes. This corroborated the findings found on Figure 2 as diluted mixture of methanol and vitamin C prevents the contact between the vitamin C and the air. The reason behind this phenomenon was in low amount of solvent, the solution is concentrated with the extracts that exposed the Vitamin C molecules closer to the air which caused in degradation [1]. It can be also observed from the three figures the amount of vitamin C extracted in the lower concentration of methanol (4.5 and 5.0 ml/g solid/solvent ratio) decreased with increasing temperature. On the other hand, high temperature (60 °C) provides enough energy for homogenous distribution of Vitamin C in the solvent contributing to the steep concentration gradient in a stretched period of extraction time.

e-ISSN 2289-7771

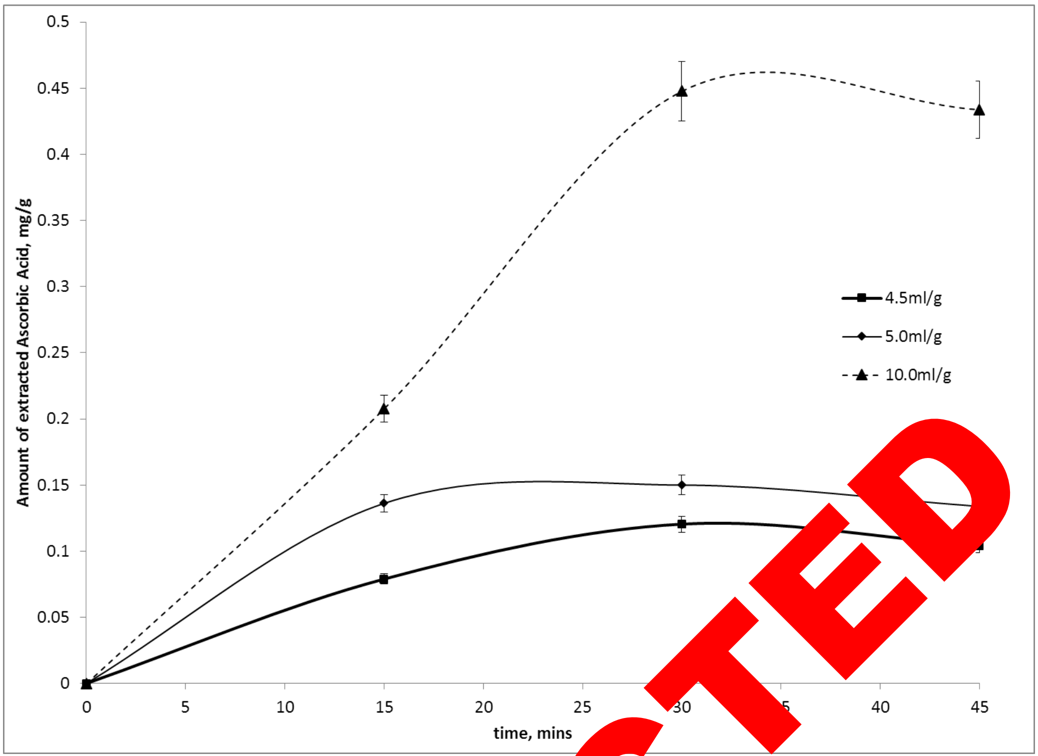

Figure 3. Extraction yield of Vitamin C from banana peel at solvent-to-solid ratio; 4.5ml/g, 5ml/g, 10ml/g; extraction temperature of 60 °C; and ethanol concentration of 60%.

It is important to study the kinetic of Vitamin C extraction from the banana peel into the solvent with the aid of the ultrasonic wave. The kinetic mechanism was studied with regard to different solvent/solid ratio at the temperature that produced Vitamin C the most that was 60 °C and with regard to different temperature at the solvent/solid ratio that extracted Vitamin C the most that was 10.0 ml/g. The linearization according to Ana et al. (2007) method (as in Eq. 1) has resulted Figure 4 and 5 respectively. Model by Ana et al. (2007) was originally inspired by Peleg model which was developed in order to study the rate of sorption (moisture content vs time) [17]. Even though, medium of study was different but Ana et al. (2007) has confirmed that the extraction curve between (concentration of antioxidant vs time and moisture content vs time) has a similarity in shape. Based on the same concept, a new model was developed by Ana et al. (2007) which assume the form of Eq. 1. It can be seen from both figures that the model fits all experimental data with R-squared values ranging from 0.8 to 0.99.

$$t/C = k_1 + k_2 t \quad (1)$$

where t is the time (min); C is the concentration of Vitamin C in the solvent at time t (mg/ml); k_1 is the extraction rate constant which is related to the extraction rate $B_o = 1/k_1$ at $t=t_o$; and k_2 is the extraction capacity constant which is the reciprocal of the concentration at equilibrium $C_e = 1/k_2$ [2].

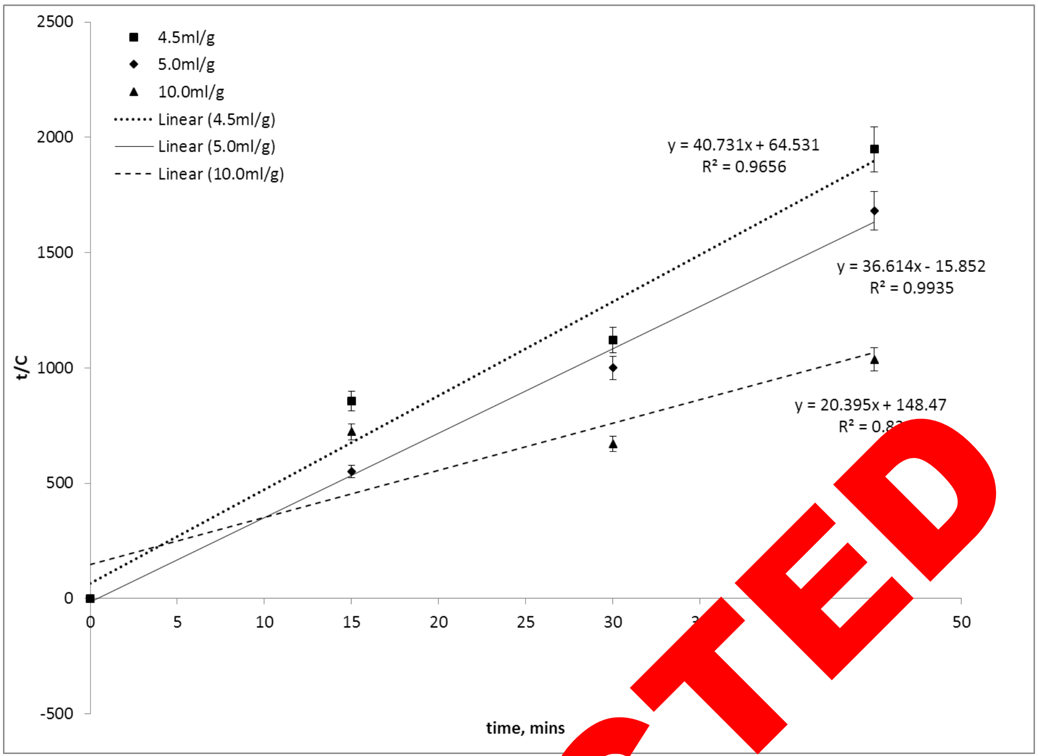

Figure 4. Kinetic model of Vitamic C extraction yield from banana peel at; different solid/solvent ratio; and fixed temperature of 60 °C.

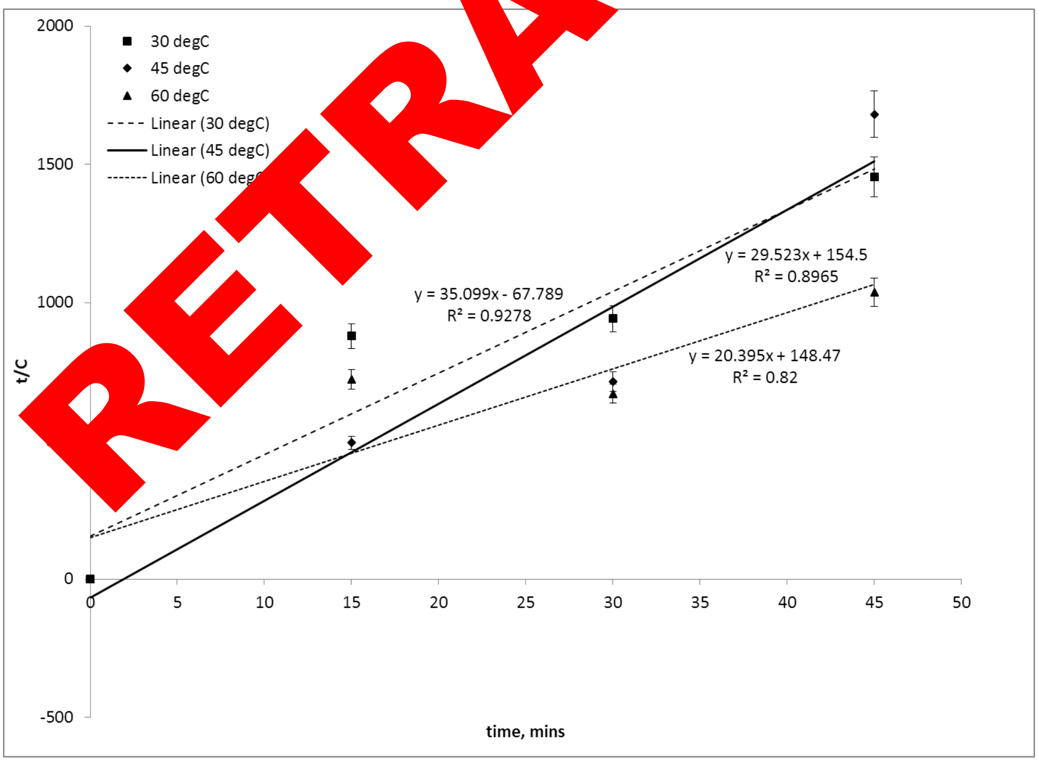

Figure 5. Kinetic model of Vitamic C extraction yield from banana peel at; different temperature; and fixed solvent/solid ratio of 10.0 mg/l.

e-ISSN 2289-7771

Table 1 enlists all of the parameters in Ana et al. (2007) model for all selected experimental data. At 60 °C, the equilibrium concentration of Vitamin C increased as the solvent/solid ratio was increased because of the high concentration gradient provided with the high solvent volume. However, the extraction rate at the initial point was reduced when changing the solvent/solid ratio from 4.5 to 10.0 ml/g.

Table 1. Ana et al. (2007) model parameters for Vitamic C extraction from banana peel.

Parameter	60 °C			45 °C	30 °C
Solvent/solid ratio (ml/g)	4.5	5.0	10.0	10.0	10.0
k_1 (L.min/g)	64.531	-15.852	148.47	-67.789	154.50
k_2 (L/g)	40.731	36.614	20.395	33.162	[illegible]
B_o (g/L.hr)	0.930	-3.785	0.404	-0.885	[illegible]
C_e (g/L)	0.025	0.027	0.049	[illegible]	[illegible]

This is because of the continuous degradation of Vitamin C in the system provided more space for Vitamin C leaching into solvent which is quicker in 4.5 ml/g solvent/solid ratio. On the other hand, the extraction rate is negative when 5.0 ml/g solvent/solid ratio was used because of the same reason discussed previously which proven that Vitamin C degradation was higher than its extraction. As the temperature was lowered, the equilibrium concentration of Vitamin C and the extraction rate decreased. The extraction rate is also negative at 45 °C showing higher degradation rate compared to the extraction rate. Although the results in this study is contrary to existing knowledge, there are also several study that experience increase in extraction rate at higher temperature. Extraction of phenolic compound from grape seed show that every increment of temperature from 20 to 80°C will resulting an increase of extraction yield from 0.071 $kg_{\text{Gallic Acid Equivalent}}$ /$kg_{\text{dry basis}}$ at 25°C to 0.130 $kg_{\text{Gallic Acid Equivalent}}$ /$kg_{\text{dry basis}}$ at 80°C after 200 minutes of continuous extraction [illegible]. In addition, extraction of phenolic content from grape pomace [19] and investigation of thermal treatment towards vitamin C contents from pomegranate juice further justified result found [illegible] where the latter study show constant concentration of vitamin C at 90°C for a period of [illegible] to [illegible] minutes [20]. From this similar study case, it is safe to assume that increase of temperature [illegible] further increase extraction yield without disregarding the possibility of antioxidant degradation at high temperature. Higher temperature may promote solubility of extracts in solvent and initiate sudden increment of diffusion rate followed by faster mass transfer rate.

4. Conclusion

Musa Acuminata was used as a precursor for Vitamin C extraction as its potential has yet to be studied. T[illegible]s affecting the performance of this solid-liquid extraction were studied. First of all, the solvent/solid ratio was varied from 4.5 to 5.0 to 10.0 ml/g. It was learnt that low solvent volume could induce high initial extraction rate (0.93 g/L.hr) but it would experience early degradation. As the solvent volume was increased, more vitamin C can be extracted (4.5 mg/g of banana peel). Secondly, the effect of temperature was investigated at 30, 45 and 60 °C where it was discovered that 60 °C was able to provide enough kinetic energy for both extraction and homogeneity of Vitamin C distribution. In fact, according to the Ana et al. (2007) kinetic model that was found to be best-fitted the empirical data, the highest equilibrium concentration of Vitamin C (0.05 g/L) was achieved at 10 ml/g solvent/solid ratio and 60 °C.

e-ISSN 2289-7771

Acknowledgements

The author gratefully acknowledges Universiti Malaysia Sarawak and Ministry of Education Malaysia for technical and financial support through Research Acculturation Grant Scheme (RAGS) no: E14099/F02/69/943/2012(44).

References

[1] F.C. Abdullah, L.V. Yap, Y. Mohammad Wali, H.S, Sundaraj, S. Khamis, Peeling the Scientific Facts of Banana. , (IAB), International Islamic Academy for Life Sciences & Biotechnology, Universiti Selangor., Shah Alam, Selangor., 2011.
[2] Y.S. Reddy, Extraction Techniques for Food Processing, 1st Editio, Gene-Tech Books, New Delhi, 2006.
[3] K. Iqbal, A. Khan, M.M.A.K. Khattak, Biological Significance of Ascorbic Acid (Vitamin C) in Human Health - A Review, Pakistan J. Nutr. 3 (2004) 5–13.
[4] M. Kassing, U. Jenelten, J. Schenk, J. Strube, A New Approach for Process Development of Plant-Based Extraction Processes, Chem. Eng. Technol. 33 (2010) 377–387. doi:10.100[illegible]eat.2009[illegible].
[5] T.-I. Lafka, V. Sinanoglou, E.S. Lazos, On the extraction and antioxidant activity of phenolic compounds from winery wastes, Food Chem. 104 (2007) 1206–1214. doi:10.1016/j.foodchem.2007.01.068.
[6] B.B. Li, B. Smith, M.M. Hossain, Extraction of phenolics from citrus peels, [illegible]urif. Technol. 48 (2006) 182–188. doi:10.1016/j.seppur.2005.07.005.
[7] G.H. Xu, J.C. Chen, D.H. Liu, Y.H. Zhang, P. Jiang, X.Q. Ye, Minerals, Phenolic Compounds, and Antioxidant Capacity of Citrus Peel Extract by Hot Water, J. Food Sci. 73 (2008) C11–C18. doi:10.1111/j.1750-3841.2007.00546.x.
[8] R. Tabaraki, A. Nateghi, Optimization of ultrasonic-assisted extraction of natural antioxidants from rice bran using response surface methodology, Ultrason. Sonochem. (2011) 1279–1286. http://www.sciencedirect.com/science/article/[illegible]135041[illegible]00976 (accessed July 15, 2014).
[9] A. Bucić-Kojić, M. Planinić, S. Tomas, M. B[illegible], Study of solid–liquid extraction kinetics of total polyphenols from grape seeds, J. Food Eng. 81 [illegible]–242. doi:10.1016/j.jfoodeng.2006.10.027.
[10] I.G. Zigoneanu, L. Williams, Z. Xu, C.[illegible]ablio[illegible], Determination of antioxidant components in rice bran oil extracted by microwave-assisted method, Bioresour. Technol. 99 (2008) 4910–8. doi:10.1016/j.biortech.2007.09.0[illegible]
[11] M.H. Eikani, F. Golmohamm[illegible], S.[illegible]mami, Extraction of pomegranate (Punica granatum L.) seed oil using superheated [illegible]xane, [illegible]ood Bioprod. Process. 90 (2012) 32–36. doi:http://dx.doi.org/10[illegible].2011.01.002.
[12] H.-F. Zhang, X.-H. [illegible]ng, L.-[illegible]ao, Y. Wang, Ultrasonic-assisted extraction of epimedin C from fresh leaves of Epime[illegible]m and extraction mechanism, Innov. Food Sci. Emerg. Technol. 10 (2009) 54–60. doi:http://dx.d[illegible]g/1[illegible]1016/j.ifset.2008.09.007.
[13] T.. Mason, L. J.[illegible]onochemistry , Theory, Applications And Uses Of Ultrasound In Chemistry, Ellis Harwood [illegible]ed, C[illegible]ster West Sussex, 1988.
[14] K.S. S[illegible]lick, Y. Didenko, M.M. Fang, T. Hyeon, K.J. Kolbeck, W.B. McNamara III, et al., Acoustic cavita[illegible]nsequences, Philos. Trans. R. Soc. A. 357 (1999) 335–353. doi:10.1098/rsta.1999.0330.
[15] N. Mehr[illegible]oost, R. Kadkhodaee, M. Taghi, H. Mousavian, Investigation of the effect of ultrasound on ascorbic ac[illegible] of fresh orange juice, in: 7th Int. Chem. Eng. Congr. Exhib. (IChEC 2011), Kish. Iran, 2011.
[16] Y. Tao, Z. Zhang, D.-W. Sun, Kinetic modeling of ultrasound-assisted extraction of phenolic compounds from grape marc: influence of acoustic energy density and temperature., Ultrason. Sonochem. 21 (2014) 1461–9. doi:10.1016/j.ultsonch.2014.01.029.
[17] A.A. Masoumi, Application of Peleg Model to Study Water Absorption in Bean and Chickpea During Soaking, (2000).
[18] A. Bucić-Kojić, H. Sovová, M. Planinić, S. Tomas, Temperature-dependent kinetics of grape seed phenolic compounds extraction: experiment and model., Food Chem. 136 (2013) 1136–40. doi:10.1016/j.foodchem.2012.09.087.
[19] N. Boussetta, E. Vorobiev, V. Deloison, F. Pochez, a. Falcimaigne-Cordin, J.-L. Lanoisellé, Valorisation of grape pomace by the extraction of phenolic antioxidants: Application of high voltage electrical discharges, Food Chem. 128 (2011) 364–370. doi:10.1016/j.foodchem.2011.03.035.

e-ISSN 2289-7771

[20] R. Paul, U. Ghosh, Effect of thermal treatment on ascorbic acid content of pomegranate juice, 11 (2012) 309–313.

Authors

Khairul Anwar Mohamad Said

Khairul Anwar Mohamad Said is a lecturer from the Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak (UNIMAS). He obtained his Masters in Engineering from Universiti Teknologi Malaysia (UTM) and his research interest is separation process including extraction and membrane.

Ibrahim Yakub

Ibrahim Yakub is a lecturer in the Department of Chemical Engineering & Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak (UNIMAS). He obtained his Masters in Engineering (Chemical Process) from Universiti Kebangsaan Malaysia (UKM). His research interest is catalyst development from biomass for energy and environmental applications.

Nurul Ain Mohamad Alipah

Nurul Ain Mohamad Alipah is a postgraduate student of Department Chemical Engineering and Energy Sustainability, Universiti Malaysia Sarawak. She obtained her Bachelor of Science degree (Pure Physics) from Universiti Teknologi Malaysia.

e-ISSN 2289-7771