IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 5, Issue 1, January 2018

"Kinetics Study and Thermal Stability of Red Onion Skin and It's use as Alternative Colorants in Food and Textiles"

Fatima Al-Qadri

Faculty of Science and Arts Shroura, Najran University, Kingdom of Saudi Arabia

Abstract: The kinetic study reactions like rate constants, half-life, and thermodynamic parameters like enthalpy activation energies (ΔE*) (ΔH*), change of activation free energy (ΔG*), change of entropy activation (ΔS*) are measured to determine the stability of anthocyanins extracted from onions skins. The extracted anthocyanins from onions skins in aqueous and ethanol solvent, were stored under darkness for one day at 5 °C. The effect of temperatures, and solvents were determined by kinetic study of the anthocyanins degradation using Spectrophotometric UV/visible techniques Thermodynamic parameters were determined, highest stabilities being observed for the anthocyanins extracted by using water at lower temperatures, such as 40°C than the stabilities of anthocyanins at higher temperatures 70 ^{0}C, and 100°C). The half-life values found for anthocyanins extracted by using water are ,($t_{1/2\ 5}$ 40=27.72 ; $t_{1/2\ 50}$= 13.86 $t_{1/2\ 70}$= 2.69; , $t_{1/2}$ 70= 6.3; $t_{1/2\ 100}$=8.66). The half-life values, for anthocyanins extracted by using ethanol were found were ($t_{1/2\ 40}$= 55.44h; $t_{1/2\ 50}$= 83.49; $t_{1/2}$ 70= 27.8; $t_{1/2\ 100}$=10.5).The rate constants for anthocyanins extracted by water at 40^{0}C, 50^{0}C, 70^{0}C,100^{0}C were (k h^{-1} =2.5, **5**, **7.5**, **81)** respectively; and the results extracted by the ethanol solvent at 40^{0}C, 50^{0}C, 70^{0}C, 100^{0}C (K h^{-1}=**1.25**, **8.3**, **25**, **66**) respectively. The effect of different temperatures on the degradation of anthocyanins from onion skins extracted by water and ethanol were determined by the found values of the activation energies were; Ea (kJ/mol) were 39.10 and 27.88 respectively and K_o (h^{-1}) 1.73, and 4.26. The temperature coefficient Q_{10} at 40–50 °C for water and ethanol were 2, and 1.1respectively, but for Q_{10} at 70–100 °C were 6.79and 2.64 respectively.

Keywords: Anthocyanins; Red-onion ,degradation kinetics, water, Ethanol.

I. INTRODUCTION

The red onion, *Allium cepa* L. (Liliaceae), contains pigments in the dried coats and outer parts of the fleshy scale-leaves of the bulbs. Their reddish-purple coloring has been attributed to anthocyanin pigments such as glycoside(s) of peonidin (Pn) and/or cyanidin (Cy).[l- 6] Four cyanidin-based anthocyanins (1-4) were isolated from the red onion, *Allium cepa* L. Pigments 1 and 3 were identified as cyanidin 3-glucoside (Cy 3-Glc) and 3-malonylglucoside (Cy 3-MaGlc), respectively, by cochromatography with standard pigments. Anthocyanins 2 and 4 were respectively determined as cyanidin 3-laminaribioside (Cy 3-Lam) and 3-malonyllaminaribioside (Cy 3-MaLam), a new anthocyanin, mainly by NMR techniques. Malonylated anthocyanins 3 and 4 were found for the first time in red onions.The colored parts of fresh bulbs of the red onion, *A. cepa* L. vaL 'Kurenai' yielded four pigments (1-4) as red amorphous powders. Chemical and UV -VIS spectral re-characterization according to the methods in the previous report[7].

Anthocyanins are the most abundant flavonoid constituents of fruits and vegetables. The conjugated bonds in their structures, which absorb light at about 500 nm, are the basis for the red, blue and purple colours of fruits, vegetables and their products. Anthocyanin pigments readily degrade during thermal processing which can have a dramatic impact on colour quality and may also affect nutritional properties. This review attempts to summarize some important aspects of anthocyanin degradation during thermal processing. Conclusions regarding the mechanisms and kinetics of anthocyanin degradation during heat treatment are postulated based on current findings.

Anthocyanins are bioactive compounds present in many fruits, vegetables and their products. They are responsible for the wide array of colours present in flowers, petals leaves, fruits and vegetables and are a sub-group within the flavanoids characterized by a C6eC3eC6-skeleton. Since anthocyanins impart a characteristic colour to fruits and vegetables they impact on a key quality parameter by influencing consumer sensory acceptance. A significant property of anthocyanins is their antioxidant activity, which plays an important role in the prevention of neuronal and cardiovascular illnesses, cancer and diabetes, among others[8].

* Author to whom correspondence should be addressed;
E-Mail: fatimaalqadri@gmail.com, Tel.: +966-558918437

The skin on the onion with a variety of useful functions as mentioned above was utilized to dye the silk material. This is not only much beneficial to the environmental protection and economic aspect by making use of the disposed skins as waste but also contributable to the development of biocompatible fabric materials through more scientific framework of the dyeing methods with onion skin pigment by analyzing the extracts and dyeing the fabric. There are many industrial plants which contain natural dyes in Turkey[9].

Kinetics of degradation of anthocyanins in foods Kinetic models are often used for an objective, fast and economic assessment of food safety. Kinetic modeling may also be employed to predict the influence of processing on critical quality parameters. Knowledge of degradation kinetics, including reaction order, rate constant and activation energy, is very vital to predict food quality loss during storage as well as thermal process treatments. One of the important factors to be considered in food processing is the loss of nutrients. Therefore, kinetic studies are needed in order to minimize the undesired change and to optimize quality of specific foods. Anthocyanins degradation under isothermal heating are reported to follow first order kinetics (Equation 1) for juice and concentrate of sour cherry[10] strawberries[11] and blackberries [12].

The use of a first-order model to describe the thermal degradation of anthocyanins has previously been reported[13] , first-order reaction can generally be expressed as Eqs. (1,2,3) with C the anthocyanin concentration at time t, C_0 the initial anthocyanin concentration (lnA/lnA_0 of onions),t the treatment time (min) and k the first-order degradation rate constant (min^{-1}). Degradation kinetics of anthocyanins or other quality parameters during thermal processing are obtained by first determining the rate constants at a given temperature against the time. The key parameters of thermal degradation kinetics i.e. half-life (T½) and activation energy are calculated using following equations

$$A_t = A_0 .\exp(-K \times t) \quad (1)$$

$$T1/2 = \log 2 /K \text{ or } T_{1/2} = 2.303/K \quad (2)$$

$$\text{Log}(K_T / K_0) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (3)$$

Where, A_t is anthocyanin concentration (mg/100 mL) at time t (min)

R is universal gas constant 8.314 $KJmol^{-1}$ C^{-1}

A_0 is initial concentration (t = 0) and $K(min^{-1})$

E_a =is activation energy ($KJ\ mol^{-1}$) is the first order degradation rate constant .

The thermodynamic parameters are of fundamental importance in the extraction of anthocyanins from onions from seeds and can be used to increase the extraction yield [14]. The thermodynamic aspects of interactions of biomolecules with halide ions are of great biological, environmental and industrial importance[15] .The knowledge of heat capacities of substances is important in their processing during various industrial applications, quality control, food engineering, drug designing, and preparation of metal complexes and is directly related to solute-solvent interactions [16-17].

The Aim of this study was to determine the degradation kinetics, including reaction order, rate constant and activation energy during their storage and thermal stability of the anthocyanins from onions extracts in different storage solvents at different temperatures.

Citation :Degradation Kinetics of Anthocyanins from European Cranberrybush (Viburnum opulus L.) Fruit Extracts. 'Effects of Temperature, pH and Storage Solvent' www.mdpi.com/journal/molecules Molecules 2012, 17, 11655-11666; doi:10.3390/molecules171011655

---

2. MATERIALS AND METHODS

2. 1 Onions:

The onions were purchased from the market, and a batch of 200 gm of the outer onions skins was grind to prepare the required samples.

2.2. Preparation of Pigment Extraction (Anthocyanin Extracts from Onion Skins) *Ethanolic and Aqueous*:

The anthocyanins Pigment are known water-soluble and therefore can be extracted by adding (300 ml distilled water and ethanol 96% to the onion skins samples (1:30 w/w). Thorough mixing was followed by centrifuging for 1 h at room temperature and Finally, the supernatant was filtered via bag filter before further analysis then at5^0C . Each sample was extracted twice. The filtrates were quantitatively transferred to a 25mL. volumetric flask and made up to the mark with the requited solvent.

2.3. Analysis

The effect of temperatures and solvents on the degradation of anthocyanins was evaluated for both aqueous and ethanolic extracts. The Half-lives t_{12}(h) ,degradation rate constant k (h^{-1}). and activation parameters Ea (kJ/mole was evaluated for both aqueous and ethanolic at four different temperatures (40°C,50°C, 70 °C, and 100°C). Aliquots of 100 mL of each extracted solution were put in test tubes, kept away from light at 5 °C (in refrigerator) , and equilibrated thermostatic water bath at(40°C,50°C,70 °C, 100°C) respectively.

2.4 Degradation Studies:

The influence of different factors (solvent, and temperatures) measurements of the samples were started after took them from the refrigerator and water baths ,5 mL aliquots of the extract and transferred to a 10 mL volumetric flask and made up to 10 mL, and the analyses were happened at time 0 h, 2, 4,6 , 8,10,12,14 hours. UV-VIS Spectrophotometer (GENESYS 10S UV-Vis v4.004) was used to measure the absorbance of the anthocyanins with time at 330-450 nm.

3.RESULTS AND DISCUSSION

3.1: Anthocyanin degradation kinetics at different temperatures :

The results of kinetic study for thermal degradation of anthocyanins in onion skins are showed by (Figs.1,2 and Table 1.).The figures and the table demonstrates that anthocyanin concentration decreases with time and that the anthocyanins are more rapidly degraded at higher temperatures. This is also reflected in the increase of k values with temperatures. The linear decreases of the anthocyanins degradation followed first order reaction kinetics (figs 1, 2).The obtained results are in agreement with those from the previous studies which showed that storage degradation of anthocyanins from various sources is described by first order reaction kinetics [18–20]. The kinetics for this reaction type can be expressed by the following equations:

$$\ln[A] = \ln[A_0] - kt \qquad (1)$$

$$t_{1/2} = -\ln 0.5 \ / k \qquad (2)$$

Where [A] = Anthocyanin concentration (mg/L) at t = time.
$[A_0]$ = initial anthocyanin concentration(mg/L).
k = reaction rate constant (h^{-1}).
t = reaction time (h).
$t_{1/2}$ = half-life (h).
The rate constants and the half-life values (Table 1) indicate a significant influence of the temperatures and solvents of the of anthocyanins.
The obtained values for the kinetic rate constants and the half-life values are summarized in Table (1).

Table 1. Kinetic parameters of degradation of anthocyanins from Onion skins extracts in different condition

Temp. (°C)	Solvent	k × 10^{-2} (h^{-1})	$t_{1/2}$ (h)
100	Water	8.1	8.66
70	Water	7.5	9.24
50	Water	5	13.86
40	Water	2.5	27.72
100	Ethanol	66	10.5
70	Ethanol	25	27.8
50	Ethanol	8.3	83.49

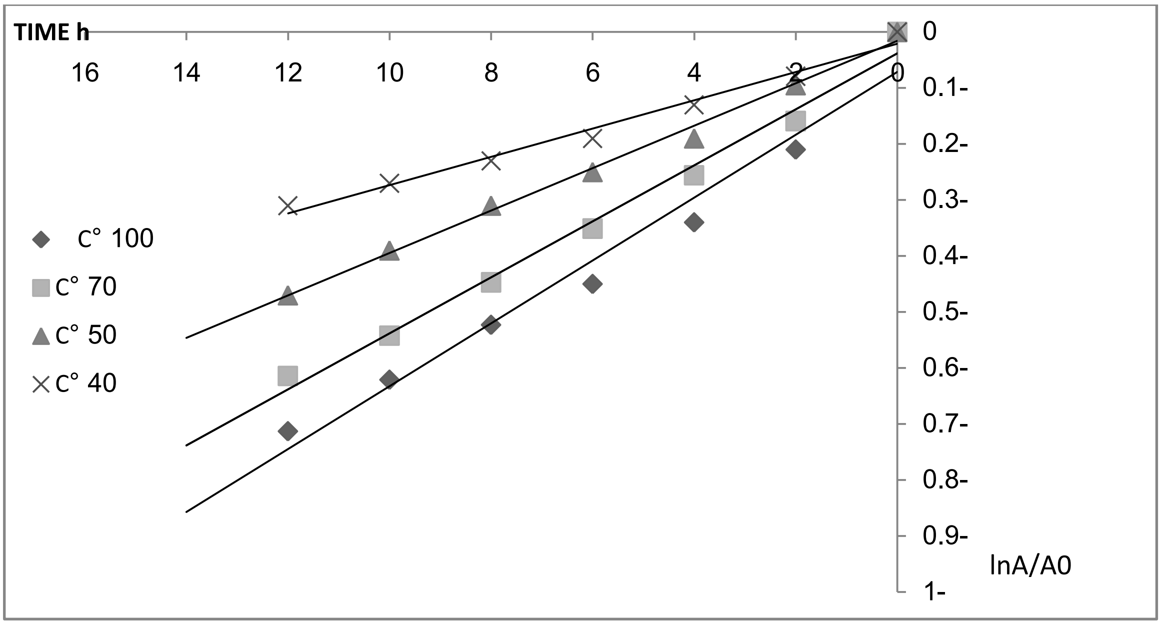

Fig 1 : Thermal Degradation of anthocyanins in onions skins aqueous extract at different temperatures (100 ^{0}C ,70^{0}C ,50^{0}C,40^{0}C) in function of time. The full lines represent the first-order model $\ln[A/A_O]$of the onions.

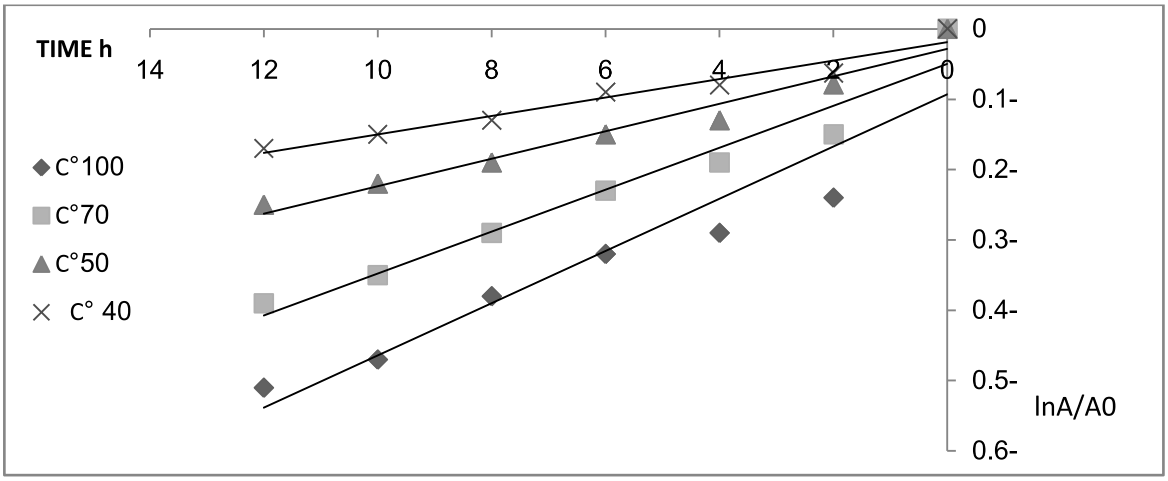

Fig 2 : Thermal Degradation of anthocyanins in onions skins ethanolic extract at different temperatures (100 ^{0}C,70^{0}C,50^{0}C,40^{0}C) in function of time. The full lines represent the first-order model $\ln[A/A_O]$of the onions.

3.2 :By comparing the half-life values, between anthocyanins extracted by water and Ethanol :

3.2.1: half-life values for anthocyanins extracted by water at different temperatures: .

By comparing the half-life values, one can conclude that, at lower temperatures, the anthocyanins of onion skin at 40°C less susceptible to degradation than they are at high temperatures the highest stabilities being observed at lower temperatures, such as, 40°C and 50°C than the stability of the aqueous anthocyanins at higher temperatures at 70 ^{0}C, and 100°C). ($t_{1/2\ 40}$= **2.5**h, $t_{1/2\ 50}$= **5h**, , $t_{1/2}$ 70= **7.5**, $t_{1/2\ 100}$=**8.1**).we observed the degradation of the anthocyanins aqueous extract less than the degradation of the anthocyanins ethanolic extracts.

3.2.2: half-life values for anthocyanins extracted by Ethanol and water at different temperatures:

The half-life values, for anthocyanins extracted by using ethanol was more significant at 40 ^{o}C less susceptible to degradation than they are at high temperatures.

($t_{1/2\ 40}$= 55.44h, $t_{1/2\ 50}$= 83.49, , $t_{1/2}$ 70= **27.8**, $t_{1/2\ 100}$=**10.5**).By comparing between the stability of anthocyanins extracted using ethanol and water, it was observed that the aqueous anthocyanins are more stable than that the anthocyanins extracted by using ethanol.

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 5, Issue 1, January 2018

3.2.3: Temperatures and Solvents effect for thermodynamic activation parameters

The thermodynamics Activation parameter such as activation energy (Ea) Enthalpy of Activation (ΔH^*), Entropy of Activation (ΔS^*) and free energy of Activation (ΔG^*), are better indicator of the solvents and temperatures effect exerted by the solvents and temperatures on the degradation and thereby the stabilities of the anthocyanins.

3.2.3.a : Activation energies (Ea) and Temperatures coefficient (Q_{10})

The thermal stability of the extracts was also evaluated. As expected, the degradation rate of anthocyanins increased with the increase of temperature. To determine the effect of temperature on the kinetics of the degradation process, the constants obtained from Equations (1) and (2) were fitted to an Arrhenius type equation (Equation (3):

$$k = k_0 e^{-Ea/RT} \quad (3)$$

where Ea = the activation energy (kJ/mol); Ko = frequency factor (h^{-1});
R = the universal gas constant (8.314 J/mol·K); T = absolute temperature (K).
The anthocyanin degradation rate constants obtained for each extract were plotted as a function of temperature (Figures 3,4). The calculated activation energies are given in Table 2.

Citation: Solvent Effect on the Enthalpy and Entropy of Activation for the Hydrolysis of Ethyl Cinnamate in Mixed Solvent SystemSingh, J Phys Chem Biophys 2017, 7:1 DOI: 10.4172/2161-0398.1000238

Table 2. Effect of temperature on the degradation of anthocyanins from onion skins extracts.

Solvent	Ea (kJ/mol)	(K_o (h^{-1})	Q10	
			40–50 °C	70–100 °C
Water	39.10	1.73	2	1.1
Ethanol	27.88	4.26	6.79	2.64

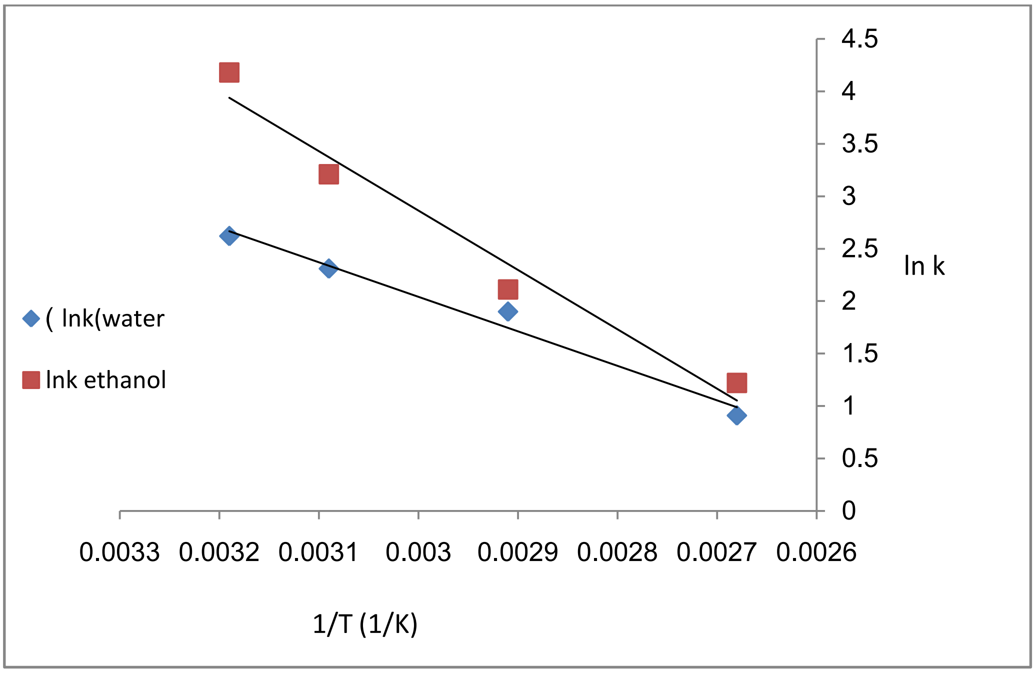

Fig 3: The Arrhenius plots for degradation of anthocyanins in onion extracts with water and Ethanol at different temperatures

IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 5, Issue 1, January 2018

High activation energy indicated that the anthocyanins extracts are more susceptible to degradation by exposure to elevated temperatures. The highest impact of the temperature on the degradation process (the highest value of Ea) was noticed for the anthocyanins extracted by ethanol . while the lowest value of the Ea (lower susceptibility to thermal degradation) was obtained for Anthocyanins extracted in water .The cross influence of the temperatures and solvents on the degradation process of the anthocyanins extracted from onion skins seems to be more significant in case of extracted in the water, The dependence of degradation rate on temperature was also evaluated by calculating the: temperature coefficient Q_{10}, according to Equation (4):

3.2.3.b : Temperatures coefficient (Q_{10}):

Temperature Coefficient Q_{10} .

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10}{t_2 - t_1}} \qquad (4)$$

where Q_{10} = the temperature coefficient, (K^{-1}); $K_{1,2}$ = rate constant (h^{-1}) at temperature $T_{1,2}$ (K).The Q_{10} values were obtained for the degradation of anthocyanins in water ,proving that the influence of the increase of the temperature on the stability of the anthocyanins for studied temperature intervals(40–50°C and 70–100 °C). The lowest temperature coefficient value (**2** K^{-1} at 40–50°C and**1.1** K^{-1} at 70- 100°C) was obtained in water indicating that lower degradations of anthocyanins and the stability of the aqueous anthocyanin.

Different Q_{10} values were obtained for the degradation of anthocyanins in ethanol show the influence of temperatures on the stability of the anthocyanins and are needed to inhibit degradation of anthocyanins, the obtained values were high (6.79 K^{-1} at at 40–50°C) and low value at (2.64 K^{-1} at 70- 100°C).

Activation energy

The results from the present study have provided detailed information regarding the stability of anthocyanins in onion skin extracts, which was strongly dependent on temperature, and solvent. Increasing temperature during heating increased the degradation rate constants of the investigated anthocyanins. The degradation rate proved to be slightly dependent on the nature of the solvent. At the different temperatures (40, 50,70 and100°C) the degradation process was faster in ethanol compared to water . In all the other investigated storage conditions, the stability of anthocyanins was higher in water. It is recommended that the onion skin anthocyanin extracts should be kept at refrigeration temperatures, in a aqueous, environment. The study of the degradation changes of anthocyanin extracts from onion skin at various temperatures, and solvents , supports the potential use of onions skins as source of natural red and yellow pigments for the food and textile industry.

3.2.3.c : Activation energies Enthalpy of Activation (ΔH*), Entropy of Activation (ΔS*) and free energy of Activation (ΔG*):

Enthalpy of Activation (ΔH*), Entropy of Activation (ΔS*) and free energy of Activation (ΔG*), are better indicator of the solvents and temperatures effect exerted by the solvents and temperatures on the degradation and thereby the stabilities of the anthocyanins. These thermodynamics Activation parameter has been calculated with help of Wyne-Jones Eyring [21] equation and absolute rate theory [22] and placed in Table 3.

Table 3: Thermodynamics Activation Parameters of the anthocyanins degradation of onion skins in Water and in ethanol Media (ΔH*and ΔG* in KJ/Mole, ΔS* in J/K/Mole).

Water	Temp (kelvin)	ΔH*	ΔG*	ΔS*
	373	36.09	64.78	**-114**
	343	36.34	57.43	**-122**
	323	36.50	43.2	**-114**
	313	36.6	25.2	**-114**

 DOI 10.17148/IARJSET.2018.519

Ethanol	373	24.78	129	**-31**
	343	25.03	91.7	**-46**
	323	25.2	56.6	**-6**
	313	25.28	57.2	**-62**

The change found in the value of three thermodynamic activation parameters

This finding is indicative of the anthocyanins degradation as explained by Absolute Reaction rate theory and supported by Elsemongy [23] and Singh [24]. From data mention in the Table 3, the values of all of three thermodynamic parameters ΔH^*, ΔG^* and ΔS^*, the value of ΔH^* and ΔS^* goes on decreasing with simultaneous increase in G* values with ethanol than water. From the fundamental thermodynamic

Equation: $\Delta G^* = \Delta H^* - T\Delta S$ (5)

Acknowledgments:

The authors are grateful for the supports for this work provided by Deanship of Scientific Research at the Najran University, KSA with grant number NU/ESCI/14/1.

CONCULISIONS

- The degradation of anthocyanins in a onions skins during thermal and different solvents described by a first-order model.
- Reaction rate constants at and half ives at different condition at different temperatures and different solvents.
- The results from the present study have provided detailed information the effect of temperatures and solvents on the anthocyanins degradation.
- The results reveals the increasing of the anthocyanins degradation rate kinetics rate constants with the increasing temperatures.
- Increasing the values of free energy with anthocyanins extracted using ethanol than water.
- Decreasing of the values of entropies and enthalpies with increasing of the free energies.

REFERENCES

1) G. M. Robinson and R. Robinson, Biochem. J., 25, 1687-1705 (1931).
2) B. J. Brandwein, J. Food Sci., 30, 680-685 (l965).
3) T. Fuleki, J. Food Sci., 34, 365-369 (1969).
4) T. Fuleki, J. Food Sci., 36, 101-104 (1971).
5) C. T. Ou, P. L. Wang, and F. J. Francis, J. Food Sci., 39, 1265-1266 (1974).
6) K. Kenmochi and 0. Katayama, Nippon Shokuhin Kogyo Gakkaishi (in Japanese), 22, 598 H605 (1975).
7) N. Terahara and M. Yamaguchi, Bull. Fac. Hort. Minami-Kyushu Univ. (in Japanese), No. 15,59-64 (1985).
8) Konczak, I., & Zhang, W. (2004). Anthocyanins-more than nature' s colours (2004). Journal of Biomedicine and Biotechnology, 2004(5), 239 - 240.
9) N.Thanker,M.Koyuncu,M.Coskun andA.Guvenc,Turk.J.Med.Sci.,26,289(1996).
10) Cemerog˘lu, B., Veliog˘lu, S., & Is xik, S. (1994). Degradation kinetics of anthocyanins in sour cherry juice and concentrate. Journal of Food Science, 59(6), 1216 -1218.
11) Garzon, G. A., & Wrolstad, R. E. (2002). Comparison of the stability of pelargonidin-based anthocyanins in strawberry juice and concentrate. Journal of Food Science, 67(4), 1288 - 1299.
12) Wang, W. D., & Xu, S. Y. (2007). Degradation kinetics of anthocyanins in blackberry juice and concentrate. Journal of Food Engineering, 82, 271 – 275.
13) Garzon, G. A., & Wrolstad, R. E. (2002). Comparison of the stability of pelargonidin-based anthocyanins in strawberry juice and concentrate Journal of Food Science, 67(4), 1288- 1299.
14) Block, E., 2010. Garlic and Other Alliums: The Lore and the Science. Royal Society of Chemistry, Burlington House. Piccadilly, London, UK.
15) Ko, M.-J., Cheigh, C.-I., Cho, S.-W., Chung, M.-S., 2011. Subcritical water extractionof flavonol quercetin from onion skin. Journal of Food Engineering 102 (4),327–333.
16) Griffiths, G., Trueman, L., Crowther, T., Thomas, B., Smith, B., 2002. Onions a globalbenefit to health. Phytotherapy Research: PTR 16 (7), 603–615.
17)Hole, C., Drew, R., Gray, D., 2000. Humidity and mechanical properties of onion skins.Postharvest Biology and Technology 19 (3), 229–237

IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 5, Issue 1, January 2018

18) Kirca, A.; Özkan, M.; Cemeroğlu, B. Effects of temperature, solid content and pH on the stability of black carrot anthocyanins. Food Chem. 2007, 101, 212–218.
19) Wang, W.-D.; Xu, S.-Y. Degradation kinetics of anthocyanins in blackberry juice and concentrate.J. Food Eng. 2007, 82, 271–275.
20)Moldovan, B.; David, L.; Donca, R.; Chişbora, C. Degradation kinetics of anthocyanins from crude ethanolic extract from sour cherries. Stud. U. Babeş-Bol. Che. 2011, 56, 243–248.
21). Wynne-Jones WF, Eyring H (1935) The absolute rate of reactions in condensed phases. J Chem Phy 3: 492-502.
22) Glasston S, Laidler KJ, Eyring H (1941) The theory of rate process. Mc Graw- Hill Newyork
23) Elsemogy MM, Abu Elamayem MS, Mussa, MNH (1975) Z Physik chem (Neuetold) 94: 69.
24) Singh AK (2016) Solvolysis rate and activation parameters of ethyl acetate in mixed dipolar organic solvent system-A solvent effect. Int J Res Appl Sci Eng Technol 4: 706-710.