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SELÇUK UNIVERSITY

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE

ENCAPSULATION OF MAHONIA (*Mahonia aquifolium*) FRUIT ANTHOCYANINS WITH APRICOT TREE GUM AND DETERMINATION OF ITS HEAT STABILITY

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MS THESIS

Department of Food Engineering

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TEZ KABUL VE ONAYI

Iliasu ALHASSAN tarafından hazırlanan "MAHONYA (*Mahonia aquifolium*) MEYVESİ ANTOSİYANİNLERİNİN KAYISI AĞACI SIZINTI GAMI İLE ENKAPSÜLASYONU VE ISIL STABİLİTESİNİN BELİRLENMESİ" adlı tez çalışması 12/06/2019 tarihinde aşağıdaki jüri tarafından oy birliği ile Selçuk Üniversitesi Fen Bilimleri Enstitüsü Gıda Mühendisliği Anabilim Dalı'nda YÜKSEK LİSANS olarak kabul edilmiştir.

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Bu tez çalışması Selçuk Üniversitesi Bilimsel Araştırma Projeleri (BAP) Koordinatörlüğü tarafından 18201132 nolu proje ile desteklenmiştir.

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Signature

Iliasu ALHASSAN

Date: 12/06/2018

ÖZET

YÜKSEK LİSANS TEZİ

MAHONYA (*Mahonia aquifolium*) MEYVESİ ANTOSİYANİNLERİNİN KAYISI AĞACI SIZINTI GAMI İLE ENKAPSÜLASYONU VE ISIL STABİLİTESİNİN BELİRLENMESİ

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Bu çalışma, *Mahonia aqufolium* meyvesi antosiyaninlerinin farklı duvar materyalleriyle (Kayısı ağacın sızıntı gamı (ATG), Gam arabik (GA), Kayısı ağacın sızıntı gamı ve Gam arabik (ATG + GA) kombinasyonu (50:50), Gam arabik ve Maltodekstrin (MD + GA) kombinasyonu (50:50) ve Kayısı ağacın sızıntı gamı ve Maltodekstrin (ATG + MD) kombinasyonu (50:50)) ile enkapsülasyonu ve kullanılan duvar materyallerinin kapsülleme veriminin araştırılması amacıyla yapılmıştır. Daha sonra kapsüllenmiş örneklerin ısıl stabilitelerinin belirlenmesi amacıyla üç farklı sıcaklıkta (35, 45 ve 50 °C) depolama yapılmıştır. Reaksiyon düzeni birinci dereceden kinetik denklemine göre uygun bulunmuştur.

Enkapsülasyon etkinliği en yüksek ATG+GA kombinasyonunda (% 98.96); en düşük ATG + MD kombinasyonunda (% 96.18) bulunmuştur. Beş duvar malzemesinin de enkapsülasyon etkinliği % 95' in üzerinde çıkmıştır. Genel olarak MD karışımlarında (ATG + MD ve GA + MD) renk bozulması önemli bulunmuştur ($P<0.01$). L *, a * ve b * CIElab parametrelerinin stabilitesi ATG'de en iyi sonucu vermiştir. Tüm duvar malzemeleri için en düşük toplam renk farkı (ΔE), 45 ve 50 °C için ATG (2.77 ± 0.23 ve 4.98 ± 0.24) de, 35 °C için GA (0.31 ± 0.97) da belirlenmiştir. ATG için aktivasyon enerjisi (EA) 37.4221 (kJ mol-1); R2 = 0.9892 iken reaksiyonun sabiti sırasıyla 35, 45 ve 50 ° C'de 0.04, 0.06 ve 0.08 gün^{-1} olarak belirlenmiştir. ATG de depolama sürecinde antosiyaninlerde daha az bozulum görülmüştür.

Anahtar Kelimeler: Antosiyanin, enkapsülasyon, kayısı ağacı sızıntı gamı, *Mahonia aquifolium,* stabilite

ABSTRACT

MS THESIS

ENCAPSULATION OF MAHONIA (*Mahonia aquifolium*) FRUIT ANTHOCYANINS WITH APRICOT TREE GUM AND DETERMINATION OF ITS HEAT STABILITY

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THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE OF SELÇUK UNIVERSITY
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This study was conducted to investigate the encapsulation efficiencies of different wall materials (Apricot tree gum (ATG), Gum Arabic (GA), Apricot tree gum and Gum Arabic (ATG+GA) combination (50:50), Gum Arabic and Maltodextrin (MD+GA) combination (50:50), and Apricot tree gum and Maltodextrin (ATG+MD) combination (50:50)) were used to encapsulate *Mahonia aquifolium* anthocyanins by freeze drying. Then the thermal stabilities of the encapsulated samples were analyzed at three different storage temperature (35, 45 and 50 °C). The order of reaction best fitted in first order equation of kinetics.

The highest encapsulation efficiency was determined in ATG+GA combination (98.96 %) and the least was found in ATG+MD (96.18 %). The encapsulation efficiencies of all the five wall materials were above 95 %.

Generally, color degradation was significant ($p<0.01$) in wall materials with MD combination (ATG+MD and GA+MD). Stability of L*, a*, and b* CIElab parameters were best in ATG. The lowest total color difference (ΔE) for all wall materials under all conditions were 2.77±0.23 and 4.98±0.24 at 45 and 50 °C for ATG and 0.31±0.97 at 35 °C for GA.

The rate constant of reaction for ATG was 0.04, 0.06 and 0.08 day-1 at 35, 45 and 50 °C respectively while the activation energy (Ea) was 37.4221 (kJ mol-1); R2 = 0.9892 appeared to protect the anthocyanins with less degradation throughout storing time.

Keywords: Anthocyanins, Apricot tree gum, Encapsulation, *Mahonia aquifolium*, stability

PREFACE

All praises and thanks be to the most High for bringing us to this far with good health, strength and knowledge to be able to carryout this study.

Above all, I would like to express my profound gratitude to my advisor; Assoc. Prof. Dr. Hacer COKLAR, whose architectural design, knowledge and efforts came out with this study. I would also like to add my deepest-heartfelt thanks to Prof. Dr. Mehmet AKBULUT, whose motivation, guidance, advice and assistance have been helping me keep moving. What a blessing to having such a wonderful advisors of your pedigree by my side. May Allah shower bounties of blessings onto your efforts and provide you with good health, strength and more wisdom to lead us throughout this journey.

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I will also want to register my gratitude to all my family and love ones whose prayers and support have brought me this far especially my wife Ayisha MOHAMMED.

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CONTENTS

SYMBOLS AND ABBREVIATIONS

Symbols

°C	: degree celcious
pH	: power of hydrogen concentration
R^2	: correlation constant
L*	: color lightness
a*	: color redness
b*	: color yellowness
C*	: Chroma
$^{\circ}h$	: hue angle
%	: percentage
β	: beta
g	: gram
$t_{1/2}$	: half-life
M	: molar
Q_{10}	: temperature coefficient
k	: rate constant of reaction
E_a	: activation energy
R	: ideal gas constant
°K	: degree kelvin
J	: joule
T	: temperature

Abbreviations

etc.	: and many more
i.e.	: that is
et al.	: and friends
BC	: before birth of Christ
DE	: dextrose equivalent
GE	: gelatin
MD	: maltodextrin
GA	: gam Arabic
ATG	: apricot tree gum
EE	: encapsulation efficiency
EP	: encapsulation productivity
RH	: relative humidity
mL	: milliliter
min	: minute
ΔE	: total color difference
a_w	: water activity
sec.	: seconds
SSC	: soluble solid content
rpm	: round per minute
SAC	: surface anthocyanin content

TAC	: total anthocyanin content
nm	: nanometer
Eqn.	: equation
D	: dilution factor
DW	: dry weight
mg	: milligram
l	: length of cell path
t	: time
kg	: kilogram
h	: hour

1. INTRODUCTION

In modern technologies, encapsulation is one of the finest and competitive technology used in the industries. Ever since it was introduced in the late 1900s, it has gained attention in sectors like pharmaceuticals, cosmetics and food industries. Encapsulation was defined by Robert and Fredes (2015) as a procedure used to protect an active compound, being it solid, liquid and/or gas from environmental conditions like light, heat, oxygen, humidity, etc. by entrapping the active compound in a matrix or polymeric wall (encapsulating agent). Encapsulation consist of two main parts i.e. the wall material or matrix and the active or core material.

Generally in the food industries, encapsulation technology has been successfully used to encapsulate food ingredients such as vitamins by Wilson and Shah (2007), fish oil by Klaypradit and Huang (2008), orange oil by Edris and Bergnstahl (2001), enzymes by Anjani et al. (2007), flavor by Madene et al. (2006), milkfat by Rosenberg and Young (1993), Lactobacillus acidophilus NCFM by Jiang et al. (2016), polyphenols by Zhong and Bhandari (2010), Bifidobacterium adolescentis by Wang et al. (2015), lycopene by Silva et al. (2012), anthocyanins of berries Robert and Fredes (2015), lipid by Adachi (1996)and protein by Erfani et al. (2018)as core or active materials and the most frequently used wall materials are gum Arabic, maltodextrin, whey protein isolate, casein and pectin.

Coloring of food products have been a major challenging component in the food producing factories for centuries. This has been so due to the mindset of individuals and consumers. Consumers mostly used color as a quality parameter when making a choice for any food product or raw material especially fruits and vegetables. During the olden days, synthetic dyes were included in food coloring until researchers discovered that some of them are carriers of toxic substances which are highly risked to human health.

In fruits and vegetables, anthocyanins are the most naturally occurring pigment. Anthocyanins are natural pigmented flavonoids that are responsible for red, purple and blue color in fruits and vegetables (Novotny et al., 2012). According to Dia et al. (2015), cyanidin, delphinidin, malvidin, pelargonidin, peonidin, and petunidin are the well-known and frequent occurring anthocyanins in nature.

Anthocyanins, being responsible for the color of fruits and flowers of the plants helps attracts insects for pollination and attention of animals including man towards the plants for their fruits (Kong et al., 2003). Anthocyanins are also known of their health

beneficiary properties. Those beneficiaries are antidiabetic, antioxidant and anticancer effects (Dia et al., 2015). Other health promoting benefits of anthocyanins includes relief of oxidative stress, prevention of cardiovascular diseases, anti-inflammatory activity, prevention of obesity, improvement of eye vision and antimicrobial activity (Zhong and Bhandari, 2010).

The characteristics features of the anthocyanins exbiting wide range of color variations from red to blue in different pH mediums and their abundance positive health properties has made it one of the most dominating natural coloring agent not only in food sector but also in textiles, cosmetics and pharmaceutical industries. Some of the sources of anthocyanins are apples, cherries, figs, eggplant, pomegranate, peach, cranberries, grapes etc.(Delgado-Vargas et al., 2000). Kırca et al. (2006) used black carrot anthocyanins as a natural colorant in fruits juices and nectars.

Wrolstad et al. (2005) notified that color quality of foodstuffs anthocyanins and their nutritional properties can be highly affected by the anthocyanins degradation of during processing and storage. Total color stabilization together with some little variation can well be achieve only when there are more aromatic acyl residue from cinnamoyl acid origin attached to the anthocyanin structures (Brouillard et al., 2003). Pigment stability can be increased by, increasing glycosidic substitution e.g. increasing cinnamic acids with sugar residue acylation,protecting the anthocyanins into getting reaction to peroxidase, Glycosidase enzymes and polyphenoloxidase, and protecting the products from light exposure (Revilla et al., 2001)

The low stability of anthocyanins and their respective colors has bring to an alert to improve their stability through encapsulation. Different sources of anthocyanins have been encapsulated and used as colorant in various literature studies (Robert et al., 2010; Tonon et al., 2010; Zhong and Bhandari, 2010; Jiménez-Aguilar et al., 2011).

Mahonia aquifolium has also been in the use in Turkey for many years as ornamental plant in Aegean, Marmara and Central Anatolia (Gunduz, 2013). This study is aimed to investigate the encapsulation efficiency of *Mahonia aquifolium* fruit anthocyanins with apricot tree gum, gum arabic and their combinations, and with maltodextrin as wall materials and then determine the stability of the encapsulated anthocyanins under storage temperatures of 35, 45 and 50 °C for 50 days.

The byproducts of this study which are encapsulated *Mahonia aquifolium* anthocyanins could be an alternative color additive in the food industries to improve the color stabilities of food products such as confectionaries, fruit juices, marmalades, jams,

etc. It could be used in industries like pharmaceuticals and cosmetics especially make-ups products.

2. REVIEW OF LITERATURE

As way back 400 BC, Egyptians used coloring in candy and wines. During the late 1800s synthetic colors got a boost in food industries which saw colors being used to decorate and sometimes mask low quality foods. Some the synthetic colors carriers of toxic substances called for law enforcement in early 1900s to control the synthetic color usage in the food industries. For the past twenty years, consumers are more conscious about the source and contents of their foods and prefers those that are totally from natural sources. This mindset of consumers has uplift the use of natural color additives in recent development of food production. The presence of consumer protection law in the legislature has been keeping color suppliers on their toe striving to improve the quality and stability of the approved colors in the food industries to meet the average demands of customers (Downham and Collins, 2000).

Day in day out, scientist keep on discovering and inventing new technologies to either develop to update the existing ones and or create a completely new technology to replace the outmoded ones. Ever since natural pigments became solely colorant material to use in coloring the food products in the industries by way of meeting the interest of the consumers, scientific researchers came out a new technology called 'encapsulation' to help fight the instability problems of the natural pigments. Today, encapsulation technology has been among the widest grown technology use in the major companies under food sector.

Speranza et al. (2017) defined encapsulation as a process whereby an active substance (lipid, flavor, anthocyanin, vitamin, etc.) is protected from external factors by enclosing it in a defensive material (wall material) to produce a varying sizes (micro, macro or Nano) of encapsulates. Encapsulation as defined above shows that almost all available food ingredients such color additive agents, vitamins, proteins, aromatic materials, lipids and oils, etc. has been used in encapsulation as active core materials as reported by Augustin and Hemar (2009). However, focusing our attention to the encapsulation of natural colorant, anthocyanins and carotenoids takes the lead.

The growing interest of anthocyanins as natural colorant is due their wide range of colors and health benefits. Although anthocyanins has vast potentials usage in the food, cosmetics and pharmaceutical industries, their application has been limited due to their low extraction yield and relative instability (Castaneda-Ovando et al., 2009). In nature, anthocyanins are extremely unstable and easily prone to degradation by external

factors such as enzymes, pH, temperature, light, oxygen, metal ions, and other factors (Wu et al., 2018). This instability problem has shun food producers away from including anthocyanins into food formulation despite the vast health promoting effects of the anthocyanins when added to human diet. Encapsulation have been applied to anthocyanins of series of different fruits and vegetables by researchers on different studies with the aim of finding the best antidote to remedy the instability problem of anthocyanins (Rein, 2005; Bilek et al., 2017; de Moura et al., 2018).

Biological properties of fruits of cranberry bush (*Viburnum opulus L.*) are known because of anthocyanins availability in their berries. Aqueous and ethanolic extracts of the fruits were stored at 2, 37 and 75 °C in the absence of light for 7 days with PH values 3 and 7 were investigated for their anthocyanins stability. Aqueous extract under 75 °C storage temperature and pH = 7 showed the lowest stability of anthocyanins with constant rate (0.3488 h^{-1}) and half-life (1.98 h). The total anthocyanin content and storage time were well correlated with coefficient determinants (R2) ranging between 0.9298 and 0.9971. The results showed kinetics first-order reaction of the anthocyanin degradation during storage under all conditions (Moldovan et al., 2012).

Roselle which is traditionally a raw material for red bright beverage is rich in anthocyanins. Their anthocyanins are mostly destructed when they get in contact to heat and different pH mediums during processing. In this study, roselle extract was investigated for antioxidant properties, anthocyanin content (in different pH mediums), color changes and heat stability by kinetic equations. A good antioxidant ability and rich anthocyanins were determined from the roselle extract. In an acidic medium, the anthocyanins showed a certain level of resistance to heat and good color stability. However, in a low acidic medium, a fast rate of anthocyanin degradation and significant color changes were observed. The anthocyanins activation energies ranged between 31.4–74.9 and 55.8–95.7 kJ/mol in low acidic and acidic mediums respectively. In their conclusion remarks of the study, they reported that roselle anthocyanins in an acidic medium could be good functional ingredient and color; however, their quality and appearance are in affected when applied to heat in a low acidic medium (Wu et al., 2018).

Cornelian cherry (*Cornus mas L.*), a hopeful natural food colorant source is known for its rich content of anthocyanins. At storage temperatures of 2, 25 and 75 °C, the stability of anthocyanins of cornelian cherry extracts with pH=3.02 in the presence

of sodium benzoate and potassium sorbate (food preserving agents) was investigated. The rate constant and half-life values of the highest stability extract were 0.48×10^{-3} h^{-1} and 1443.8 h respectively under storage temperature of 2 °C without addition any preservative. Anthocyanin extract of highest rate constant degradation value was 82.76 $\times 10^{-3}$ h^{-1} at storage temperature 75 °C without any preservative. The degradation of cornelian cherry fruit anthocyanins under all investigated storage conditions were in compliance with kinetics first order reaction. The preservatives had small influence on the stability of the anthocyanins in aqueous solution (Moldovan and David, 2014).

Anthocyanins are color main contributors. In red wine, Color is among the important features when evaluation their sensory quality. Cabernet Sauvignon wine was investigated for CIELAB color values and Monomeric anthocyanins during fermentation by using spectrophotometry and HPLC-MS. In their results, 14 monomeric anthocyanins were detected. The anthocyanins detected were correlated negatively to the values of L*, b* and H* and positively to the values of a* and C*. While cyanidin-3-O-glucoside was highly influenced, malvidin 3-O-glucoside was minimally influenced on the color values compared to equal concentrations of all the anthocyanins detected. In their remarks, they said that the degree of color on every single monomeric anthocyanin is influenced by their acyl groups on the glucoside, structures, molecular steric structure and the substituents on the B-ring (Han et al., 2008).

Apart from the core materials (active materials), wall materials (encapsulating agents) are another most important entity in encapsulation. The choice of which wall material to use in encapsulating natural pigments hasn't been easy so far. Though gum Arabic and Maltodextrin have frequently in use as wall materials in anthocyanins encapsulation. Depending on the source of the anthocyanins, several other alternatives of wall materials has been given a trial.

Selim et al. (2008) investigated the effect of Maltodextrin D.E. 10, Maltodextrin D.E. 20, and gum Arabic as wall materials on the stability of encapsulated roselle (*Hibiscus sabdariffa L.*) anthocyanins and found that maltodextrin DE 20 was the most efficient wall material to extend the shelf life of roselle anthocyanins during different storage conditions.

In another similar study, maltodextrin, gum Arabic, combination of maltodextrin and gum Arabic, and soluble starch as wall materials were used during the encapsulation of anthocyanins from Hibiscus sabdariffa L. to determine their kinetic degradation and color stability during storage at 4, 25 and 37 °C for 105 days. Their

results showed that the highest encapsulation efficiency was encapsulates under 4 °C with combination of maltodextrin and gum Arabic as wall material. At the same storage condition had little impact on a* and b* values and also showed reduce rate of degradation under all storage conditions (Idham et al., 2012b).

Akhavan Mahdavi et al. (2016) also encapsulated barberry (*Berberis vulgaris*) extract which is a rich source of anthocyanins using combination of maltodextrin and gum Arabic (MD + GA), maltodextrin and gelatin (MD + GE), and maltodextrin (MD) as wall materials. After the encapsulation they found that capsules with MD + GA as wall material appeared as the best wall materials among the rest to encapsulate the anthocyanins of barberry.

In a different study on anthocyanins, the stability and color of encapsulated freeze-dried anthocyanin of saffron petal's extract with different wall materials (gum Arabic (AG), maltodextrin DE 7 and 20) were analyzed. The analytic results of the encapsulates after 10 weeks storage showed that gum Arabic was the most efficient wall material and protected the stability of the anthocyanin during storage (Mahdavee Khazaei et al., 2014).

The powdered açai juice was analyzed for anthocyanin stability and antioxidant activity from day 1 to day 120. The juice was spray dried encapsulated with maltodextrin 10DE, maltodextrin 20DE, gum Arabic and tapioca starch as wall materials during encapsulation. Storing the encapsulated samples under temperatures of 25 and 35 °C, and water activities of 0.328 and 0.529 did not had any negative impact on the anthocyanin stability throughout the storage time. The results also showed that Maltodextrin 10DE was the most efficient among the wall materials that best kept the stability of the anthocyanins under all conditions during the 120 days storage (Tonon et al., 2010).

Again, lowbush blueberries extract containing anthocyanins was encapsulated by freeze-drying using three different dextrose equivalents (DE) of maltodextrin as wall materials to investigate how well the encapsulated anthocyanins could be used as colorant and functional ingredient in the food industry. Comparing the freeze dried extract to the encapsulated anthocyanins proved that the shelf life of the freeze dried encapsulated anthocyanins has been better extend, henceforth slows the retardation of anthocyanin during storage under 70, 80 and 90 °C (Celli et al., 2016).

The main raw material for this study was *Mahonia aquifolium* fruit. *Mahonia aquifolium* fruit is a perennial shrub growing up 1.5 m of height. It is widely grown in

British Columbia. In 1822, it was ushered in Europe as an ornamental plant. Its fruits, roots and leaves are used in natural colorant production in North America and in Europe (Sorokopudov et al., 2017). In their study, the morphological and phytochemical properties of four varieties of *Mahonia aquifolium* found in the Central Anatolia region of Turkey were investigated. Through careful analysis, they came out that *Mahonia aquifolium* is a rich source of anthocyanins, antioxidants and phenolic and significant difference were seen among the varieties. They concluded that the antioxidant properties of the fruit could make it useful in pharmacological and food industry (Gunduz, 2013).

Coklar and Akbulut (2017) reported that 70% of the total anthocyanin in *Mahonia aquifolium* fruit juice is cyanidin-3-O-glucoside. In a different study of berries anthocyanins, Rein (2005) also mentioned cyanidin-3-O-glucoside as the most quantified anthocyanin in berries as reported by many studies. The profile composition of anthocyanins detected in the juice of *Mahonia aquifolium* fruit were cyanidin-3-O-rutinoside (45.57±2.03), cyanidin-3-O-glucoside (253.40±7.27), malvidin-3-O-glucoside (25.64±1.66), peonidin-3-O-glucoside (12.89±1.41), pelargonidin-3-O-glucoside (12.56±0.71) , delphinidin-3-O-glucoside (6.71±1.84), and delphinidin-3-Orutinoside (3.38±0.79) mg/100 g FW (Coklar and Akbulut, 2017).

It is at the brim of becoming one of the major raw material to be use in food industry in the coming century. Significant amount of carbohydrates, vitamin C and several other minerals we found in the fruit through the chemical composition analysis. Anthocyanins were also present in the fruit which could also serve as a natural colorant material (Sorokopudov et al., 2017).

Tao et al. (2017) freeze dried encapsulated blueberry anthocyanins with gum Arabic, maltodextrin, whey protein isolate and β-cyclodextrin as wall materials. They made an experimental design using simplex lattice mixture. A successful application of genetic algorithm with artificial neutral network was used to control the effect formulation composition on encapsulation efficiency (EE) and productivity (EP). The optimum formulation provided by the approach of genetic algorithm with artificial neutral network were four. Whey protein isolate provided the highest content among the wall materials used. According to the optimum formulations, the values of encapsulation efficiency (EE) and encapsulation productivity (EP) were above 82 and 96 % respectively. Among the encapsulated anthocyanins in different formulations, despite the differences in glass transition temperature, particle size and bulk density,

there were similarities in color property, moisture content, crystallinity and water activity in all the encapsulated samples. The results of optimum formulations protected the degradation of encapsulated blueberry anthocyanins during thermal treatment.

Two wall materials, almond gum and gum Arabic were used during the encapsulation of β-carotene. Assessing the two wall materials functionality, the encapsulate β-carotene powders from the two materials were used as colorant in cake. Kinetic degradation and surface color changes of freeze dried powders with gum Arabic as wall material were investigated during 70 days storage at relative humidities 10, 45 and 80 %. The degradation of β-carotene (loss in red color) fitted in first order kinetic reaction. β-carotene degradation and reduction in red color were directly dependent on increasing relative humidity (RH) till the samples collapsed at 80 % RH. The results proved that almond gum best protected β-carotene degradation and also provided homogenous color to cake better than gum Arabic (Mahfoudhi and Hamdi, 2015).

Jiménez-Aguilar et al. (2011) used spray drying method to encapsulate blueberry anthocyanins with mesquite gum as the wall material. They were then investigated the variations in the color and compounds concentration found in the encapsulated powders. The soluble solid concentration of the ethanolic extract of blueberry was arrange to 35 %. Spray drying of the samples were done feeding rates 8.5, 9.1 and 9.6 mL min^{-1} and inlet temperatures at 140 and 160 °C. The samples with 9.1 $mLmin^{-1}$ feeding rate and inlet temperature 140 °C stored in the dark at 4 °C for 4 weeks found to provide lower degradation of antioxidant activity (15%) anthocyanins (7%) and phenolics (10%). total color difference (ΔE) was 5 and final values for L, C and H were 39.87, 47.83 and 28.59 respectively.

Pitalua et al. (2010) studied the antioxidative activity of beetroot juice encapsulated with gum Arabic as wall material when the samples were stored at 5 different water activities (0.110, 0.326, 0.521, 0.748 and 0.898 aw) for 45 days. Results of the samples stored at 0.110, 0.326 and 0.521 aw showed no significant differences in redox potential, betalain concentration, antioxidant activity and color. However, there was significant differences in the samples at water activities 0.748 and 0.898. At 0.748 and 0.898, as betalains degradation was progressing, antioxidant activity was increasing. They ending saying that product stability during storage are influenced by water adsorption.

Betz and Kulozik (2011) encapsulated bilberry extract which is rich in anthocyanins with whey protein gels as wall materials. They therefore made an

assessment on how manufacturing conditions such as sample morphological properties, emulsifier addition and stirrer speed at pH 1.5 and 3. The outcome of the study was that microcapsules manufactured at pH 1.5 was preferable for bilberry anthocyanin encapsulation with whey protein gel to pH at 3. The reason was that interactions between bilberry anthocyanins and whey proteins was detrimental. They projected that emulsion method of protein based encapsulation.

Robert et al. (2010) used maltodextrin and soybean protein isolate as wall materials when encapsulating polyphenols and anthocyanins of pomegranate (Punica granatum) juice by spray drying. The stability of encapsulated powders of bioactive compounds from pomegranate juice during 56 days stored at 60 °C was investigated. The encapsulation efficiency of the polyphenols was significantly higher in soybean protein isolate as wall material and the anthocyanins was found in maltodextrin. In terms of stability, maltodextrin provided better protection to polyphenols as soybean protein isolate did to anthocyanins. Apart from polyphenols with maltodextrin as wall materials, all the microcapsules of the bioactive compounds from pomegranate when added to yogurt provided similar similar stability strength to non-encapsulated bioactive compounds.

Osorio et al. (2010) analyzed the individual anthocyanins from Bactris guineensis fruit using chromatography. While 87.9 % of constituting cyanidin3-glucoside and cyanidin-3-rutinoside, peonidin3-glucoside, cyanidin-3-(6-O-malonyl) glucoside, cyanidin-3-sambubioside and Peonidin-3-rutinoside were available in minor concentrations. Physicochemical characteristics of four ethanol extracts of the anthocyanins were obtained by soxhlet extraction and osmotic dehydration. HPLC-PDA was used to monitor the anthocyanins composition. Anthocyanin extracts with highest concentration were spray dried with maltodextrin as wall material. Stability of the microcapsules after storage showed first order kinetic reaction. Rate constant of reaction increased by humidity and temperature. The storage condition low degradations of the anthocyanin pigments was determined to be less than 76 % humidity and below 37 °C.

By using spray drying, Bakowska-Barczak and Kolodziejczyk (2011) encapsulated black currant (*Ribes nigrum L.*) polyphenols with different dextrose equivalent maltodextrin (DE 11, 18 and 21) and inulin as wall materials. They evaluated the stability of the encapsulated samples stored at 8 and 25 °C for 12 months. Microcapsules with maltodextrin DE 11 gave excellent drying yield and also protected the polyphenols the better than maltodextrins DE 18 and 21 during storage. The

microencapsulated powders again demonstrated considerable antioxidant activity prior to storage and after storage.

Several fruit extracts rich in anthocyanins has been usually used as food colorant in the food industries. Rapid loss and poor stability of the natural pigments has been a major challenge. Effects of ferulic acid and rutin on blackberry anthocyanins as copigments were investigated during storage. The anthocyanin of blueberries degradation followed first order kinetics during storage at different temperatures under light. Anthocyanin stability affected much with light than higher temperatures. Copigments addition significantly decreased anthocyanin losses and also increased the half-lives of the spray dried powders than powders without copigments. They assumed that effective stabilization of the powder may be credited to the copigments antioxidative properties and hydration control of the anthocyanins. Degradation of anthocyanins didn't correlate with color changes but could cause formation of polymers and colored derivatives during storage (Weber et al., 2017).

Malacrida et al. (2015) microencapsulated turmeric oleoresin with gelatin and modified starch by freeze drying. Stability of the samples were evaluated during storage under different light and temperatures. Encapsulated samples were in the dark at -20, 25 and 60 °C and 25 °C with light for 6 weeks. The samples were analyzed for total phenolic contents, curcumin and color. Curcumin retention had no significant effect with all the wall materials. Wall material with gelatin (1 g/100 g) + modified starch (30 g/100 g) and mechanical homogenization showed best conditions for encapsulated turmeric oleoresin. Stability of encapsulated samples were higher at -20 °C and least at 25 °C under light.

Syamaladevi et al. (2012) used spray drying to encapsulate powders of red raspberry with gum Arabic as the wall material. Prior to spray drying, puree of raspberries were treated with or without high pressure homogenizers. Physicochemical property analysis of the dried samples was done. Smaller median particle size of the samples produced with pressure homogenizer than those that were not treated with pressure homogenizer was determined. At equal water activities, water contents and glass transition temperatures of encapsulated powders were insignificant ($p > 0.05$). High porosity and apparent density raspberry encapsulated powders whose purees were treated with high pressure homogenization. The bigger particle size of encapsulated raspberry samples whose puree wasn't treated with high pressure homogenization produced higher water solubility index and hygroscopicity. Encapsulated powders that

went through high pressure homogenization produced greater anthocyanin concentration with low L*, a* and b* values.

Mandavi et al. (2016) applied combinations of maltodextrin and gelatin (MD+GE), gum arabic and maltodextrin (GA+MD), and maltodextrin (MD) as three wall materials when encapsulating barberry anthocyanins. The stability of the encapsulated samples were studied at different temperatures (4, 25, 35 and 42 °C) and relative humidities (20, 30, 40 and 50 %) under light illumination for 90 days. Apart from the non-encapsulated samples of anthocyanins, there was convincing increase in half-lives (t1/2) of the encapsulated samples during storage. Combination of GA+MD as wall material protected the anthocyanins of barberry the best with greater encapsulation efficiency and lower degradation rate at all storage temperatures. The encapsulated anthocyanins were applied when coloring jelly powder as a replacement of synthetic color. Hygroscopicity, ash content, moisture content, acidity and texture of the jelly were insignificant including the control sample, however, solubility and syneresis of colored jelly reduced significantly.

Silva et al. (2013) encapsulated jaboticaba extracts with maltodextrin (MD), gum arabic and maltodextrin (GA+MD) and Capsul™ and maltodextrin (CA+MD) as wall materials by spraying drying method at 140, 160 and 180 °C inlet temperatures. Overall color difference, hygroscopicity, moisture content and anthocyanin retention parameters were chosen for simultaneous optimization by using the approach of desirability. Encapsulated sample with MD as wall materials at inlet air temperature of 180 °C achieved the highest desirability (0.7–0.8). From the analysis of scanning electron microscopy, samples with GA+MD as wall material formed more homogeneous particles recommended in spray dried encapsulates.

Mohd Nawi et al. (2015) investigated how different wall materials effected the physicochemical properties of encapsulated Ipomoea batatas anthocyanins by microwave-assisted drying method. Anthocyanins of purple sweet potato powders were analyzed for morphology, hygroscopicity, water activity, color, dissolution time and moisture content by powder characterization method. Gum arabic (GA), maltodextrin (MD), gum arabic and maltodextrin (GA+MD) combination were used as wall materials to encapsulate anthocyanins of purple sweet potato. Samples with GA+MD produced best quality powder with the least water activity and moisture content values. There were changes in L, a*, b*, chroma and hue in the encapsulated powders to the initial ones.

Laokuldilok and Kanha (2017) used maltodextrin of different dextrose equivalent (DE 10, 20 and 30) produced from broken black glutinous rice as wall material to encapsulate black glutinous rice (bran fraction) anthocyanins. The encapsulated samples were spray dried at 140, 160 and 180 °C inlet temperatures. The impact of increasing inlet temperatures increased encapsulation efficiency, and reduced surface anthocyanin content, total anthocyanin content and antioxidant activities of the encapsulates. Samples with maltodextrin DE 20 as wall material provided higher and or similar values of total anthocyanin content and antioxidant activities compared to those with maltodextrin DE 10 as wall material. The results also indicated that increasing inlet temperatures and dextrose equivalent reduced L*, a*, b* and Chroma but increased hue value. Also, spray dried samples were brighter than freeze dried samples. The stability of spray dried samples were much higher than freeze dried samples.

3. MATERIAL AND METHOD

3.1. Material

The material used in this study was *Mahonia aquifolium* fruit collected in Alaeddin campus of Selcuk University, Konya/ Turkey, grown for landscaping purpose. The fruits were collected in 2016 and stored in a deep freezer (-18 °C) until their fruit juice (anthocyanins) were extracted for the study.

Apricot tree gum (ATG), gum Arabic (GA) and maltodextrin (MD) were the wall materials used. Apricot tree gum exudates were collected from apricot trees grown in Battalgazi, Malatya in 2016. Gum arabic and maltodextrin were purchased from Sigma.

3.1.1. Extraction of juice (anthocyanins) from *Mahonia aquifolium* fruit

Samples of the freeze fruits were mashed in a plastic tube immediately after removing them from the freezer without allowing it to thaw. They were then heated at 90 °C for 10 sec and immediately cooled to a room temperature in an ice water bath to terminate the enzymatic activity of the juice. They were then centrifuged (Nuve, NF 800R, Turkey) at 8000 rpm for 5 minutes to enable easy separation of the juice from the residue. Extraction of the fruit juice was completed after a maceration enzyme solution was added to the residue and submerged in a digital precise shaking water bath (WSB-30; Daihan Scientific, Korea) at 50 °C for 30 minutes. Centrifugation was repeated to remove the remaining anthocyanins from the residue. The soluble solid content (SSC) of the extract (anthocyanins) was measured as 8 °Brix with the help of a refractometer (HSR-500, Atago, Japan).

3.1.2. Encapsulation procedure

Fruit juice (anthocyanins) of mahonia fruit was encapsulated after extraction. A total of five wall materials were used during encapsulation. The wall materials were Apricot tree gum (ATG), Gum Arabic (GA), Apricot tree gum and Gum Arabic (ATG+GA) combination, (50:50), Maltodextrin and Gum Arabic (MD+GA) combination, (50: 50) and Apricot tree gum and Maltodextrin (ATG+MD) combination (50:50). For each wall material, 500 mL of extract was mixed during encapsulation. The extract in a beaker was premixed with the appropriate amount of wall material on a hotplate magnetic stirrer (MSH-20D; Daihan Scientific, Korea) at room temperature such that the SSC of the mixture will become 20 °Brix. The mixtures were then encapsulated by using a homogenizer (WiseMixTM HG-15D; Daihan Scientific, Korea) at 10000 rpm for 2 minutes. The encapsulated anthocyanin samples were freeze at a temperature of -18 °C before drying them in a freeze dryer (Labogene ScanVac Coolsafe110-4, Lynge, Denmark).

3.1.3. Storage of samples

Freeze-dried encapsulated anthocyanins of *Mahonia aquifolium* fruit were manually grinded into powder and seize to achieve equal particle sizes. For each of the five wall material, equal amounts of powdered encapsulate were measured into 30 separate eppendorf tube with lid top. The samples were stored an oven at 35, 45 and 50 °C (Nuve, EN 500, Turkey) for 50 days. For an interval of 5 days, samples (one from each wall material) from each storage temperature were removed and kept at +4 °C till analysis day.

3.2. Method

3.2.1. Determination of encapsulation efficiency (EE)

0.2 g of powdered encapsulate was mixed with an appropriate ratio of metanol:water (1:1, v:v) solution and vortexed. The mixture was then made to stand in an ultrasonic water bath (Elma, T1-H-20, Germany) for 20 minutes. The dispersion was then centrifuge (Nuve, NF 800R, Turkey) for 5 min at 9000 rpm. The supernatant was

used for total surface monomeric anthocyanin analysis and the surface anthocyanin content (SAC) was determined.

Again, total monomeric anthocyanin content was analyzed using 0.2 g powdered encapsulate sample and mixed with an appropriate ratio of metanol:acetic-acid:water (50:8:42, v:v:v) solution and then follow the same procedure as used in the above. The supernatant was used to analyze the total anthocyanin content (TAC). The EE of the powdered encapsulates were calculated according to eqn. 3.1. (Akhavan Mahdavi et al., 2016).

$$EE\ (\%) = \left(\frac{(TAC - SAC)}{TAC} * 100\right) \quad (3.1)$$

3.2.2. Total monomeric anthocyanin content

The total monomeric anthocyanin content of encapsulates were determined by following the protocol used by Akbulut and Coklar (2015) with a slight change. Powders of the encapsulated samples (200 mg) were dissolved in methanol: water: acetic-acid (50:42:8, v:v:v) solution. The dispersion was sonicated (Elma, T1-H-20, Germany) for 20 min after 1 min vortex. From the sonicator, it was centrifuged (Nuve, NF 800R, Turkey) at 9000 rpm for 5 min. The supernatant was separated from the residue.

Equal volumes of the supernatant were measured in two separate test tubes. One of the tubes was diluted with pH 1.0 buffer (potassium chloride, 0.025 M) and the other too was diluted with pH 4.5 buffer (sodium acetate, 0.4 M). The mixtures were vortex and allow to stay for 30 min after which the wavelengths were measured at 515 and 700 nm and the absorbance difference was calculated in the expression given below eqn. 3.3. The total monomeric anthocyanin content of the extracts was calculated according to Eqn. 3.2.; the results were expressed in mg of cyanidin-3glucoside/100 g DW (Ko et al., 2017).

$$\text{Total monomeric anthocyanin content}\left(\frac{\text{mg}}{\text{L}}\right) = \frac{\text{A}\times\text{MW}\times\text{D}\times 10^3}{\text{l}\times\varepsilon} \quad (3.2.)$$

Where;

$$A = (A_{515\ nm} - A_{700\ nm})_{pH\ 1.0} - (A_{515\ nm} - A_{700\ nm})_{pH\ 4.5} \quad (3.3.)$$

$$MW\ (\text{molecular weight of cyanidin} - 3 - \text{glucoside}) = 449.2$$

$$\varepsilon\ (\text{molecular absorbance of cyanidin} - 3 - \text{glucoside}) = 26900 M^{-1} cm^{-1}$$

$$\text{Dilution factor}(D) = \text{dilution ratio of extract}$$

$$l = \text{length of cell path (1 cm)}$$

3.2.3. Color analysis

Analysis of the color of the encapsulated mahonia anthocyanins was determined by Konika Minolta CM-5 model colorimeter (Konika-Minolta, Osaka, Japan). From fig. 3.1, CIElab color system parameters for L* was an indication for lightness varying from white (+L*) to black (-L*), a* for reddish (+a*) and greenish (-a*) and b* for yellowish (+b*) and bluish (-b*). Prior to the analysis, encapsulated powders were diluted in water. Total color change (ΔE) were calculated from the eqn. 3.4. (Weber et al., 2017). Chroma (C*) and hue (°h) values are indications of color intensity or saturation and the location and angle of the colors on the diagram respectively (Akbulut and Coklar, 2008).

$$\Delta E = \sqrt{(\Delta L *^2 + \Delta a *^2 + \Delta b *^2)} \quad (3.4.)$$

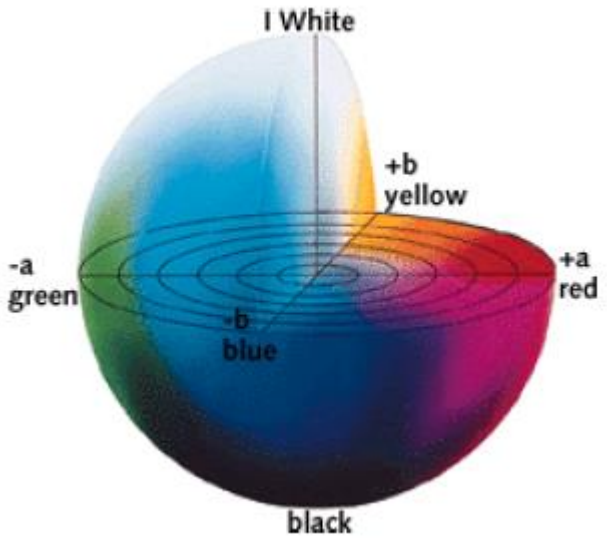

Figure 3. 1. Positions of color parameters L*, a* and b* on the Hunter scalar

3.2.4. Kinetics modelling of *Mahonia aquifolium* anthocyanins degradation

The degradation of encapsulated *Mahonia aquifolium* anthocyanins were investigated after storing them for a period of time under different temperatures. The kinetics parameters investigated were rate constant of reaction (k), half-life ($t_{1/2}$), activation energy (E_a) and temperature coefficient (Q_{10}).

3.2.4.1. Reaction rate constant (k)

The reaction rate constant was determined by plotting the natural logarithmetic values of the anthocyanin concentration on the y-axis vs. the time (day) on the x-axis. The linear line was obtained which fits in the first order of kinetic reaction equation. The rate constant of reaction (k) becomes the slope of the equation. Kinetic first order of reaction equation is shown in eqn. 3.5.

$$\ln C = -k.t + \ln C_0 \quad (3.5.)$$

Where,

C_0 : concentration of *Mahonia aquifolium* anthocyanins at t=0

C : concentration of *Mahonia aquifolium* anthocyanins after t (min.)

k : reaction rate constant (min^{-1})

t : time (min.)

3.2.4.2. Activation energy (E_a)

To determine the effect of temperature on antocyanin degradation throughout the storage, activation energy (Ea) values were calculated via Arrhenius equation in logarithmic form expressed in eqn. 3.6.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \cdot \frac{(T_2 - T_1)}{T_1 \cdot T_2} \quad (3.6.)$$

where;

k_1: Rate constant at T_1

k_2: Rate constant at T_2

R: Ideal gas constant, 8.314 J/mol ^oK

E_a: Activation energy, J/mol ^oK

3.2.4.3. Temperature Coefficient (Q_{10})

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10}{(T2 - T1)}} \quad (3.6.)$$

3.2.4.4. Half-life of reaction

Half-life is a terminology used to defined the period at which the quality of any material or substance to degrade to 50 % of its shelf life. It is denoted as $t_{1/2}$. The period taken for the *Mahonia* aquifolium anthocyanins during storage at 35, 45 and 50 °C to degrade 50 % of its life span was determined from eqn. 3.7. (Labuza, 1984).

$$t_{1/2} = \ln 2/k$$

(3.7.)

4. RESULTS OF THE STUDY AND DISCUSSION

4.1. Encapsulation Efficiency (EE)

In Table 4.1 and Figure 4.1 are the results of the encapsulation efficiencies (EE) of *Mahonia aquifolium* fruit anthocyanins with Apricot tree gum (ATG), Gum Arabic (GA), Apricot tree gum and Gum Arabic (ATG+GA) combination, (50:50), Maltodextrin and Gum Arabic (MD+GA) combination, (50: 50) and Apricot tree gum and Maltodextrin (ATG+MD) combination (50:50). The results indicated Apricot tree gum and Gum Arabic (ATG+GA) combination as the most efficient wall material with encapsulation efficient value of 98.96±0.19 %. Apricot tree gum equally hold shoulder to shoulder to gum Arabic with almost the same efficient capacity. Gum Arabic (GA),

having taken the second highest encapsulation efficiency position next to Apricot tree gum and Gum Arabic (ATG+GA) combination has proven the reason why it has been commonly used in encapsulation as wall material. This is due that gum Arabic has high emulsifying and stabilizing characteristic features. In the study of food hydrocolloids, Dickinson (2003) reported that the emulsifying and stabilizing properties are highly associated to the protein content in gum Arabic. Apricot tree gum could also have similar emulsifying and stabilizing property to gum Arabic since both has nearly the same protein content.

Table 4. 1. Encapsulation Efficiency of different wall materials on *Mahonia aquifolium* anthocyanins

Wall material	Encapsulation Efficiency (%)
GA	98.58±0.56a
ATG	98.49±.040a
ATG+GA	98.96±0.19a
ATG+MD	96.18±0.18b
GA+MD	97.50±0.20ab

GA: Gum Arabic, ATG: Apricot Tree Gum and MD: Maltodextrin

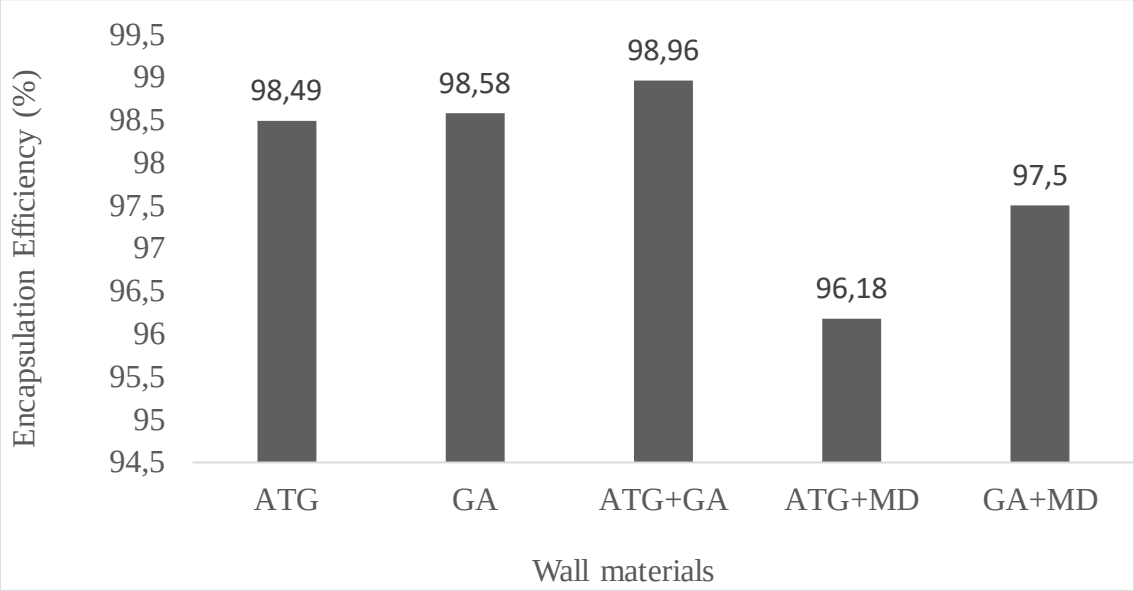

Figure 4. 1. Graphic showing the Encapsulation efficiency (EE) of different wall materials on *Mahonia aquifolium* anthocyanins.

GA: Gum Arabic, ATG: Apricot Tree Gum and MD: Maltodextrin

It was brought to attention the magnificent role played by maltodextrin in defining the encapsulation efficiencies of apricot tree gum (ATG) and gum Arabic (GA). Significant differences were observed in GA and/or ATG when either of the two was combined with maltodextrin and used as wall material in reference to the efficiencies of only GA or ATG as wall material. The efficiency loss of the wall materials (Gum Arabic (GA) and Apricot tree gum (ATG)) when combined with maltodextrin could be the influence of some compounds or elements within the chemical composition of maltodextrin. Also MD could have a highest endothermic feature to GA and ATG. There could be that MD encapsulated samples may have bigger pores that allows easily penetration of heat into the core material in comparison to the samples without MD in their wall material. The effectiveness of the combination of gum Arabic (GA) and maltodextrin (MD) was not as it was reported by Xue et al. (2019) on red-fleshed apple, Akhavan Mahdavi et al. (2016) on barberry, Idham et al. (2012a) on roselle and Burin et al. (2011) on grape anthocyanins as the best wall material. The reason could be either material difference or the high efficiency ability of apricot tree gum (ATG) which has been tremendously improved gum Arabic (GA) efficiency to maltodextrin. While there was synergistic effect on EE between ATG and GA, however MD combination of either ATG or GA had antagonistic effect on the efficiency of encapsulation. The encapsulation efficiencies between the wall materials were statistically significant ($P<0.01$).

4.2. Anthocyanin content and degradation kinetics of encapsulated *Mahonia aquifolium* anthocyanins during storage at different temperatures.

4.2.1. Anthocyanin content of encapsulated *Mahonia aquifolium* at different levels of storage.

Table 4.2 is showing the results of mahonia *fruit* monomeric anthocyanin content determined after storage at 35, 45 and 50 °C.

Table 4. 2. Anthocyanin concentration (mg/kg) in mahonia fruit encapsulated with apricot tree gum and gum Arabic and stored at different temperatures

	ATG			GA		
Time(day)	**35°C**	**45°C**	**50°C**	**35°C**	**45°C**	**50°C**
0	2378.79	2378.79	2378.79	2435.77	2435.77	2435.77
5	2374.02	2216.24	1905.35	2291.19	2050.23	1979.84
10	2296.03	1947.38	1907.33	2278.25	1890.20	1659.93
15	2155.76	1920.51	1810.56	2171.30	1864.24	1505.93
20	2164.06	1863.75	1724.69	2168.39	1813.83	1488.40
25	2147.35	1854.51	1705.67	2184.38	1793.07	1507.71
30	2064.16	1746.75	1646.02	2137.68	1608.53	1392.27
35	1984.03	1702.39	1599.89	2065.98	1593.46	1335.03
40	2021.85	1703.57	1582.02	2071.12	1533.71	1158.03
45	2001.82	1699.06	1369.43	2022.98	1511.05	1050.21
50	1916.42	1697.28	1477.38	1935.74	1486.81	971.59

Apricot tree gum: ATG, Gum arabic: GA

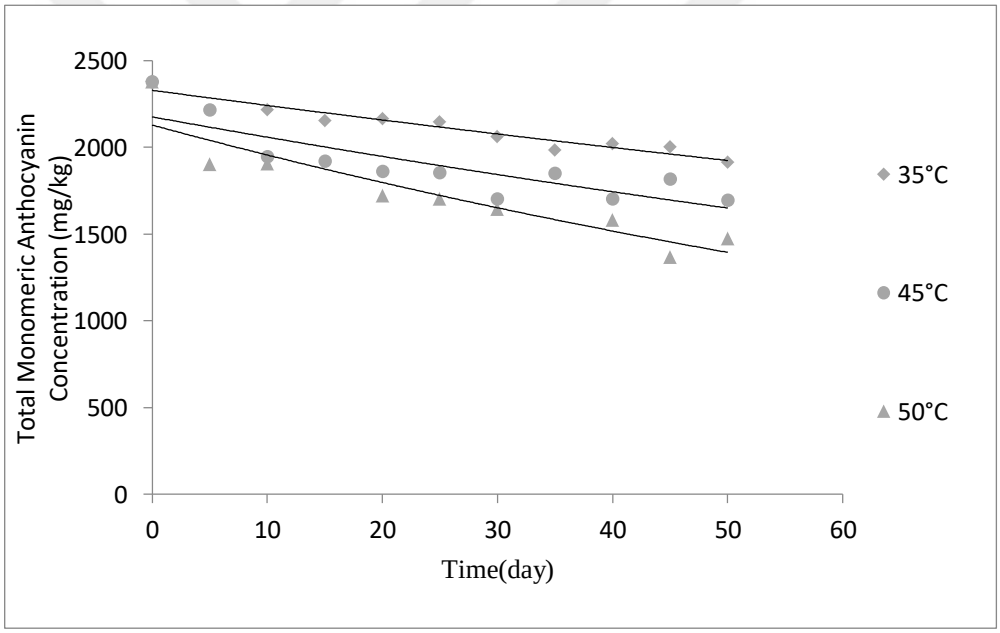

Figure 4. 2. Degradation of mahonia anthocyanins encapsulated with apricot tree gum. Geometric figures point out the storage temperature (◊:35 °C, o: 45 °C, and Δ: 50 °C).

The degradation of the anthocyanins encapsulated with gum Arabic (GA) can be seen in figure 4.3. Out the three storage temperatures, it was only samples stored at 35 °C that were able to protect their anthocyanins level not much differing from their initials prior to storage. There were sharp losses in the anthocyanins as the the storage temperatures were increased to 45 and 50 °C. from the figure we clearly observe that the 50 °C slope fell deeply down followed by the 45 °C slope as compare to 35 °C.

There was significant difference between the slopes. The samples that were stored at 50 °C had greater anthocyanin degradation while the least loss of anthocyanins was recognized at 30 °C.

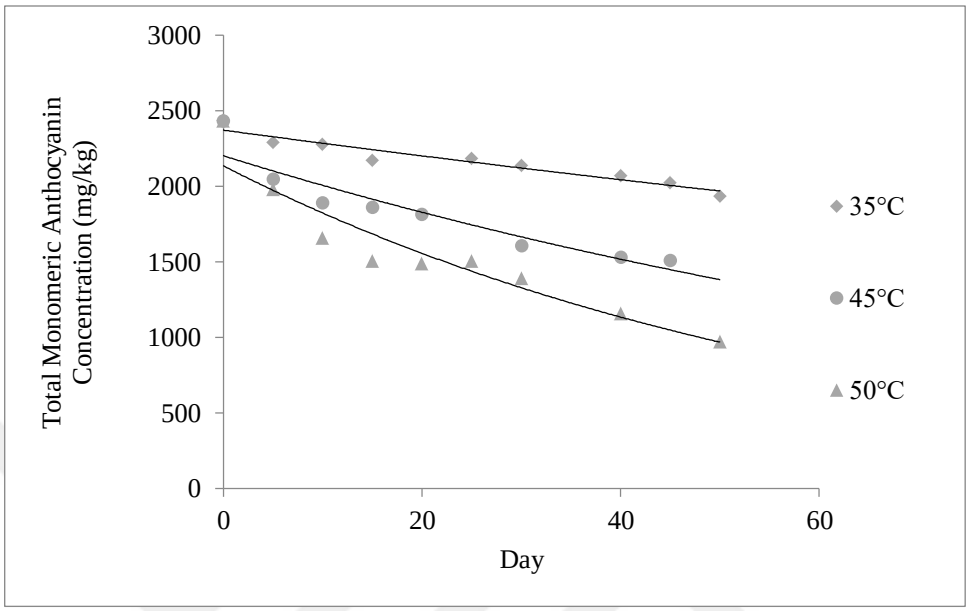

Figure 4. 3. Degradation of mahonia anthocyanins which encapsulated with gum arabic during storage at different temperatures. Geometric figures point out the storage temperature (◊:35 °C, o: 45 °C, and Δ: 60 °C).

Results from the above table (Table 4.2) were obtained when the anthocyanins concentrations (mg/kg) of the encapsulated powders with ATG or GA were determined after storage under different temperatures. Initial concentrations of anthocyanins with ATG and/or GA at 35, 45 and 50 °C were 2378.79 and 2435.77 (mg/kg) respectively, whereas the final concentrations were 1916.42, 1697.28 and 1477.38 (mg/kg) for ATG and 1935.74, 1486.81 and 971.59 (mg/kg) for GA at 35, 45 and 50 °C respectively. Despite higher anthocyanin concencentration in GA samples at the initials, ATG anthocyanin concentrations under all conditions appeared higher than those of GA samples except at 35 °C after storage. Lower anthocyanin degradation in samples with ATG could be that ATG has higher solubility to GA as wall materials. Syamaladevi et al. (2012) explained that solubility is a vital instant property needed in encapsulated powders which subjected to rehydration when applied as color additives to food formulation. They further included that higher solubility materials could be attributed to higher distribution of particle size.

Table 4. 3. Anthocyanin concentration (mg/kg) in mahonia fruit encapsulated with apricot tree gum-gum Arabic (1:1) and stored at different temperatures.

	ATG-GA		
Time(day)	**35°C**	**45°C**	**50°C**
0	2358.46	2358.46	2358.46
5	2259.90	2236.40	1895.65
10	2229.29	2156.34	1785.12
15	2251.50	1829.99	1632.79
20	2174.64	1853.13	1476.59
25	2159.13	1811.98	1453.87
30	2098.51	1790.15	1404.99
35	2101.78	1721.65	1355.04
40	2066.89	1627.91	1306.16
45	2077.75	1510.46	1150.35
50	1956.84	1416.25	1125.19

Apricot tree gum-gum Arabic mixture: ATG-GA

The degradation of the anthocyanins encapsulated with the combination of apricot tree gum and gum Arabic (ATG+GA) were examined at 35, 45 and 50 °C stored temperatures. The results is indicated in figure 4.3. The anthocyanins were less degraded at lower temperature (35 °). From the figure 4.3, the 35 °C slope was nearly horizontal showing that there was almost no lost in the stability of the anthocyanins throughout the 50 days storage. However, a sharp lost in the anthocyanins occurred when the temperatures were increased to 45 and 50 °C. The instability nature of the anthocyanins was more severe at 50 to 45 °C slopes. A significant difference in the anthocyanins degradation could be observed in figure 4.4.

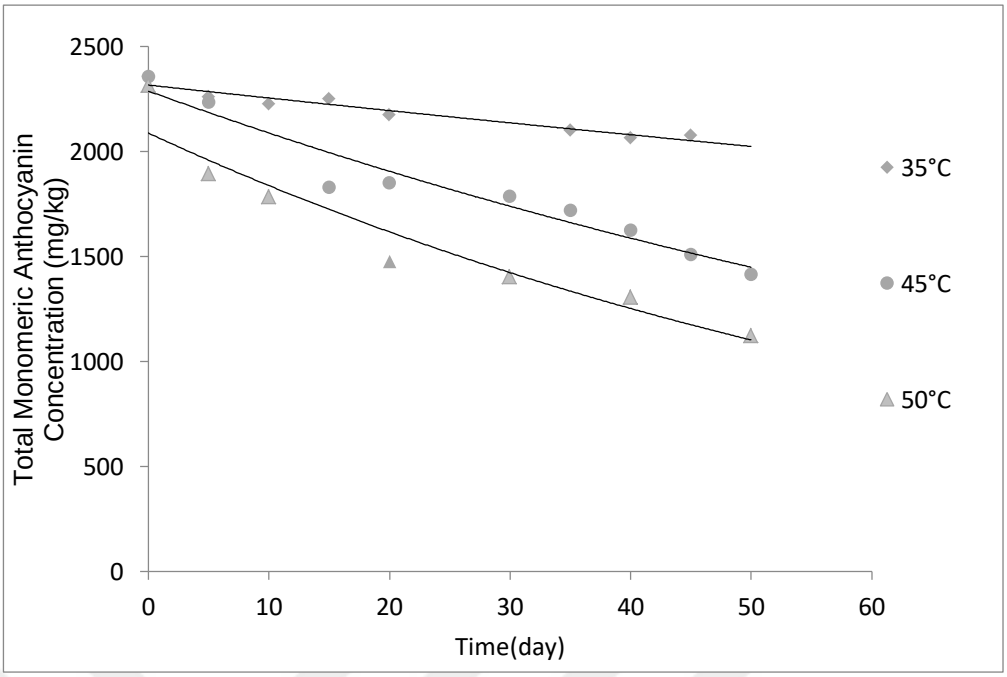

Figure 4. 4. Degradation of mahonia anthocyanins encapsulated with apricot tree gum and gum arabic mixture during storage at different temperature. Geometric figures point out the storage temperature (◊:35 ^{o}C, o: 45 ^{o}C, and Δ: 60 ^{o}C).

Evaluation of anthocyanin concentration (mg/kg) in samples with ATG-GA was analysed after storing the samples under 35, 45 and 50 °C for 50 days. The results is presented in Table 4.3. We could observe that temperature difference affected the anthocyanin degradation significantly more especially at 50 °C. Except at 50 °C where considerable changes in anthocyanin concentration were seen, only minor changes were found along the storage slopes of samples at 35 and 45 °C.

Our results follows what Moldovan and David (2014) reported on thermal stability of anthocyanins from cornelian cherry. They also found degradation of the anthocyanins stored at 22 and 75 °C were 1.8 and 172.1 times faster than those stored at 2 °C respectively. In this regard we could analytically come into an agreement that the stability of anthocyanins are hugely affected by storage temperatures, i.e they easily loses their stability when exposed to higher temperatures (Guo et al., 2018).

Table 4. 4. Anthocyanin concentration (mg/kg) in mahonia fruit encapsulated with apricot tree gum-maltodextrin (1:1) and gum Arabic-maltodextrin (1:1) and stored at different temperatures.

	ATG+MD			GA+MD		
Times(day)	**35°C**	**45°C**	**50°C**	**35°C**	**45°C**	**50°C**
0	2417.13	2417.13	2417.13	2499.44	2499.44	2499.44
5	2334.76	1967.46	1805.07	2335.00	2014.72	2176.97
10	2297.27	1802.66	1490.56	2316.07	1807.45	1440.61
15	2164.77	1626.53	1376.42	2252.63	1674.34	1354.97
20	2098.75	1647.96	1325.26	2173.86	1497.98	1303.48
25	2074.72	1487.62	1297.50	2060.16	1560.03	1042.47
30	2065.69	1450.38	1276.37	1976.12	1413.68	1022.61
35	2056.89	1415.58	1059.12	1953.18	1385.32	971.41
40	1964.97	1403.89	918.04	1959.85	1307.11	991.44
45	1826.47	1359.03	885.62	1845.27	1210.42	995.17
50	1848.14	1309.44	835.56	1828.34	1120.89	810.16

Apricot tree gum-Maltodextrin mixture: ATG+MD Gum Arabic-Maltodextrin mixture: GA+MD

Figure 4.5 shows the behavioral response of *Mahonia aquifolium* anthocyanins encapsulated with apricot tree gum and maltodextrin combination (ATG+MD) as wall material when stored under three different temperatures (30, 45 and 50 °C) for a 50 days long. The three slopes are a representation of the rate of change in the anthocyanins stability with temperature difference. All the storage temperatures negatively afftected the stability of the anthocyanins. There was frequent degradation of the anthocyanins along the slopes in the three storage conditions. The highest degradation of the anthocyanins were observed at each storage period under 50 °C in comparison to their correspondent stages at 35 and 45 °C.

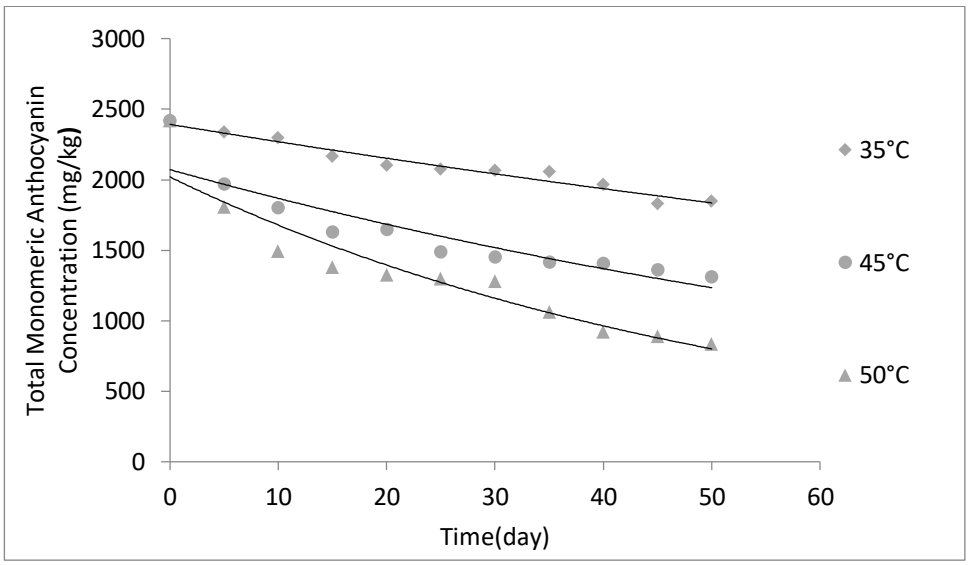

Figure 4. 5. Degradation of mahonia anthocyanins which encapsulated with apricot tree gum and maltodextrin mixture during different temperature. Geometric figures point out the storage temperature (◊:35 °C, o: 45 °C, and Δ: 50 °C).

The kinetic degration of the anthocyanins were also investigated in samples that were encapsulated with the combination of gum Arabic and maltodextrin (GA+MD) as wall material. The outcome of the investigation is demonstrated in figure 4.6. The stability of the anthocyanins were poorly protected at storage temperature 50 °C which saw sharply degradation along the slope. In relationship to the anthocyanins of the samples stored at 45 and 50 °C, the anthocyanins of the samples kept under 35 °C had lowest degradation and henceforth better protected the stability of the the mahonia fruit anthocyanins.

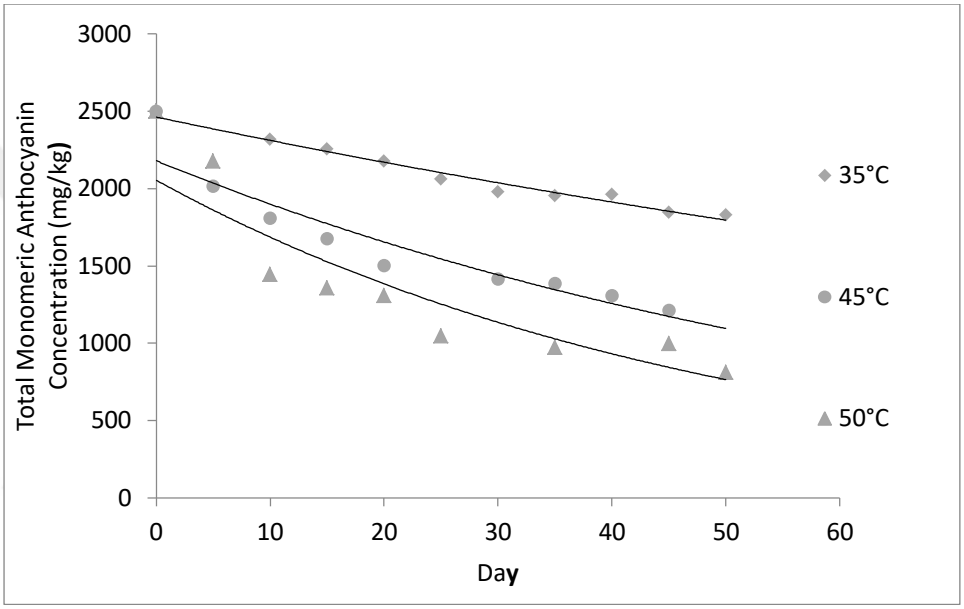

Figure 4. 6. Degradation of mahonia anthocyanins which encapsulated with gum Arabic and maltodextrin mixture at different storage temperature. Geometric figures point out the storage temperature (◊:35 ^{o}C, o: 45 ^{o}C, and Δ: 60 ^{o}C).

Going through the results (Table 4.2-4.4), concentrations of mahonia fruit anthocyanins at room temperature prior storage were 2378.79 (mg/kg) for ATG, 2435.77 (mg/kg) for GA, 2358.46 (mg/kg) for ATG+GA, 2417.13 (mg/kg) for ATG+MD and 2499.44 (mg/kg) for GA+MD as wall materials. Anthocyanin concentration in GA+MD as wall material was the most accumulated anthocyanin content with respect to the other wall materials at the initial state. The rate of degradation of anthocyanins in the various wall materials were directly proportional to temperature increase. Anthocyanins in samples with wall materials possessing maltodextrin (ATG+MD and GA+MD) had the highest degradation in comparison to anthocyanins with wall materials without maltodextrin (ATG, GA, and ATG+GA). Despite the low initial concentrations in the anthocyanins with ATG as wall material,

we could realize at the 50th day of storage under 45 and 50 °C for all wall materials that ATG retained the most anthocyanin content. This phenomenon could be reported that ATG as wall material is the best wall material to enhance anthocyanin stability against temperature increase compare to gum arabic and maltodextrin.

In Kırca et al. (2006) stated in their study of anthocyanin stability of different fruit nectars and fruit juices from black carrot that the stability of grapes and apples are higher than citrus fruits and supported their statement that lower content of ascorbic fruits has high anthocyanin degradation. *Mahonia aquifolium* fruit which is classified under berries could have low ascorbic content and as such its anthocyanins may also have higher stability to citrus, grapes and apples juices.

4.2.2. *Mahonia aquifolium* anthocyanin kinetic degradation of different wall materials during storage

Table 4.5 represents the kitenic degradation results of mahonia fruit anthocyanins encapsulated with five different wall materials after a 50 days storage at 35, 45 and 50 °C. Using the values of the results indicated in Tables 4.2 to 4.4, the degradation of the anthocyanins with respect to temperature and time changes were calculated through the following kinetic parameters: reaction rate constant (k), half-life (t1/2), activation energy (Ea) and temperature coefficient (Q10). The kinetic study of the mahonia anthocyanin degradation for all the wall materials followed first order reaction as illustrated in figures 4.2 – 4.6. The order of reaction for anthocyanins degradation has also been found in different studies to be in first order kinetics (Xiong et al., 2006; Selim et al., 2008; Weber et al., 2017; de Moura et al., 2018).

Table 4. 5. Reaction rate constant (k), activation energy (E_a), half-life ($t_{1/2}$) and Q_{10} value for encapsulated mahonia anthocyanins encapsulated with different wall materials which stored at different temperature.

Wall material	Temperature (^oC)	k (day^{-1})	R^2	Ea, kJ mol^{-1}	R^2	Half life ($t_{1/2}$) (day)	Q_{10} (35-50 ^oC)
Apricot tree gum	35	0.004	0.9389	37.4221	0.9892	173.287	1.5874
	45	0.006	0.8368			115.525	
	50	0.008	0.8653			86.643	
Gum Arabic	35	0.004	0.9246	74.8435	0.9892	173.287	2.5198
	45	0.009	0.8988			77.016	
	50	0.016	0.9353			43.322	
Apricot tree gum+ Gum arabic	35	0.003	0.9297	77.1074	0.9274	231.049	2.6580
	45	0.009	0.9452			77.016	
	50	0.013	0.9407			53.319	
Apricot tree Gum +Maltodextrin	35	0.005	0.9507	70.9766	0.9681	138.629	2.4351
	45	0.010	0.8633			69.315	
	50	0.019	0.9267			36.481	
Gum Arabic +Maltodextrin	35	0.006	0.9719	66.7880	0.9991	115.525	2.2314
	45	0.014	0.9289			49.511	
	50	0.020	0.8493			34.657	

4.2.2.1. Reaction rate constant (k)

The figure (4.2) shows the graphic of degradation of mahonia fruit anthocyanins encapsulated with apricot tree gum (ATG) at 30, 45 and 50 °C. From the origin, the x-axis indicates the storage time and the y-axis indicates the anthocyanin concentration in apricot tree gum at different temperatures. Reaction rate constants (k) of apricot tree gum were 0.004, 0.006 and 0.008 day^{-1} at temperatures of 35, 45 and 50 °C respectively (Table 4.5). The rate constant (k) of apricot was directly proportional to temperature. The coefficient of correlation (R^2) for apricot tree gum was more than 80 % at the various temperatures. The least correlation coefficient (R^2) was found at storage temperature of 45 °C while the highest being found at 35 °C. The order of correlation coefficients (R^2) wasn't in consistence with temperature and hence didn't have any much relation to the anthocyanin degradation. Likewise, the anthocyanin concentration, rate constant (k) and correlation coefficient (R^2) were all highest at 35 °C storage state.

Per each wall material, the kinetic results for rate constant of reaction(k): correlation coefficient(R^2) during the degradation of mahonia anthocyanins were 0.004:0.9389, 0.006:0.8368 and 0.008:0.8653 for apricot tree gum, 0.004:0.9246, 0.009:0.8988 and 0.016:0.9353 for gum Arabic, 0.003:0.9297, 0.009:0.9452 and 0.013:0.9407 for apricot tree gum+ gum Arabic, 0.005:0.9507, 0.010:0.8633 and 0.019:0.9267 for apricot tree gum+ maltodextrin, and 0.006:0.9719, 0.014:0.9289 and

0.020:0.8493 for gum Arabic+ maltodextrin in sequential order of 35, 45 and 50 °C as storage temperatures(Table 4.5). The rate constants (k) of apricot tree gum, gum Arabic and apricot tree gum+ gum Arabic at 35 °C were almost having the same effect to the degradation of the anthocyanins. As temperature increases the intensity of anthocyanin degradation also increased in all the wall materials.

Similarly, Idham et al. (2012b) reported roselle anthocyanins that increase in temperature increase the rate constant of reaction (k) among all the wall materials they used with only two as an exception. Anthocyanin degradation at 45 and 50 °C were more severe in gum Arabic+ maltodextrin, followed by apricot tree gum+ maltodextrin. We could see from Table 4.5 that the rate constant of reaction (k) was always speeding wherever maltodextrin is involved. On the other, the rate constant of reaction (k) was quiet slower in the absence of maltodextrin causing less degradation of mahonia anthocyanins.

In agreement to our results, reports of Laokuldilok and Kanha (2017) on anthocyanins extracted from black glutinous rice and Kirca et al. (2007) on anthocyanins of strawberry jam stated that increase in storage temperature enchances reaction rate constant (k) and decreases the half life ($t_{1/2}$) of the anthocyanins.

4.2.2.2. Half-life ($t_{1/2}$)

Half-life ($t_{1/2}$) is that parameter of kinetics which helps producers to be able to predict the life span of the products produce. In this study, half-life ($t_{1/2}$) could be defined as the time interval needed for the mahonia anthocyanins concentration to reduce to 50 % of the initial concentration.

The half-life ($t_{1/2}$) values for apricot tree gum, gum Arabic, apricot tree gum+ gum Arabic, apricot tree gum+ maltodextrin and gum Arabic+ maltodextrin at 35,45 and 50 °C were 173.287, 115.525 and 86.643; 173.287, 77.016 and 43.322; 231.049, 77.016 and 53.319; 138.629, 69.315 and 36.481; and 115.525, 49.511 and 34.657 days respectıvely. At all storage temperatures for all wall materials, there were constant declining of half-life ($t_{1/2}$, day) values with increasing temperature. At 35 °C, while the half-lives ($t_{1/2}$, day) of ATG (100%) and GA (100 %) were same; significant differences were found of in the values of their half-lives ($t_{1/2}$, day) when the temperatures were 45 and 50 °C. At all conditions, the most favorite wall material that caused less degradation

of the anthocyanins were the samples with ATG+GA stored at 35 °C which it will have to take 231.049 days to reduce to 50% of the initial concentration. The lowest half-life ($t_{1/2}$, day) values which shows highest anthocyanins degradation occurred in samples with GA+MD as wall material at all temperatures (35, 45 and 50 °C).The half-life ($t_{1/2}$) of the encapsulated mahonia anthocyanins with wall material used in this study had better protected the anthocyanins to what Celli et al. (2016) reported on lowbush blueberry.

Selim et al. (2008) investigated the half-lives of encapsulated roselle (Hibiscus sabdariffa L.) fruit anthocyanins with maltodextrin DE 10 and 20, and gum arabic as wall materials as affected by different a_w. The results of samples with maltodextrin DE 20 was seen as the most effective wall material to elongated the shelf life of the anthocyanins. The values of the half-lives were 433.1 (a_w=0.43), 238.96 (a_w=0.53), 80.58 (a_w=0.64), and 94.93 (a_w=0.75) days.

4.2.2.3. Activation energy (E_a) and temperature coefficient (Q_{10})

Table 4.5 contains the how different wall materials protected the degradation mahonia fruit anthocyanins with respect to the rate of change in activation energy (E_a, kJ mol^{-1}) and temperature coefficient (Q_{10}, 35-50 °C).

Temperature is one of the factors known to highly cause the degradation of anthocyanins during storage. In order to predict the impact of encapsulated mahonia anthocyanins to temperature during storage, activation energy (Ea, kJ mol-1) and temperature coefficient (Q10) values of the samples were calculated.

From Table 4.5, the calculated values of activation energy (Ea, kJ mol-1) for samples with ATG, GA, APTG+GA, ATG+MD and GA+MD as wall materials were 37.4221, 74.8435, 77.1074, 70.9766 and 66.7880 kJ mol-1 respectively. Consequent values for temperature coefficients (Q10) were 1.5874 °C for ATG, 2.5198 °C for GA, 2.6580 °C for ATG+GA, 2.4351 °C for ATG+MD, and 2.2314 °C for GA+MD.

Xiong et al. (2006) studied the degradation of black currant anthocyanins with different temperatures (60, 80 and 100°C) and pH varying from 2.4 to 6.8. The activation energy (E_a, kJ mol^{-1}) energies of the various anthocyanins were higher in the anthocyanins treated with low pH levels (acidic) than in a higher pH levels (basic). This shows that the efffect of temperature to the degradation of the anthocyanin were stable at higher pH than at low pH.

Moldovan and David (2014) analyzed the dependence of degradation of anthocyanins from cornelian cherries on temperature coefficient (Q10) between temperature of 2-22 and 22-75 °C. The Q10 values of anthocyanin samples stored between 2-22 °C varied from 1.277 to 1.346. Those samples stored between 22-75 °C had higher Q10 values. They explained that anthocyanins at more sensitive to higher temperatures which increases their rate of degradation during storage.

4.3. Color analysis

Color of products to be precise fresh fruits and vegetables is postulated to be a quality indicator by most consumers. This encourages researchers to include color analysis of their samples during their research studies. Here, the effect of different wall materials on the color of encapsulated mahonia fruit berries were investigated at different temperatures (35, 45, and 50 ° C) for 50days. From table 4.6, 7, 8, 9 and 10 shows the L*, a* and b* hunter color parameters of the various wall material encapsulates. The initial values of L*,a* and b* parameters for encapsulated mahonia anthocyanins were 59.20±0.16, 47.91±0.48 and 27.56±0.42 for Apricot Tree Gum (ATG) as wall material, 57.84±0.10, 52.36±0.25 and 26.53±0.32 for Apricot Tree Gum (ATG) and Gum Arabic (GA) as wall material, 56.33±0.15, 57.53±0.35 and 28.94±0.06 for ATG and Maltodextrin (MD) combination as wall material, 55.38±0.01, 59.71±0.62 and 31.39±2.40 for GA+MD as wall material and 57.53±0.02, 55.70±0.00 and 26.20±0.00 for GA as wall material respectively.

The highest a* and b* values were recorded in the sample encapsulated with GA+MD as wall material representing the wall material that best protected the reddish and yellowish color parameters of the anthocyanins at the initial stage compare to the other wall materials. However, the highest L* (lightness) value was seen in ATG as wall material at the initial. Contrary, Idham et al. (2012b) reported gum Arabic as the wall material with the highest initial value for L* in their study of anthocyanins from Hibiscus sabdariffa L. encapsulated with different wall materials. When MD was combined to ATG (ATG+MD) and GA (GA+MD) significant increase in a* parameter was observed in both; however, MD improved a* value for ATG better than GA.

Stability of red pigments are high in acidic (lower pH) solutions (Brønnum-Hansen et al., 1985) and MD is known of its acidic feature in aqueous solution and

camouflaged the real color (a*) samples with inclusion MD as their wall to appear as if they improved the a* value to the other non-MD wall material samples.

Table 4. 6. Effects of different temperature on the color parameters (L*, a* and b*) on *Mahonia aquifolium* anthocyanins encapsulated with Apricot Tree Gum during storage.

	35 °C			45 °C			50 °C		
Time(day)	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
0	59.20±0.16	47.91±0.48	27.56±0.42	59.20±0.16	47.91±0.48	27.56±0.42	59.20±0.16	47.91±0.48	27.56±0.42
5	57.88±0.00	48.54±1.66	28.32±0.00	57.39±0.02	52.48±0.27	28.17±0.34	57.58±0.13	52.04±0.11	27.86±0.45
10	58.03±0.35	50.39±0.08	27.92±0.76	56.99±0.00	49.37±2.68	28.05±0.00	58.04±0.11	51.86±0.15	27.83±0.30
15	59.50±2.12	52.88±0.00	29.86±1.46	57.32±0.13	52.26±0.20	28.09±0.27	56.90±0.77	51.69±0.00	28.47±0.00
20	57.56±0.20	51.64±0.16	28.42±0.02	57.51±0.45	52.01±0.05	28.26±0.27	58.60±0.55	51.65±0.14	28.07±0.53
25	57.54±0.08	52.21±0.41	27.82±0.07	55.46±2.08	49.48±2.55	28.25±0.00	57.23±1.64	51.19±0.00	28.06±0.00
30	59.00±0.00	47.05±0.25	28.43±0.00	58.86±0.60	51.25±0.20	27.32±0.67	59.74±0.21	50.73±0.05	28.33±0.17
35	57.91±0.44	52.10±1.08	27.98±0.20	58.16±0.15	52.02±0.11	27.83±0.20	59.09±0.41	51.10±0.09	28.70±0.18
40	57.67±0.00	49.65±2.79	27.27±0.00	57.19±1.82	48.97±2.08	27.39±0.00	57.39±2.83	48.02±1.90	29.39±0.00
45	57.76±0.38	52.20±0.58	27.41±0.32	58.58±0.03	52.13±0.16	28.23±0.02	57.95±0.58	51.16±0.00	29.61±0.00
50	58.09±0.94	50.61±0.01	27.49±0.17	61.02±0.00	47.30±0.31	29.51±0.00	60.27±0.75	49.48±0.77	31.92±0.17

CIElab color parameters results of *Mahonia aquifolium* anthocyanins with Apricot Tree Gum as the wall material is presented below (Table 4.6). Temperature difference didn't have much effect on a*(redness), increase in yellowish color with temperature and L* was approximately constant with temperature difference throughout storage. At 35°C, no significant difference in values of L*, a* and b* during storage as they all remained almost unchanged. In comparison to the control sample, the red color degradation was affected much at storage temperature 50 to 45 °C which caused a reduction in its brighteness level taken samples at day-50 as the baseline. Also it was observed that yellowness of the samples were in parallel with increasing the storage temperature.

Table 4. 7. Effects of different temperature on the color parameters (L*, a* and b*) on *Mahonia aquifolium* anthocyanins encapsulated with Apricot Tree Gum and Gum Arabic combination during storage.

	35°C			45 °C			50 °C		
Days	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
0	57.84±0.10	52.36±0.25	26.53±0.32	57.84±0.10	52.36±0.25	26.53±0.32	57.84±0.10	52.36±0.25	26.53±0.32
5	60.41±0.01	48.14±0.50	25.39±0.23	59.17±0.00	50.21±0.00	25.16±0.00	59.22±0.25	50.13±0.04	25.03±0.41
10	60.55±0.00	47.10±0.00	25.33±.0.00	58.84±0.43	49.98±0.04	24.99±0.00	59.99±0.66	49.75±0.30	25.02±0.61
15	60.12±0.01	49.13±0.52	25.22±0.33	59.77±0.69	49.33±0.16	24.95±0.47	59.85±0.00	46.78±2.41	24.80±0.63
20	59.59±0.04	49.41±0.46	25.29±0.21	59.84±0.85	49.40±0.36	24.58±0.00	61.00±0.50	45.62±3.01	25.59±0.00
25	59.39±0.00	50.54±0.00	25.09±0.00	61.49±0.00	48.23±0.00	23..81±0.00	61.24±1.10	48.27±0.92	25.75±0.30
30	59.87±0.29	49.90±0.05	24.88±0.46	60.16±0.71	49.24±0.45	25.18±0.39	61.61±0.00	46.12±0.82	26.77±0.09
35	59.83±0.08	49.96±0.42	24.90±0.32	61.06±1.58	48.55±1.09	25.18±0.75	62.50±0.28	43.69±2.15	27.03±0.77
40	59.71±0.03	50.12±0.06	24.49±0.08	61.74±0.00	48.41±0.00	24.95±0.00	61.28±0.00	44.01±3.97	27.63±0.00
45	59.59±0.00	49.75±0.00	24.83±0.00	60.82±1.16	48.84±0.82	25.89±0.33	61.69±1.06	47.07±1.46	28.21±0.65
50	59.45±0.11	49.85±0.00	24.93±0.07	61.72±1.39	47.65±1.57	26.20±0.14	62.03±0.00	45.72±0.00	31.04±0.00

L*: lightness, a*: redness, b*: yellow

From Table 4.7, the values of L*, a* and b* for ATG+GA as wall material is presented. the lightness(L*) of the anthocyanins became more brighter as the redness keep diminishing throughout the 50 days of storage under temperatures 35,45 and 50 °C. Meanwhile, discrepancies were detected in the yellowish parameter along the storage line at all temperatures.

Table 4. 8. Effects of different temperature on the color parameters (L*, a* and b*) on *Mahonia aquifolium* anthocyanins encapsulated with Apricot Tree Gum and Maltodextrin combination during storage.

	35°C			45 °C			50 °C		
Time(Day)	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	56.33±0.15	57.53±0.35	28.94±0.06	56.33±0.15	57.53±0.35	28.94±0.06	56.33±0.15	57.53±0.35	28.94±0.06
5	57.44±0.00	55.41±0.00	26.66±0.00	58.32±0.00	53.10±0.84	25.99±0.00	58.94±0.44	52.38±0.59	25.19±0.27
10	57.92±0.27	55.10±0.49	26.71±0.01	59.31±0.37	52.14±0.65	24.92±0.19	62.03±0.19	49.68±0.32	24.06±0.13
15	57.70±0.32	54.90±0.42	26.76±0.01	59.95±0.16	50.085±1.53	24.66±0.00	62.32±2.37	46.91±0.69	24.40±0.00
20	58.10±0.24	54.73±0.36	26.30±0.03	62.87±0.48	49.07±0.74	23.73±0.14	63.64±0.91	45.69±0.00	25.26±0.31
25	57.96±0.00	54.32±0.00	26.49±0.00	61.8±0.34	50.31±0.19	24.57±0.01	65.54±0.16	42.83±0.49	26.79±0.21
30	57.60±0.49	54.26±0.12	26.27±0.11	63.35±0.79	46.66±0.29	24.52±0.01	64.99±0.00	43.31±0.00	29.39±2.07
35	58.36±0.22	54.16±0.28	25.94±0.01	63.11±0.92	47.11±0.00	24.99±0.01	66.03±0.00	42.01±4.03	28.89±1.89
40	58.20±0.01	54.11±0.00	25.74±0.00	64.25±0.30	46.53±0.42	25.45±0.19	66.30±0.00	39.60±0.00	29.38±2.00
45	58.68±0.40	53.69±0.44	25.62±0.09	63.15±1.23	45.91±0.00	25.92±0.38	68.46±0.00	32.88±0.01	32.64±3.51
50	58.55±0.20	53.51±0.38	25.54±0.07	64.13±0.00	43.67±0.01	26.11±0.10	68.29±0.01	29.67±0.00	36.86±6.43

L*: lightness, a*: redness, b*: yellowish

Examining the color of encapsulated anthocyanins with combination of APT+MD as wall material, small increase in L* and decrease in a* parameters were observed at 35 °C. At 45 and 50°C, the lightness parameter became darker while the redness was fading. Despite yellow color parameter was falling under temperatures 35

and 45 °C, increasing yellow color tendency was recorded at 50 °C during the last 20 days of storage (Table 4.8).

Table 4. 9. Effects of different temperature on the color parameters (L*, a* and b*) on *Mahonia aquifolium* anthocyanins encapsulated with Gum Arabic and Maltodextrin combination during storage.

	35 °C			45 °C			50 °C		
Time(day)	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	55.38±0.01	59.71±0.62	31.39±2.40	55.38±0.01	59.71±0.62	31.39±2.40	55.38±0.01	59.71±0.62	31.39±2.40
5	56.41±0.00	58.36±0.65	29.10±2.25	58.60±0.00	56.77±1.02	27.31±2.50	60.08±0.00	55.11±1.90	26.77±2.58
10	57.05±0.01	58.16±0.76	28.74±2.58	59.97±0.75	53.51±0.95	24.49±0.30	60.91±0.01	53.14±2.04	26.66±1.95
15	57.06±0.00	57.28±1.41	27.45±3.45	60.82±0.01	53.54±1.06	25.35±1.09	61.95±0.01	50.04±1.37	26.01±0.93
20	57.60±0.01	57.83±0.88	28.33±2.52	61.34±0.00	53.07±1.77	26.14±1.93	62.13±0.03	48.65±0.20	26.99±1.23
25	58.34±0.02	57.77±0.00	27.23±2.29	61.40±0.01	52.23±1.68	26.26±1.65	61.68±3.00	47.35±4.06	28.26±0.81
30	57.61±0.01	57.73±0.01	26.27±3.46	61.49±0.00	52.52±2.02	26.75±1.91	62.39±0.01	47.58±0.17	28.41±1.02
35	59.06±0.02	57.76±0.00	27.11±2.62	61.03±0.00	51.29±3.15	26.39±2.48	62.80±0.01	45.67±3.70	29.69±0.42
40	59.03±0.00	56.44±1.11	27.02±2.45	62.04±0.01	51.58±2.70	27.28±1.67	63.70±0.01	44.37±0.03	30.45±1.24
45	59.30±0.00	54.86±0.02	26.95±2.40	62.64±0.01	49.77±2.45	27.66±1.35	64.23±0.01	41.87±0.01	31.30±0.21
50	58.17±0.01	52.86±0.01	25.64±3.35	61.96±0.01	48.28±2.70	27.49±1.38	64.65±0.01	38.54±0.02	35.38±0.91

L*: lightness, a*: redness, b*: yellowish

Similarly to the results from the other wall materials, there was nearly acceleration of L* and constant retardation of a* at all storage conditions when GA+MD mixture was used as the encapsulation agent (Table 4.9). The b* parameter had variation response to temperature different. Basically, there was up and down variations in b* parameter throughout storage at 35, 45 and 50°C. However, samples that were stored at 50 °C were more yellowish followed those stored at 45 °C and the least yellowish samples were detected in samples that were stored at 35 °C. The brightest samples were observed in those that were at 50 °C compared to the the samples that were stored at 35 and 45 °C.

Table 4. 10. Effects of different temperature on the color parameters (L*, a* and b*) on *Mahonia aquifolium* anthocyanins encapsulated with Gum Arabic during storage.

	35°C			**45 °C**			**50 °C**		
Time(day)	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	57.53±0.02	55.70±0.00	26.20±0.00	57.53±0.02	55.70±0.00	26.20±0.00	57.53±0.02	55.70±0.00	26.20±0.00
5	56.07±0.36	57.62±0.36	27.66±0.56	56.57±0.36	57.02±0.76	27.04±0.94	57.84±0.61	54.02±1.08	24.67±0.76
10	56.36±0.16	57.57±0.40	27.37±0.65	57.48±0.40	55.77±1.24	26.26±0.88	59.88±1.05	52.01±1.71	24.19±0.60
15	56.44±0.33	57.37±0.31	27.11±0.47	58.14±0.31	55.25±0.62	25.83±0.34	60.77±0.77	50.68±1.83	24.62±0.28
20	56.19±0.51	57.47±0.18	27.33±0.25	60.31±0.01	52.25±2.87	25.45±0.65	61.69±1.12	48.39±3.06	25.51±0.31
25	56.75±0.13	57.08±0.45	27.03±0.61	59.07±0.45	53.69±1.49	26.31±0.53	60.61±0.53	50.18±1.45	26.02±0.02
30	56.88±0.21	56.97±0.39	26.82±0.43	59.54±0.39	52.60±3.01	26.95±0.64	61.88±0.21	47.80±1.30	26.94±0.41
35	57.20±0.25	56.45±0.39	26.37±0.32	59.30±0.39	53.31±1.53	26.82±0.30	61.72±0.69	48.17±1.56	27.32±0.23
40	57.28±0.17	56.27±0.77	26.48±0.56	59.88±0.77	52.28±1.77	27.00±0.09	60.01±3.75	48.03±0.01	30.98±0.01
45	57.50±0.04	56.07±0.04	26.12±0.38	59.81±0.46	52.17±1.06	27.31±0.17	59.66±0.33	50.42±0.75	30.41±0.12
50	58.04±0.21	55.77±0.21	25.80±0.56	59.75±0.51	52.25±1.24	27.51±0.16	60.75±1.14	50.45±0.01	33.55±0.01

L*: lightness, a*: redness, b*: yellowish

In the case when gum Arabic (GA) was used as the wall material during the anthocyanins encapsulation, there wasn't any significant changes in L*, a* and b* values at 35 °C. The values of L*, a* and b* of the samples that were stored at 45 and 50 °C responded positively to temperature. While an increase in L* and b*, the value of a* saw a decrease at the last day of storage (45 and 50 °). However, degradation of a* was more severe at 50 °C than 45°C (Table 4.10).

The reduction in a*(redness) could be as a results of the mahonia anthocyanins degradation with effect of heat during storage (Idham et al., 2012b). Red color is essentially retain in solution when the flavylium cation A is maintained (Chandra et al., 1993). It could be that the wall materials which didn't have MD in their combinations best maintained the flavylium cation and hence were able to better improve the stability of mahonia anthocyanins red color.This could be that red pigments are sensitive to higher temperatures and therefore during processing of products with red color, the choice of processing temperature must be duly considered.

Table 4. 11. Total color difference for mahonia anthocyanins with different wall materials during storage at 35, 45 and 50 °C

	ΔE		
Wall material	**35 °C**	**45 °C**	**50 °C**
ATG	2.99±0.73	2.77±0.23	4.98±0.24
GA	0.31±0.97	4.36±1.11	9.65±0.38
ATG+GA	3.42±0.09	6.15±2.19	9.06±0.30
ATG+MD	5.71±0.12	16.15±0.37	31.94±1.96
GA+MD	9.44±0.13	14.5±0.80	24.15±0.46

Apricot tree gum: ATG, Gum arabic: GA, Maltodextrin: MD

The impact of temperature on the various wall materials used during this study to the color of the *Mahonia aquifolium* anthocyanins was clearly interpreted by the total color change (ΔE) of L*, a* and b* parameters. The anthocyanins were best protected at 35 °C by gum Arabic(GA) followed by Apricot Tree Gum (ATP) and the least protected wall material was the combination of gum Arabic and maltodextrin (GA+MD). When the temperatures were increased to 45 and 50 °C, ATG took the lead as the overall best wall material with the least degradation of the anthocyanins color. Meanwhile the highest color degradation occurred in samples with ATG+MD at 45 °C (16.15±0.37) and 50 °C (31.94±1.96) and GA+MD at 35 °C (9.44±0.13) as wall material. It was observed that inclusion of MD to either GA or ATG speeded color degradation significantly though GA showed better resistance to ATG. This can ascertain that MD could be a bad insulator to heat compare to the other wall materials used during this study.

Wu et al. (2018) studies of color change in relation to different pH (1-7) and temperature on roselle extract anthocyanins reported that when the total color difference (ΔE) is greater than 12, human eyes are able to clearly distinguish the colors formed. In relation to the color difference obtained from this study, it is only samples stored at 45 and 50 °C with encapsulated materials of ATG+MD and GA+MD that could be differentiated with human eyes because their ΔE values were above 12. They also added that color of anthocyanins are relatively stable in acidic mediums at lower temperatures (Wu et al., 2018). Just as determined in this study, Silva et al. (2013) also found the highest total color difference (ΔE) in *Myrciaria jaboticaba* extract encapsulated with the combination gum Arabic and maltodextrin (GA+MD) as wall material in comparison to the other wall materials used in the study.

The total color difference (ΔE) which falls within the range of 0 and 1.5 is considered as small indicating that the color samples are almost the same as the original through visual observation (Silva et al., 2013). This can be confirmed that the color of

mahonia anthocyanin samples that were stored at 35 and 45 °C with wall materials ATG (100 %) amd GA (100 %) were nearly similar to the original color.

Acerola pulp and residue of acerola extracts were microencapsulated by spray and freeze dried using maltodextrin and gum arabic as wall materials. The L* parameter of the control (L* >95) was the brighest as compared to the rest of the encapsulated samples. All the parameters (L*, a*, b*, C* and H) fell within the first quadrant displaying better red and yellow colors which were in line with our results (Rezende et al., 2018).

The results of Chroma (C*) and hue (h) of the encapsulated anthocyanins of different wall materials are shown in Table 4.12. - 4.16. The control values of the Chroma (C*) and Hue (h) were respectively recorded as 55.27±0.20 and 29.91±0.62 for ATG; 58.70±0.08 and 26.87±0.39 for ATG+GA; 64.40±0.29 and 26.71±0.18 for ATG+MD; 67.48±1.66 and 27.70±1.56 for GA+MD; and finally 61.55±0.01 and 25.19±0.01 for GA. The highest color saturation of the control samples was found in the encapsulate sample with gum Arabic and maltodextrin combination (GA+MD) as wall material. However, highest initial value for hue angle was measured in encapsulate with Apricot Tree Gum (APT) as wall material. Throughout storage, there were irregular changes in chroma (C*) and hue (°h) values at temperatures 45 and 50 °C for the five wall materials. Figuring out the control values of chroma (C*) and hue (°h) before and after (50th day) storage at 45 and 50 °C, however, a degrading C* and upgrading h values were recorded for all the five different wall materials. Sanchez et al. (2015) similarly reported an increasing L* and decreasing C* values during their study of cherry juice anthocyanins. The chroma and hue values for the various wall materials did not follow any constant pattern at 35 °C storage temperature. For instance, while chroma and hue values along the storage periods were declining for ATG+MD and GA+MD as wall materials, increasing C* (color saturation) was determined for ATG as wall material.

In Table 4.12, hue (°h) and chroma (C*) values of mahonia anthocyanins thermal degradation is displayed. The range of C* values at storage temperatures 35, 45 and 50 °C were 55.27±0.20 - 60.02±0.01; 55.27±0.20 - 59.33±0.05; and 55.27±0.20 - 59.11±0.00 respectively. Also, the values for hue ranged from 29.91±0.62 to 31.01±0.00; 29.91±0.62 to 31.80±0.01; and 29.91±0.62 to 32.83±0.55 at 35, 45 and 50 °c respectively. Looking at the chroma values between the three storage temperature, we could say that Apricot Tree Gum (ATG) as encapsulating agent well protected the

color saturation (chroma values, C*) from increasing storage temperature and henceforth there wasn't any definite change in the C* values among the samples stored under 35, 45 and 50 °C. Likewise, the effect of temperature increase did not affected the hue values (h) of samples with ATG as wall material as they fell in the first quadrant of the color plane. At the last storage period (50th day), as temperature increases hue angle was moving further from zero causing the color of the anthocyanins with ATG to change from deep-red to light-red along with diminishing color saturation.

Table 4. 12. Effects of different temperature on the color parameters (C* and °h) on *Mahonia aquifolium* anthocyanins encapsulated with Apricot Tree Gum during storage.

	35°C		45 °C		50 °C	
Time(day)	C*	°h	C*	°h	C*	°h
0	55.27±0.20	29.91±0.62	55.27±0.20	29.91±0.62	55.27±0.20	29.91±0.62
5	57.64±0.00	29.43±0.01	59.56±0.08	28.22±0.41	59.03±0.12	28.16±0.43
10	57.61±0.44	28.98±0.62	59.12±0.01	28.33±0.01	58.85±0.01	28.22±0.32
15	60.02±0.01	28.24±0.01	59.33±0.05	28.26±0.32	59.01±0.01	28.85±0.01
20	58.94±0.15	28.82±0.06	59.18±0.09	28.52±0.25	58.78±0.37	28.52±0.39
25	59.16±0.33	28.06±0.25	59.20±0.01	28.50±0.02	58.38±0.00	28.73±0.00
30	55.17±0.00	31.01±0.00	58.08±0.49	28.06±0.50	58.11±0.04	29.18±0.17
35	59.14±0.86	28.25±0.66	59.00±0.01	28.14±0.22	58.61±0.16	29.32±0.11
40	59.10±0.01	27.48±0.01	57.93±0.01	28.22±0.00	57.92±0.01	30.50±0.01
45	58.97±0.67	27.71±0.02	59.27±0.13	28.44±0.09	59.11±0.00	30.20±0.14
50	58.22±0.70	28.18±0.19	56.01±0.02	31.80±0.01	58.89±0.56	32.83±0.55

C*: color saturation, °h: hue angle

In the table below, the results of chroma (C*) and hue (°h) color parameters of *Mahonia aquifolium* anthocyanins with combination of ATG+GA as wall material stored at three different temperatures for 50 days are presented (Table 4.13). Both parameters (C* and °h) were almost the same to each other in respect to difference in storage temperatures. Even if the differences were insignificant, we could realize that as C* values were falling, °h values were rising between the starting day (day zero) and last day (day 50) of storage at all temperatures, except °h at 35 °C.

Table 4. 13. Effects of different temperature on the color parameters (C* and °h) on *Mahonia aquifolium* anthocyanins encapsulated with Apricot Tree Gum and gum Arabic combination during storage.

	35°C		45 °C		50 °C	
Time(day)	C*	°h	C*	°h	C*	°h
0	58.70±0.08	26.87±0.39	58.70±0.08	26.87±0.39	58.70±0.08	26.87±0.39
5	54.43±0.34	27.81±0.46	56.16±0.01	26.62±0.01	56.03±0.21	26.54±0.36
10	53.48±0.01	28.27±0.01	56.16±0.32	27.13±0.55	55.69±0.54	26.70±0.43
15	55.22±0.31	27.18±0.55	55.27±0.35	26.83±0.36	55.37±0.01	28.00±0.63
20	55.50±0.31	27.11±0.40	55.46±0.60	27.03±0.41	54.95±0.01	27.52±0.24
25	56.51±0.01	26.36±0.01	53.79±0.00	26.27±0.01	54.71±0.95	28.08±0.18
30	55.76±0.17	26.50±0.44	55.30±0.55	27.08±0.17	53.32±0.75	30.15±0.36
35	55.81±0.23	26.49±0.48	54.69±1.31	27.41±0.17	53.60±0.01	31.77±0.54
40	55.78±0.02	26.04±0.09	54.46±0.01	27.26±0.01	55.37±0.01	29.94±0.01
45	55.60±0.01	26.52±0.01	55.28±0.88	27.93±0.10	54.89±0.92	30.97±1.37
50	55.74±0.03	26.57±0.06	55.70±0.01	27.90±0.01	53.96±1.30	34.17±0.01

C*: color saturation, °h: hue angle

The color intensity (C*) and hue angle of anthocyanins that was encapsulated with ATG+MD mixture and stored during a 50 days period under temperatures of 35, 45 and 50 °C were measured. The results could be referred from table 4.14. From the table, the intensity of the color (C*) at 35 °C decreased throughout the storage period unlike the other samples at 45 and 50 °C where there were fluctuations in both C* and °h values throughout the storage time. The color intensities (C*) among samples stored under various temperatures was highest at 35 °C and diminished along with increase in temperature. Whiles the hue angle was seen to be increasing with storage temperature increase from 35→45→50 °C. The effect of temperature increase to decreasing C* and increasing °h could be well noticed at the last storage period of the samples since there were up and downs in the values of C* and °h along the storage time.

Table 4. 14. Effects of different temperature on the color parameters (C* and °h) on *Mahonia aquifolium* anthocyanins encapsulated with Apricot Tree Gum and Maltodextrin combination during storage.

	35°C		45 °C		50 °C	
Time(day)	C*	°h	C*	°h	C*	°h
0	64.40±0.29	26.71±0.18	64.40±0.29	26.71±0.18	64.40±0.29	26.71±0.18
5	61.49±0.01	25.70±0.01	58.32±1.56	25.72±0.01	58.12±0.65	25.68±0.02
10	61.23±0.44	25.86±0.20	57.79±0.67	25.54±0.12	55.20±0.34	25.84±0.03
15	61.08±0.38	25.99±0.19	57.20±0.01	24.77±0.77	52.38±0.12	26.40±1.45
20	60.72±0.31	25.66±0.17	55.22±0.01	25.81±0.21	53.54±1.18	28.18±1.05
25	60.44±0.01	26.00±0.01	55.99±0.17	26.03±0.10	50.52±0.53	32.03±0.10
30	60.29±0.07	25.83±0.15	52.34±0.62	26.94±0.65	48.69±2.52	32.24±0.01
35	60.06±0.26	25.60±0.11	53.33±0.01	27.37±0.58	51.13±2.24	30.39±0.01
40	59.92±0.01	25.44±0.01	53.03±0.28	28.68±0.40	52.97±2.44	29.62±0.01
45	59.49±0.44	25.52±0.11	54.53±1.62	29.74±0.01	51.24±2.38	32.91±0.00
50	59.30±0.37	25.51±0.10	53.88±3.05	30.78±0.01	53.38±0.90	34.11±0.01

C*: color saturation, °h: hue angle

The results of hue (°h) and chroma (C*) values of mahonia anthocyanins encapsulated with GA+MD are demonstrated in Table 4.15 during storage at 35, 45 and 50 °C. In comparison to the control sample (t=0) and the end of storage sample (t=50), a falling in chroma (C*) and rising in hue (°h) values could be observed at 45 and 50°C. Chroma (C*) and hue (°h) values were inversely affected by temperature increase (35>45>50 °C). Thus, as color saturation was accelerating, hue angle was decelerating with increase intemperature. At 35 °C the two color parameters (C* and °h) responded in the same direction to temperature by decreasing with time when the control sample was compared to the final sample.

Table 4. 15. Effects of different temperature on the color parameters (C* and °h) on *Mahonia aquifolium* anthocyanins encapsulated with Gum arabic and Maltodextrin combination during storage.

	35°C		45 °C		50 °C	
Time(day)	C*	°h	C*	°h	C*	°h
0	67.48±1.66	27.70±1.56	67.48±1.66	27.70±1.56	67.48±1.66	27.70±1.56
5	65.24±1.59	26.46±1.51	63.02±2.00	25.64±1.65	61.28±2.83	25.85±1.40
10	64.90±1.82	26.25±1.75	58.85±0.98	24.59±0.12	59.45±2.69	26.61±0.81
15	63.57±2.76	25.51±2.26	59.24±1.42	25.33±0.52	56.39±1.63	27.46±0.20
20	64.42±1.90	26.05±1.66	59.17±2.44	26.19±0.93	55.64±0.77	29.01±1.01
25	63.08±1.80	25.55±1.53	58.47±2.25	26.67±0.71	55.16±3.90	30.94±1.45
30	64.93±3.04	25.03±2.23	58.94±2.66	26.95±0.76	55.42±0.67	30.83±0.81
35	62.74±2.22	25.55±1.68	57.68±3.93	27.18±0.76	54.50±3.33	33.13±1.76
40	62.60±2.06	25.54±1.59	58.35±3.17	27.86±0.21	53.82±0.73	34.45±1.07
45	62.28±2.18	25.60±1.49	56.94±2.80	29.07±0.01	56.74±4.34	33.78±3.19

50	60.62±3.25	24.93±2.07	55.56±3.03	29.67±0.15	53.66±0.73	41.31±1.97

C*: color saturation, °h: hue angle

Gum Arabic (GA) was one of the wall materials used to encapsulate the *Mahonia aquifolium* anthocyanins. The effect of different temperatures on color intensity (C*) and hue angle °h) of samples that were encapsulated with this wall materials (GA) were investigated for a 50 days period. The results are shown table 4.16. At t=0, the values of C* and °h were 61.55±0.01 and 25.19±0.01; whiles at t=50, C* and °h were 61.45±0.70 and 24.83±0.28, respectively. This shows that there wasn't any significant effect of temperature on the chroma (C*) and hue angle (°h) of the samples stored 35 °C. On the hand, there were slightly changes in the values of color intensity and hue angle of the samples that were stored under 45 and 50 °C. Observation of the changes in the chroma values (C*) and hue angles showed that there were losses in C* and gains in °h for samples stored at both 45 and 50 °C, despite the fluctuations that occurred throughout storage time.

Table 4. 16. Effects of different temperature on the color parameters (C* and °h) on Mahonia aquifolium anthocyanins encapsulated with Gum arabic during storage.

	35 °C		45 °C		50 °C	
Time(day)	C*	°h	C*	°h	C*	°h
0	61.55±0.01	25.19±0.01	61.55±0.01	25.19±0.01	61.55±0.01	25.19±0.01
5	63.91±0.56	25.65±0.32	63.11±1.09	25.37±0.48	59.39±1.30	24.54±0.23
10	63.75±0.65	25.42±0.37	61.65±1.50	25.21±0.25	57.36±1.80	24.95±0.18
15	63.45±0.48	25.29±0.26	60.99±0.70	25.06±0.05	56.34±1.76	25.93±0.55
20	63.64±0.27	25.43±0.13	58.12±2.87	26.00±0.67	54.72±2.56	27.88±1.78
25	63.15±0.66	25.34±0.33	59.79±1.57	26.11±0.17	56.53±1.28	27.43±0.70
30	62.96±0.53	25.21±0.20	59.11±2.98	27.17±0.79	54.87±0.93	29.42±1.04
35	62.30±0.49	25.04±0.11	59.68±1.50	26.71±0.41	55.38±1.24	29.58±1.00
40	62.19±0.94	25.20±0.17	58.84±1.61	27.33±0.72	53.15±0.54	31.31±4.77
45	61.85±0.58	24.98±0.14	58.89±1.90	27.66±0.79	58.88±0.71	31.10±0.28
50	61.45±0.70	24.83±0.28	59.05±1.17	27.78±0.43	58.96±1.63	37.71±4.09

C*: color saturation, °h: hue angle

The interpretation of Reyes and Cisneros-Zevallos (2007) regarding the effect of pH on the red and purple-flesh potatoes (Solanum tuberosum L.) stated that anthocyanins stability were inversely proportional to pH increase. The color retention of the samples (pH-3) stored at 25 °C in the dark were 68 % for purple flesh potatoes and grape, 86 % for red flesh, and 92 % purple carrot anthocyanins. de Moura et al. (2018) analyzed the effect of varying pressure and feeding values on the color stability of

Hibiscus sabdariffa L. calyces anthocyanins and found that C* and °h parameters rose to a pressure of 0.23 bar. The feeding values for the highest and lowest C* color values were 1.30 mL/min and 1.61 mL/min respectively.

5. SUMMARY AND RECOMMENDATIONS

5.1 Results

This study was carried out to determine the impact of apricot tree gum as a wall material to encapsulate mahonia (*Mahonia aquifolium*) fruit anthocyanins in comparison to the two most widely used wall materials during anthocyanin encapsulation. Stability of the encapsulated samples during storage temperatures of 35, 45 and 50 °C for 50 days were also investigated. A total of five wall materials (Apricot tree gum (ATG), Gum Arabic (GA), Apricot tree gum and Gum Arabic (ATG+GA) combination (50:50), Gum Arabic and Maltodextrin (MD+GA) combination (50:50), and Apricot tree gum and Maltodextrin (ATG+MD) combination (50:50) were used during the encapsulation of *Mahonia aquifolium* anthocyanins.

The highest Encapsulation efficiency was determined as 98.96±0.19 % in samples with apricot tree gum and gum Arabic (ATG+GA) as wall material, followed by gum Arabic (GA) (98.58±0.56 %) and the least was found as 96.18±0.18 % in sample with apricot tree gum and maltodextrin (ATG+MD) as wall material. Maltodextrin had syneresis effect on the efficiencies of apricot tree gum (ATG), and gum arabic (GA).

The results of anthocyanin concentration in the encapsulated samples during storage showed mahonia anthocyanin degradation. Anthocyanin degradation was largely affected at higher storage temperatures. Among the wall materials, the lowest degradation occurred apricot tree gum (ATG) under all temperatures; i.e. stability of the anthocyanins were higher in samples withb ATG. combination of gum arabic and maltodextrin (GA+MD) produced the least protection to the stability of mahonia anthocyanins was compared to the rest at all temperatures.

Kinetic stability results of all wall materials used followed first order of kinetic reaction. The lowest values of reaction rate constant (k), activation energy (E_a) and temperature coefficient (Q_{10}) were $3.0*10^{-3}$ (35 °C), $6.0*10^{-3}$ (45 °C) and $8.0*10^{-3}$ (50 °C) day^{-1} for k, 37.4221 kJ mol^{-1} for E_a and 1.5874 for Q_{10} occurred in samples with apricot tree gum (ATG) with exclusion of k at 35 °C which occurred in samples with combination of apricot tree gum and gum Arabic (ATG+GA). The highest half-live ($t_{1/2}$) values at 45 and 50 °C were 115.525 and 86.643 days respectively which were determined in samples with ATG as wall material. At 35 °C, the highest half-life value

was 231.049 days which occurred in samples with combination of apricot tree gum and gum Arabic (ATG+GA) as wall material, representing the overall highest half-live values at all storage temperatures.

According to the kinetic results, except at 35 °C, all results were in favor of samples having apricot tree gum (ATG) as their wall material. Thus, mahonia anthocyanins are best protected when encapsulated with apricot tree gum (ATG) than maltodextrin (MD), gum Arabic (GA) and their fractions. Nevertheless, lower rate of anthocyanin degradation and higher half-lives at higher storage temperatures (45 and 50 °C) have greater improvement on the stability of anthocyanins and a good material in realization of anthocyanin stability is apricot tree gum. At lower temperature (35 °), there were synergistic effect on the kinetic parameters between mahonia anthocyanin samples with APT and GA as wall materials.

Color of anthocyanins is of much concern so long as color continue to be a quality parameter looking at the side of a consumer. The redness (a*) of the anthocyanins was greater in GA+MD samples at 35 °C and it decreased when 45 to 50 °C. The values of L* varied between 55.38±0.01 and 68.46±0.00 and that of b* ranged from 24.19±0.60 to 36.86±6.43, at all storage temperatures. Samples with GA+MD recorded highest chroma values at 35, 45 and 50 °C whiles hue was highest at 50 °C for GA+MD, 35 and 45 °C for ATG.

For total color difference (ΔE), the stability of anthocyanin color was more effective with samples encapsulated with gum Arabic at 35 °C, however, the stability of mahonia anthocyanin color was better at 45 and 50 °C with apricot tree gum as wall material.

5.2 Recommendations

The world until now still fighting with its armours to protect the instability of anthocyanins. Out of more than million studies on anthocyanins, the instability problem of anthocyanins is yet to find a remedy. This study was embarked to also do its quota on solving if not all but reduce the intensity of the problem of anthocyanin instability.

Throughout this study, all the criterias that we investigated ends up to one material. Apricot tree gum as a wall material produced excellent results we never dream of especially when gum arabic and maltodextrin is included in the race.

Though there could be minusis and plusis, we can ascertain that encapsulated *Mahonia aquifolium* fruit anthocyanins shows that apricot tree gum could be used to improve the stability of anthocyanins.

We therefore recommend researchers who are still into finding the solution to anthocyanins to also give a try to apricot tree gum (ATG) as this is the first ever study of using apricot tree gum as wall material in anthocyanin encapsulation.

The high rate of apricot plantation across the globe and the low cost of its gum exudate when adopted as compare to gum arabic and maltodextrin could uplift the use of natural coloring anthocyanins in food formulation.

In a nut shell apricot tree gum could be use as one of the wall materials in anthocyanin encapsulation. The usual long awaiting delivery of wall materials (gum Arabic and maltodextrin) from abroad in addition to the high cost of import and taxes of these materials will be reduced considerable especially in Turkey since this material will be available in the local markets when the need arises.

Finally, the products of this study (encapsulated anthocyanins with apricot tree gum (ATG) as wall materials) could be used as color additive in pharmaceuticals, cosmetics in products like make-ups, and more especially in food industries for coloring products like fruit juices, confectionaries and colored milk products.

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