UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES

PRODUCTION OF SUMAC, APPLE, CARROT AND GRAPE CONCENTRATES BY FREEZE CONCENTRATION

M. Sc. THESIS
IN
FOOD ENGINEERING

BY
GÜLAY ÖZKANLI
FEBRUARY 2013

Production of Sumac, Apple, Carrot and Grape Concentrates by Freeze Concentration

M.Sc. Thesis

in

Food Engineering

University of Gaziantep

Supervisor

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by

Gülay ÖZKANLI

February 2013

REPUBLIC OF TURKEY
UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
NAME OF THE DEPARTMENT

Name of the thesis: Production of Sumac, Apple, Carrot and Grape Concentrates by Freeze Concentration

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Exam date: 18.02.2013

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Gülay Özkanlı

ABSTRACT

PRODUCTION OF SUMAC, APPLE, CARROT AND GRAPE CONCENTRATES BY FREEZE CONCENTRATION

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M.Sc. in Food Eng.

Supervisor: Prof. Dr. Ali Rıza TEKİN

February 2013

71 pages

Fruit juices contain high amounts of water; so it is beneficial to concentrate them as much as possible to reduce the microbial spoilage and cost of transportation. Various methods are used to produce fruit concentrates. Among them, freeze concentration can be considered as a non-thermal concentration technique. The quality properties of the original juice will not, therefore be altered appreciably after being concentrated.

In this study, sumac, apple, grapes and carrot juices were thawed as a function of time at different temperatures (10 to 25° C) and initial concentrations (1 to 40 ^{o}Brix) to see the effect of these parameters on the degree of separation. The present method can be named as “differential freeze concentration” due to its dependency on time.

As expected, the degree of separation decreased with increase in the initial concentration, thawing temperature and time for all juices. The size and pH values of the samples being thawed were also observed to affect the degree of separation. Thus, increase in size and decrease in the pH values of the samples, resulted in increase in degree of separation.

Key Words: Freeze concentration, fruit concentrate, fruit juice

ÖZET

DONDURARAK KONSANTRE METODUYLA SUMAK, ELMA, HAVUÇ VE ÜZÜM KONSANTRELERİ ÜRETİMİ

ÖZKANLI, Gülay

Yüksek Lisans, Gıda Mühendisliği Bölümü

Tez Danışmanı: Prof. Dr. Ali Rıza TEKİN

Şubat 2013

71 sayfa

Meyve suları yüksek miktarda su içerir; bu nedenle, mikrobiyal bozulma riskini ve nakliye masraflarını azaltmak için bunları mümkün olduğu kadar konsantre etmek gerekir. Meyve sularını konsantre etmek için değişik metotlar kullanılmaktadır. Bunlardan, dondurarak konsantre etme, ısıl olmayan metotlardan biri olarak kabul edilmektedir. Orijinal meyve suyunun kalite özellikleri, bu yüzden, elde edilen meyve konsantresinde fazla değişikliğe uğramamaktadır.

Bu çalışmada sumak, elma, üzüm ve havuç suları dondurulduktan sonra, zamana bağlı olarak, farklı sıcaklıklarda (10 - 25° C) ve başlangıç konsantrasyonlarında (1-40 ^{o}Brix) tavlanmaya tabi tutulmuş, bu değişkenlerin meyve sularının konsantre edilme derecesine etkileri araştırılmıştır. Zamana bağlı olması nedeniyle, bu metot "diferansiyel dondurarak konsantre etme" metodu diye adlandırılabilir.

Beklendiği gibi, konsantre edilme derecesi, -tüm meyve suları için- başlangıç konsantrasyonu, tavlama sıcaklığı ve zaman arttıkça azalma göstermiştir. Tavlanan örneklerin büyüklüğü ve pH değerlerinin de konsantre edilme derecesini etkilediği gözlenmiştir. Böylece, örnek büyüklüğünde artış ile pH değerlerinde düşüş, konsantre edilme derecesinde artışa neden olmuştur.

Anahtar Kelimeler: Dondurarak konsantre etmek, meyve konsantresi, meyve suyu

To my parents…

ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to my supervisor, Professor Dr. Ali Rıza Tekin for his continuous support and patience throughout my thesis study. His immense knowledge and logical way of thinking have been invaluable to me. His understanding, encouraging, academic and personnel guidance have been helped me in all the time of research and writing of this thesis.

I would like to thank to my committee members, Assoc. Prof. Dr. Abuzer Çelenkli and Assist. Prof. Dr. Bülent Belibağlı for their useful discussions and suggestions throughout the study.

Most importantly, none of this would have been possible without the love and patience of my family. They are always beside me during the happy and hard moments and motivate me.

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CHAPTER 1

INTRODUCTION

1.1. Concentration of Fruit Juice

Concentration can be defined as the removal of excess water to reduce volume and weight. Fruit juices contain large amounts of water. So, fruit juices are generally pasteurized or concentrated after squeezing to enhance storage life. Concentration processes reduce the water content from about 75 – 90% to 25 – 35%. That is, the soluble solid content is increased up to 65 – 75%. The concentration of fruit juices has several advantages like economical packaging, transportation and storage as well as microbiological stability (Ramteke et al., 1993).

Various methods are available to remove water from liquid food products. Different kinds of concentration methods such as evaporative concentration, membrane concentration (reverse osmosis), and freeze concentration can be applied commercially (Thijssen, 1975).

1.2. Evaporative Concentration

Evaporation is known as the oldest technique for concentration. At first, fruit juice was concentrated by vacuum evaporation in 1920s. The separation principle of evaporation is the difference in volatilities (vapor pressure) with producing a liquid and a vapor phase. Evaporation removes the solvent, generally water, from solution to increase the solute concentration. The liquid flows through a tube while heat is applied to the outside of the tube. The solvent boils and it is separated from the concentrated liquid. Main components of this system are: A feed preheater and a feed distribution system. The feed preheater is used to bring the feed nearly to the boiling point and the feed distribution system is used to distribute the feed among the tubes (Heldman and Lund, 2007).

Evaporative concentration has several advantages: It causes to decrease the water activity and increases the storage stability of foods. The cost of evaporative concentration systems is generally low so this method is still used widely (Ramteke et al., 1993). On the other hand, evaporation causes loss of volatile substances and aromas of foods. In addition, some foods are heat sensitive so evaporation is not preferred for these type foods (Ramaswamy and Marcotte, 2006a). Moreover; evaporator consumes much energy (Ramtake et al., 1993).

1.2.1. Some Application of Evaporative Concentration in the Food Industry

Evaporation is used for fruit products to concentrate fruit juices. Jams and jellies are produced from fruit juices and purees and pastes are produced from vegetable juices by evaporation, also. In addition, this technique is used for dairy products to concentrate milk, whey and lactose before drying process. It is used for refining sucrose from sugar beet and cane in sugar industry. Salt is produced by evaporation of sea water (Heldman and Lund, 2007).

1.3. Membrane Concentration (Reverse Osmosis)

Reverse osmosis works on the principle of the presence of pressure gradient. The separation is provided by different combined solubilities and diffusivities of species in membrane. This method reduces loss of aroma and flavor so a good quality product is obtained and it consumes low energy (Jiano et al., 2004). In addition, the equipment is not expensive (Cassano et al., 2007). However, high concentrated juice in reverse osmosis system is limited because of high osmotic pressure (Cassano et al., 2007) and the high organic concentration and pH values are not suitable to membranes (Lemmer et al., 2000).

Reverse osmosis was used for desalination by U.S. Department of the Interior, Office of Saline Water in 1953. In 1970s, it was used in the chemical industry e.g. textiles, oil recovery, paint, pulp and paper. The food and biotechnology industries used this technology in the 1980s. This method was then modified to micro-filtration and nanofiltration, so application of membrane technology has been widened (Heldman and Lund, 2007).

1.3.1. Some Applications of Membrane Concentration in the Food Industry

Membrane concentration is used in water treatment, waste treatment, demineralized sea water and desalination. In dairy industry, lactose is produced by this method. Membranes can be applied to fruit juice process for clarification, concentration and acidification (Heldman and Lund, 2007). Other applications of membrane system are concentrated egg white (Conrad et al., 1993; Elaya and Gunasekaran, 2002), coffee and tea extracts, and concentrated flavor compounds (Heldman and Lund, 2007).

1.4. Freeze Concentration

The other commercial method is the freeze concentration and this study is related with this method. Freeze concentration has several advantages. It does not use up much energy (Cassano et al., 2007). The latent heat of phase transition from water to steam is 540 kcal/kg while the latent heat of phase transition from water to ice is 76 kcal/kg so energy is saved by freezing concentration (Yuping and Baomin, 2001; Canovas et al., 2005). Freeze system is worked at low temperatures so corrosion is not significant, thus it requires less maintenance. The most important advantage of this method is that, the characteristics of the original product do not change due to lower temperatures. It also reduces microbiological activity (Lee and Lee, 1999). Freeze concentration is carried out in closed systems so oxidation and denaturation are prevented. This technique is selected to produce a high quality concentrated liquid food and it is suitable for new product development. In fact, it is extremely reliable; it can be both batch and continuous. The process can be used for different products from small volume to large volume. A freeze concentration pilot plant apparatus was shown in Figure 1.1. For freeze concentration, water removal capacity is between 5 and 30,000 kg/hour in industry. Various configurations with capacities ranging from 100 to 400,000 tons per year have been installed (http://www.gea-messo-pt.com).The freeze concentration is not to become widespread due to it's the high price of the equipment (Shamsudin, 2000). The degree of concentration is limited like reverse osmosis (Cassano et al., 2007) and it is not used for cheap juices (Ramaswamy and Marcotte, 2006a). Sensory quality is nearly the same for both freeze concentration and reverse osmosis (Sanchez et al., 2009).

1.4.1. History of Freeze Concentration

Anton Maria Lorgna was issued the first article about freezing process in Italy in 1786 (Nebbia and Menozzi, 1968). He used this method to desalinate sea water. His work was important to develop some refrigerating devices. The difficulties in establishing a simple equipment to produce drinking water was pointed out in 1940s (Parker, 1942). The development of freeze concentration put forward commercial scale. It was used to purify p-xylene in the chemical and petroleum industry in the 1950s. Then, this system was applied to different industrial areas like wastewater treatment, chemical industry, pulp and paper industry, and food industry etc. Generally, this technique has been the most successful in food industry. Warezak (1969) developed the clathrate process in which one component molecules were trapped within the crystals structure of another physically. In this way, freeze concentration was used in beet industry in 1951 and it was used to concentrate vinegar solution in 1959 in a commercial scale (Englezos, 1992).

Figure 1.1. Freeze Concentration Pilot Plant

1.4.2. Some Application of Freeze Concentration in the Food Industry

Generally freeze concentration is used in food and chemical industry. It has been applied to various food samples because it is independent of the food composition (Lemmer et al., 2000).

Some examples can be given why this method is used in food industry. Wine and beer production is aimed to prevent loss of alcohol and flavors by freezing which occurs before fermentation because sugar, not alcohol, is concentrated. Concentration of coffee and tea before freeze drying is necessary for flavor retention.

Preconcentration is essential before freeze drying so freeze concentration is selected to flavor containing liquid foods (Karel, 1975). Especially heat-sensitive fruit juices which are not suitable for the application conventional concentration processes can be deformed physically by extensive heat. This system is therefore used to prevent loss of aroma and prevent any thermal damage (Jusoh et al., 2009). Freeze concentration is also used in dairy industry for new product development, high quality ingredients, and improved final products etc. (Karel, 1975). According to Lemmer et al. (2000), the concentration of wastewater is preferred due to economic reasons. Preconcentration of wastewater is carried out by two methods which are evaporative and freeze concentration. Wastewater contains organic components and salts. High organic concentration and pH values are not suitable for membranes. By freeze concentration system, pure water stream is improved from the wastewater and this stream is used to prepare demineralized water again. 75% of the water in the wastewater can be recovered by this method. This technique has been the best preserved method of freshness of food product until now. It is an improvable method to become commercial (Lemmer et al., 2000). Freeze concentration presents new opportunities in a wide variety of applications.

1.4.3. Freeze Concentration Process

The freeze concentration is a sophisticated method because it fits very well into modern food processing plant. Freeze concentration can be carried out by several ways due to equipment and refrigerant alternatives; so a number of conduits, pumps and controls can be added to the system. Therefore, several freeze-concentration process systems can be imagined. For a single stage process is composed of minimum two components which are a crystallizer or a freezer and a separator (wash column). A multi-stage process is a more appropriate system for industry and its production rate is higher as well as consuming lower energy **(**Rane and Jabade, 2002).

The basic principle of freeze concentration is solid-liquid phase equilibrium. The solution has the solvent as water and soluble components. The freeze concentration separates water from soluble solid without affecting the other components at low temperatures. This condition is important for sensory properties of the original food because lower temperatures protect to preserve quality of the original food (Jusoh et al., 2009). The freezing temperature of solution is reduced by the presence of solute so it freezes below pure water freezing temperature (Yuping and Baomin, 2001; Canovas et al., 2005). Freeze concentration removes heat from aqueous solution and one component crystallizes. It is obvious that freeze concentration removes water as ice crystals; thus water content is lowered in solution and remained part gets highly concentrated solution (Jusoh et al., 2009). The basic components of a freeze concentration unit are crystallizer and wash column.

1.4.3.1. Function of Crystallizer

The crystallizer is a container with a cooling jacket. The inner wall of crystallizer is scraped by rotating blades. The outer wall of crystallizer is cooled by a circulating refrigerant which produces small ice crystals, called nuclei. These ice crystals are removed heat from the solution. It is achieved by a scraped surface heat exchanger (SSHE) at high supercooling and low residence times. Then, these ice crystals pass the recrystallizer for growing large spherical ice crystals **(**Rane and Jabade, 2002; http://www.gea-messo-pt.com). The system is required to get large and symmetrical ice crystals because large crystals are separated easily. Large ice crystals are required to minimize removing a portion of solid within water, also (Wenzelbergel, 1951). Paddle crystallizer is accomplished rather softly stirring thick slurry of ice crystals and allowed growing the bigger crystals from smaller ones (Muller, 1967). The each crystal separation shows different degree of clumping of the crystals (Kessler, 1986). Definitely, the function of crystallizer produces ice crystals and grows these crystals.

1.4.3.2. Function of Wash Column

The function of wash column is separation of the concentrated liquid and ice crystals efficiently by unique device. The separation can be achieved by centrifugation, vacuum filtration, filter pressing as well as wash column. According to Mellor's article (1978), the result of the efficiencies of separation technique was noted as 50% for centrifuging, 71% for vacuum filtration, 89–95% for filter pressing and 99.5% for wash columns. Wash column is a vertical enclosed cylinder whose bottom is operated by feeding ice concentrate. Ice crystals are removed by gravity, hydraulic pressure, or mechanically such as piston and screw. For removing all traces of concentrated liquid, a compressed ice crystal bed is washed with melted ice.

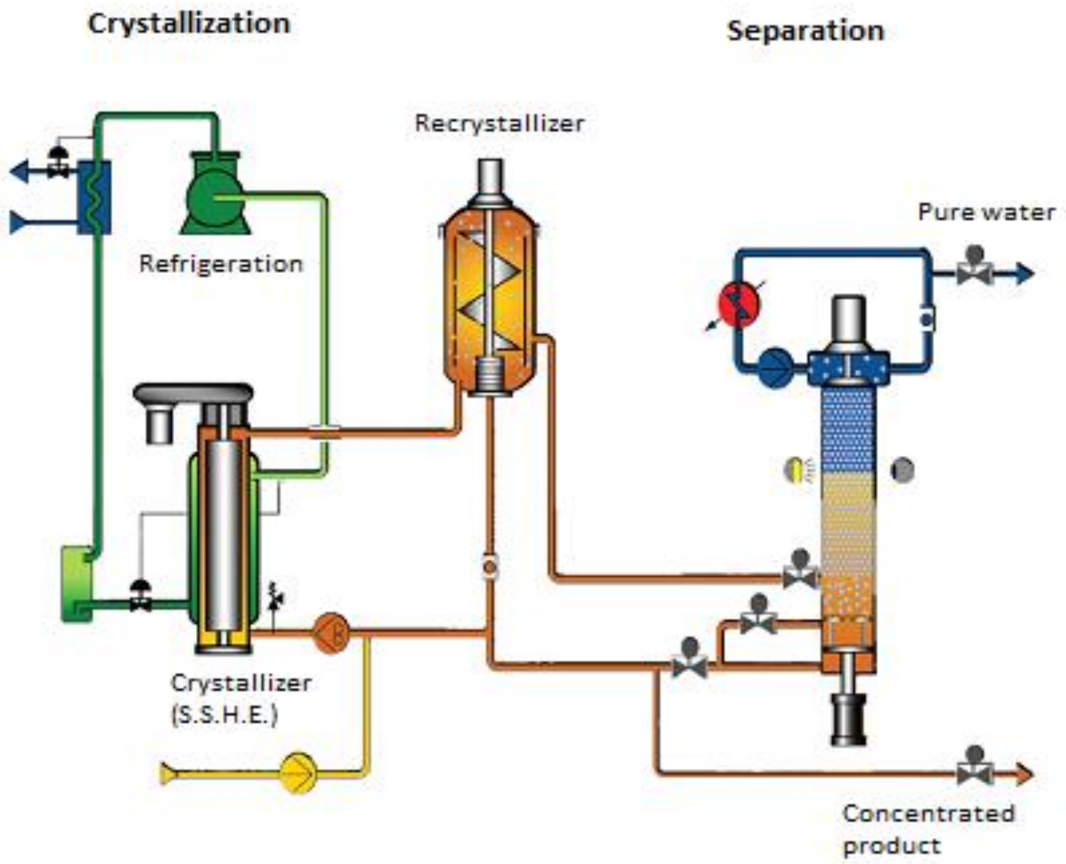


Figure 1.2. Freeze concentration system for concentrated juice production (adapted from http://www.gea-messo-pt.com).

A concrete example can be given for a freeze concentrator which has a scraped-wall heat exchanger attached to an adiabatic recrystallizer tank as shown in Figure 1.2. The liquid sample is pumped from feed tank into the heat exchanger. Basically, the solution is cooled to a temperature which is nearly freezing point by a feed heat exchanger. The juice flows over the refrigerated surface. Small ice crystals are formed due to high supercooling and short residence times. This crystal slurry is passed to the recrystallizer in where it is blended with larger crystals (Lemmer et al., 2000). The recrystallizer tank is used to grow these small ice crystals which form desired pure ice size. Larger crystals have a higher equilibrium temperature than smaller crystals and the big ice crystals affect smaller ones which melt and recrystallize on the surface of larger crystals (Gibbs-Thompson effect). Then, ice and concentrated juice are separated at wash column. The concentrated juice is discharged through a filter plate and ice crystals are apart from the concentrate. The wash column is rinse due to remove adhering concentrate from the ice crystals (Myerson and Ginde, 1993).

1.4.4. Freezing Techniques

1.4.4.1. Suspension Freeze Concentration

The freezing technique or cryoconcentration technology is based on suspension crystallization method. Generally, the suspension crystallization is known as first system of freezing technique (Huige and Thijssen, 1972; Hartel and Espinel, 1993). This system is also known as crystallization process which forms in two phases. Ice nuclei are formed in initial phase and the growth of ice nuclei in the solution occurs in second phase. As a result; suspended ice crystals are formed in the liquid sample. The ice growth rate of suspension freeze concentration is different from other methods, the growth rate is lower than the others but this provides higher ice purity than the others. However, a limitation presents the size of ice crystals (Aider and Halleux, 2008) and the concentration degree is limited. In addition, it is complicated system which contains surface-scraper heat exchanger, re-crystallization, washing tower for producing seed ice, growth ice crystals and separation of ice crystals, respectively (Miyawaki et al., 2005). The scraped surface heat exchanger needs to produce ice seeds to provide ice growth. The size of ice crystals are enlarged in a ripening vessel. Moreover, a filtration system is used to separate ice crystals from concentrated liquid (Widehem and Cochet, 2003).

Suspension crystallization is difficult for separation of ice crystals from the concentrated solution. Therefore, Ostwald ripening mechanism is used to grow large ice crystals (Huige and Thijssen, 1972). Ostwald ripening is defined as water vapor tends to transfer from higher vapor pressure area to lower vapor pressure area at a constant temperature. Higher vapor pressure is in the surface of small crystals and lower vapor pressure is in the surface of larger crystals. However, the most important problem is caused by temperature fluctuation. When the temperature of frozen storage is increased, small ice crystals melt, so the amount of water rises. If the temperature is decreased, the form of nucleus does not continue, so water refreezes on the surface areas of large crystals. Therefore, the number of ice crystals decreases and the crystal size increase.

Ice nucleus begins to grow in a solution, ice phase is formed and solutes are not accepted in this phase. The interfacial tension between ice and mother liquor is low, concentrate adheres to the crystal surface. As a result, a modification is observed in solid-liquid equilibrium temperature. Equilibrium temperature increases decreasing solute concentration, thus, supercooling increases in front of the interphase which can cause instability for growth of ice crystals. Ice nucleation agents are recommended to avoid impurities during initial supercooling in the ice phase. Ice nucleation agents are known as insoluble materials, biogenic and non biogenic origin. Biogenic ice nucleation agent reduces the supercooling degree by increasing ice nucleation temperature. Non biogenic is not preferred for application of food products (Petzold and Aguilera, 2009). The suspension freeze concentration method has been used concentrated coffee extract, fruits juice like apple, berry and kiwi juices etc. (Deshpande et al., 1982; Braddock and Marcy, 1985), milk (Hartel and Espinel, 1993) and wastewater treatment (Heist, 1979).

1.4.4.2. Progressive Freeze Concentration

The second system is known as layer crystallization. Crystallization of water in the solution forms as an ice layer on a cold surface (Muller and Sekoulov, 1992; Flesland, 1995). This technique is called progressive freeze concentration. It is easy separation due to not necessary other unit operations. Thus, progressive method is very different technique in the crystallization process especially from the suspension crystallization method (Miyawaki et al., 2003). Because progressive method produces a single ice crystal while the suspension method produces many small ice crystals. The method is based on cooling surface in a crystallization vessel. Ice and mother solution is to be separated easily with this way (Miyawaki et al., 2003), but impure ice crystals can be produced.

For progressive freeze concentration, Wakisaka et al. (2001) experienced nearly 1.4 fold concentrated glucose solution to represent wastewater. As well as this, average 135 kg ice was produced in 70 minutes by batch operation. In an article by Miyawaki et al. (2005) used sucrose solution, coffee extract and tomato juice for progressive freeze concentration and their results gave high yield and productivity on account of proof tubular ice system suited to progressive freeze concentration. Raventos et al. (2006) studied sugar solutions such as glucose, fructose and sucrose in progressive freeze concentration which produced 31.2° Brix sucrose from 5° Brix sucrose in 16.6 hours in a successful conclusion. This method has been used to purify organic materials (Atwood, 1973; Gilbert, 1991), aqueous and organic solutions (Matthews and Coggeshall, 1959; Shapiro, 1961), concentrated impurities in organic solvent (Matthews and Coggeshall, 1959), waste water treatment and low thermal energy regeneration (Miyawaki et al., 2009). However; productivity of progressive freeze concentration is lower than suspension freeze concentration (Jusoh et al., 2009). New designs have been aimed high efficiency and productivity. Suspension and progressive freeze concentration are shown in Figure 1.3.

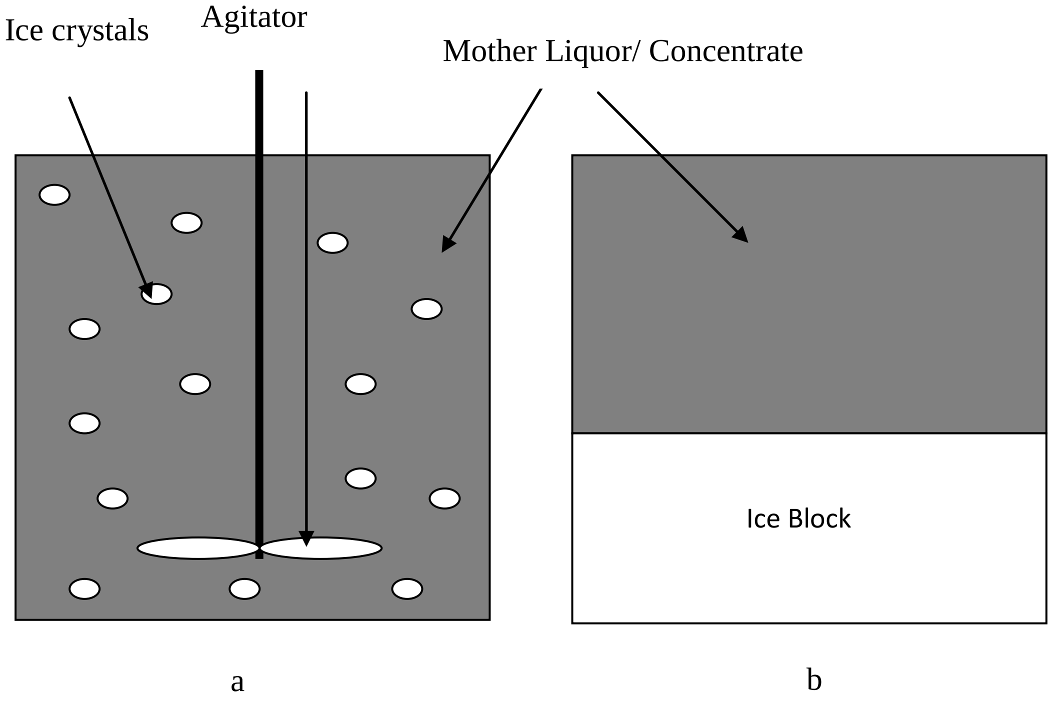


Figure 1.3. (a) Suspension Freeze Concentration and (b) Progressive Freeze Concentration (Miyawaki et al., 2003; Sanchez et al., 2009).

Concentration is purposed of reduction of volume and this phenomenon can be described as effective partition constant value, K, calculated from the concentration and volume of liquid and solid phases (Gu et al., 2008). Effective partition constant is related to initial concentration. This constant is increased by initial concentration. The higher initial concentration, the higher K value but efficiency of the system is lower (Miyawaki et al., 1992). According to Miyawaki (1998), the effective partition coefficient of solute between ice and liquid phases at the ice–liquid interface is the important factor of this process efficiency at progressive cryoconcentration technology. It is defined as:

$$K = C_S / C_L \tag{1}$$

Where C_S is solute concentration in the ice while C_L is the solute concentration in the solution phase. The K value is calculated experimentally. Equation (1) can be obtained from a mass balance, and is defined as:

$$C_L V_L = - C_S \, dV_L + (C_L + dC_L)\,(V_L + dV_L) \qquad (2)$$

where V_L is the liquid volume and C_L is the liquid concentration. ($-dV_L$) is defined as a small volume increase in the ice phase and (dC_L) is the solute concentration increase in the solution phase. It is assumed that complete mixing in the solution phase and no mixing in the ice phase. Combining equation 1 and 2:

$$(dC_L / C_L) / (dV_L / V_L) = K-1 \qquad (3)$$

If K is assumed constant equation (3) is rewritten as:

$$(1-K) \log (V_L / V_O) = \log (C_O / C_L) \qquad (4)$$

Where V_O is the liquid volume at time zero and V_L is the liquid volume at an arbitrary time and C_O and C_L are the concentration of solute in the solution at the corresponding time. K value is between 0 and 1 and this means that when K=0, freeze concentration does not occur and when K=1 freeze concentration occurs completely. K is calculated from this equation and a straight line is observed from graph of log (C_O/ C_L) versus log (V_L/ V_O) (Miyawaki et al., 2005). The effective partition coefficient is the noticeable coefficient of solute between ice phase and bulk liquid phase experimentally. The concentration polarization model analyzes the effective partition coefficient on the solute concentration distribution near the ice–liquid interface, and the advance rate of the ice front (u) and the mass transfer coefficient (k) at the ice–liquid interface are stated as functions. The partition coefficient is defined at following equation (Miyawaki et al., 1998):

$$K = K_O / [K_O + (1 - K_O) \exp(-u/k)] \qquad (5)$$

Where K_O is defined as the limiting partition coefficient representing the partition coefficient of solute at the ice–liquid interface. K_O is response the partition coefficient at an infinitesimal advance rate of ice front (u tends to 0) and at infinite mass transfer coefficient (k tends to ∞) because K is equal to K_O in Eq. (5).

A mass balance equation compared with theory is used:

$$W_{pred} = (C_{FS} - C_I) / (C_{FS} - C_H) \qquad (6)$$

Where W_{pred} is defined as predicted ice mass ratio (kg ice/ kg solution), C_I is the initial solutes concentration (ºBrix), C_{FS} is the final solutes concentration (ºBrix) and C_H is the solutes concentration of ice (ºBrix) (Pradistsuwana et al., 2003).

The efficiency of each concentration stage is calculated by following equation:

$$Efficiency\ (\%) = [1- (C_H/ C_{FS})] *100 \quad (7)$$

Where C_{FS} is the concentration solutes in the liquid phase (ºBrix) and C_H is the concentration of solutes (ºBrix) in the ice formed at the end of each concentration stage.

The impurity of ice is defined as soluble solid remaining in the ice. The relative impurity of ice is determined as the ratio of ice concentration and the concentration in the concentrated juice at the end (Sanchez et al., 2010).

$$Impurity\ ratio\ (\%) = (C_F/C_{FS})*100 \quad (8)$$

For freeze concentration requires large and spherical ice crystals because large ice crystals provides very easy separation and requires short time. So, optimal operation parameters should be selected. Refrigerant temperature, crystal growth rate and agitation rate should be controlled due to heat and mass rates. Moreover, the average distribution coefficient (K) was defined as:

$$K= W_{ice}/ W_S \quad (9)$$

Where W_{ice} and W_S are the solute mass fraction in ice (wt %) the solute, the solute mass fraction in the bulk solution (wt %), respectively (Sanchez et al., 2011).

1.4.4.3. Block Freeze Concentration

The third procedure is defined as block crystallization. A liquid solution is frozen completely and then the temperature at the center of the product is decreased below the freezing point. After that, this frozen solution is thawed and the concentrated part is separated from ice. If the thawing temperature is controlled, it is possible to achieve process efficiency higher than 90%, so solute in the ice crystal is decreased successfully (Aider and Halleux, 2008). The phenomenon of these methods produced ice by different heat extraction. The advantage of block concentration is that it is easier than the others. That is, the equipment usage is easy due to no moving parts

(Sanchez et al., 2009). Complete block technology is influential procedure for concentrated liquid foods which have high nutritive value and organoleptic properties (Aider et al., 2007; Aider and Halleux, 2008).

Partial block freeze technology is new and effective technique. A liquid solution is firstly introduced in a crystallizer chamber and then passed a pipe, in which a cryogen is circulated, is occurred partially frozen from the center.

A block freezer is based on separation of solution at low temperatures. Refrigeration machine provides a block of ice. The block of ice is to be separated by gravitation. Further perfection of the block freezers can be carried out at the expense of intensification of the processes of heat transfer and mass transfer in the boundary layer (Burdo et al., 2007). This technology is succeed in aromatic compounds from grape seeds, fruit juices, coffee extract and concentrate milk whey (Aider and Halleux, 2008).

1.4.4.4. Eutectic Freeze Concentration

Different method is used to separate inorganic salts from aqueous solution by crystallization of both solute and ice at the same time. This technique is called as eutectic freeze concentration (Vaessen et al., 2002). The solution is cooled down below the eutectic temperature which can be defined as the melting point dependent on ratio of ingredients in solution for frozen heterogeneous liquid food. The ratio of mixture affects melting point which is as far as low. Moreover, the crystal size distribution is important because it affects performance of the downstream separation equipment. An example for eutectic cryoconcentration, it can be applied to the purification of waste water streams with high soluble salts. Aqueous electrolyte solutions can be distinguished into pure water as ice and salt. Gravitation achieves separation between salt and ice crystals which have different densities (Vaessen et al., 2002; Vaessen et al., 2003). Eutectic cryoconcentration technology has been investigated by Stepakoff et al. 1974. The system requires equipment which is composed of solid/ solid separator, filters, wash column, pumps etc. This technique has been recently modernized so it requires low energy consumption, and provides high purity of products (Van der Ham et al., 1998).

1.5. Aim of the Present Study

The freeze concentration method is important because of maintaining original properties of foods. Among different freeze concentration methods, block freeze concentration is adopted in this study due its simplicity and applicability under laboratory conditions. In addition, the degree of separation was analyzed by a differential melting process which is time dependent. This method is unique, because no similar methods have not been observed in the literature.

In this study, separation of high-concentrated soluble solids from ice was accomplished for varied initial concentrations of various fruit juices at different temperatures. The effect of the frozen samples size on the degree of separation of the soluble solids from the ice was also studied at different time intervals.

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

2.1.1. Sumac Juice

Sumac berries were supplied from sumac trees in the campus of University of Gaziantep. After harvesting sumac berries in clusters, they were destemmed. Then, these berries were screened to separate unripe flower residues and impurities. They were soaked and leached in distilled water. The suspended insoluble materials in the sumac juice were removed by filtration.

2.1.2. Apple Juice

Apple juice was purchased from a local market in Gaziantep. 100% apple juice, not containing added sugar, was selected.

2.1.3. Grape Juice

Grape juice was purchased from a local market in Gaziantep. 100% grape juice, not containing added sugar, was selected.

2.1.4. Carrot Juice

Carrots were purchased from a local market in Gaziantep. Carrots were washed to remove impurities. Carrot juice was obtained by using hard fruit squeezer.

2.1.5. Water

Distilled water was used for adjusting concentration of juices. It was supplied from the Food Engineering Department, General Chemistry Laboratory, water distilling unit.

2.2. Preparation of Concentrated Juices

These samples were concentrated using two types evaporators: a rotary evaporator (Bibby, RE 100, Rotary Evaporator) and a laboratory type rising film evaporator

(Armfield FT 22-A, Rising Film Evaporator).

2.3. Variation of pH Value of Concentrated Juices with Concentration

The pH value of various fruit juices at different concentration was measured with a digital pH meter (WTW 2A10-1012, Germany). The measurement was done at room temperature 23 ± 2 ºC.

2.4. Titratable Acidity of Juices

Titratable acidity was measured by titration with 0.1 N NaOH. The sample was titrated with 0.1 N NaOH using a few drops of 1% phenolphthalein solution as indicator until a pink color was observed.

2.5. Measurement of Concentration of Juices

The concentration of solutes was measured in terms of ºBrix using Pocket PAL-1 and Pocket PAL-2, ATAGO hand refractometer. The accuracy of these refractometers was ± 0.1 with a measurement range of 0-53 ºBrix for Pocket PAL-1 and 45-93 ºBrix for Pocket PAL-2. Results were expressed as Brix degrees. The measurements were made at the different temperatures (10, 15, 20 and 25ºC).

2.6. Preparation of Juices with Varied Concentration

Various concentration of juices were prepared. Samples with various soluble solid contents (1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35 and 40 ºBrix) were prepared by dilution of the original concentrated juice. They were prepared for each sample.

2.7. Analysis of Separation of Juice from Ice

100 mL of each sample was placed in 150 mL bottles. These samples were frozen in a deep freezer of a refrigerator at -18 ºC. Then, they were thawed at different temperatures (10, 15, 20 and 25 ºC) in a temperature-controlled oven (Binder, Germany). This experiment was shown in Figure 2.1. The bottle was put in this oven. Frozen juice began to melt. Then, melting portion was collected in a small beaker. The concentration of melting portion was measured at 5-minute time intervals during melting. All experimental measurements were made in double with samples prepared from the same concentrated juice. The same procedure was used for 250, 500 and 750 mL of samples at 10ºC.

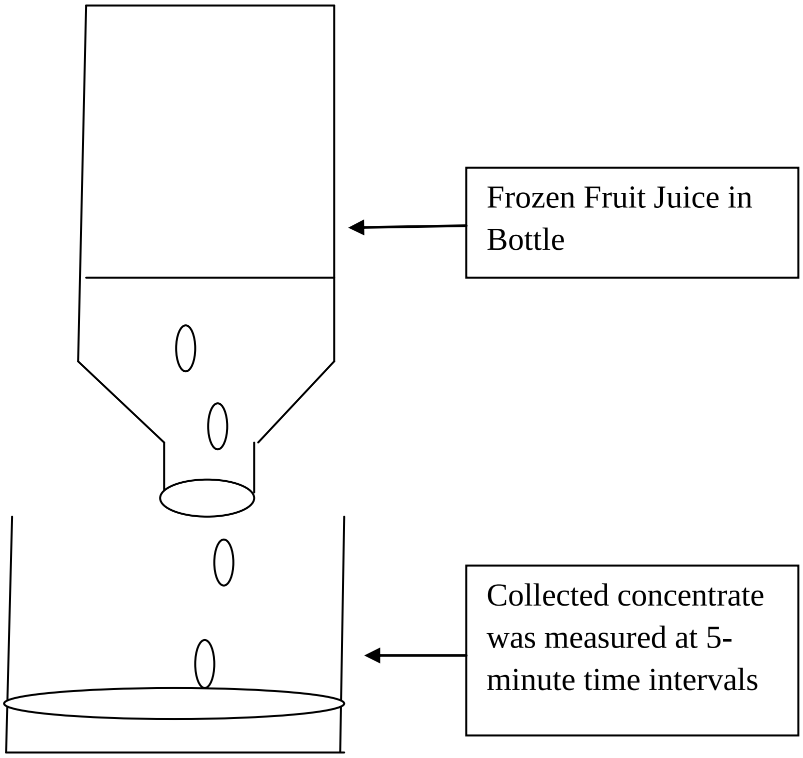


Figure 2.2. The experimental set-up of the system

2.8. Statistical Analysis

Exponential decay model was observed to be the best fitted model for all data. The parameters of the models were calculated by the NLIN (non-linear) and linear procedures of the Sigma Plot (Scientific Graph System, version 11.00).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. The Effect of Initial Concentration on Degree of Separation

Different samples at constant initial concentrations were thawed as a function of different temperatures. During the experiment, separation of the concentrated juice from ice was observed. The degree of separation could be dependent upon initial concentrations of the juice. This behavior is clearly shown in Tables 3.1– 3.4. Thus, the degree of separation decreased with increasing initial concentration of the juice. In other words, an inverse relationship between the initial concentration and the degree of separation was found. The concentration of the first drop of juice (having an initial concentration of 1 ºBrix) was observed to be 20 ºBrix. The concentration of the first drop of juice (having an initial concentration of 20 ºBrix) was observed to be 40 ºBrix. The concentration of the first drop of juice (having an initial concentration of 40 ºBrix) was increased to 48 ºBrix.

Table 3.1. Concentration of the first drop of sumac juice at different initial concentrations at 10 ºC

Initial Concentration (ºBrix)	Concentration of the First Drop (ºBrix)	Degree of Separation (Concentration of the First Drop/ Initial Concentration)
1	26.1	26.10
2	28.2	14.10
3	32.0	10.67
4	33.1	8.28
5	34.4	6.88
10	39.1	3.91
15	42.5	2.83
20	42.9	2.15
25	43.7	1.75
30	44.8	1.49
35	46.9	1.34
40	47.6	1.19

Table 3.2. Concentration of the first drop of apple juice at different initial concentrations at 10 ºC

Initial Concentration (ºBrix)	Concentration of the First Drop (ºBrix)	Degree of Separation (Concentration of the First Drop/ Initial Concentration)
1	24.3	24.30
2	28.4	14.20
3	30.2	10.07
4	30.5	7.63
5	30.7	6.14
10	40.8	4.08
15	42.6	2.84
20	44.7	2.24
25	45.8	1.83
30	47.5	1.58
35	47.7	1.36
40	48.5	1.21

Table 3.3. Concentration of the first drop of grape juice at different initial concentrations at 10 ºC

Initial Concentration (ºBrix)	Concentration of the First Drop (ºBrix)	Degree of Separation (Concentration of the First Drop/ Initial Concentration)
1	26.6	26.60
2	27.3	13.65
3	29.7	9.90
4	31.1	7.78
5	31.9	6.38
10	39.7	3.97
15	41.1	2.74
20	44.9	2.25
25	45.6	1.82
30	46.5	1.55
35	47.8	1.37
40	48.8	1.22

Table 3.4. Concentration of the first drop of carrot juice at different initial concentrations at 10 ºC

Initial Concentration (ºBrix)	The Concentration of the First Drop (ºBrix)	Degree of Separation (Concentration of the First Drop/ Initial Concentration)
1	23.2	23.20
2	24.5	12.25
3	25.4	8.47
4	26.2	6.55
5	28.7	5.74
10	30.7	3.07
15	33.4	2.23
20	35.5	1.78
25	37.1	1.48
30	40.2	1.34
35	41.1	1.17
40	42.4	1.06

3.2. Effect of Concentration on the pH Value of Different Juices

pH was measured at room temperature for different fruit juices. Table 3.5 shows

Table 3.5. Variation of pH with concentration for different juices

Concentration (ºBrix)	pH (Sumac Juice)	pH (Apple Juice)	pH (Grape Juice)	pH (Carrot Juice)
1	2.94	3.78	3.75	6.64
2	2.93	3.76	3.74	6.61
3	2.91	3.74	3.73	6.57
4	2.86	3.73	3.72	6.53
5	2.80	3.68	3.71	6.46
10	2.76	3.66	3.70	5.99
15	2.69	3.64	3.67	5.86
20	2.61	3.63	3.66	5.63
25	2.59	3.63	3.65	5.57
30	2.55	3.58	3.64	5.47
35	2.49	3.56	3.64	5.43
40	2.38	3.55	3.63	5.35

variation in pH values by changing concentration for each sample. According to these results, pH values of the concentrates did not change with concentration significantly. Values of pH slightly changed for buffer solution. Therefore, these concentrates were observed to behave like buffers.

3.3. Titratable Acidity of Different Samples

Titratable acidity is a measure of the total amount of acid present in the solution. The titratable acidity of a solution occurs for any acid that loses protons in an acid- base reaction.

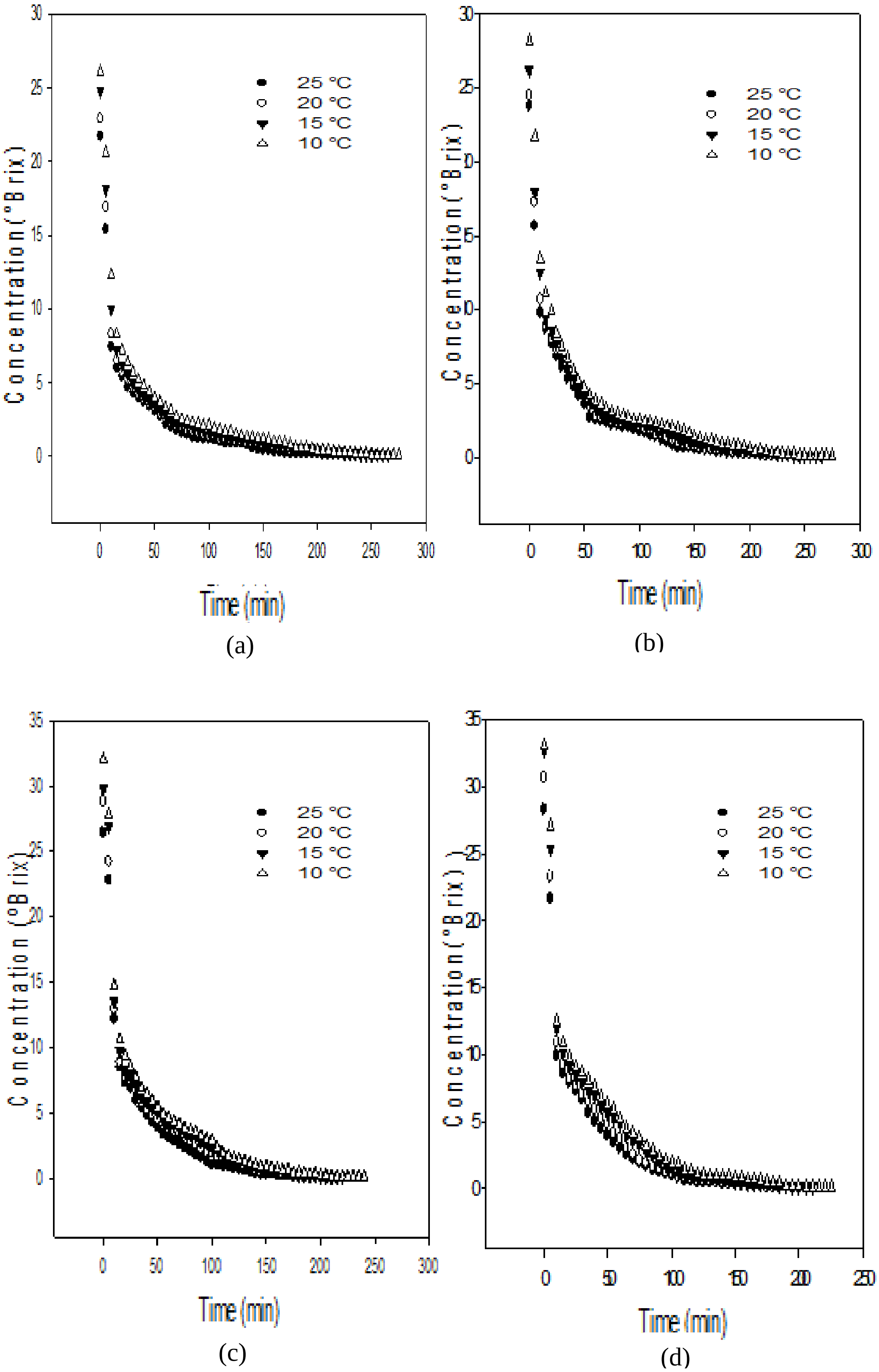
Table 3.6. Titratable acidity of different fruit juices

Sample	ºBrix	Titratable Acidity (g/100 mL)	Corrected Titratable Acidity (g/100 mL)
Sumac	1.5	1.69	12.28
Apple	10.9	2.79	2.79
Grape	10.6	1.23	1.26
Carrot	3.5	0.32	0.99

3.4. Effect of Temperature on the Concentration of Sumac Concentrates

In this study, four temperatures were studied 10, 15, 20 and 25 ºC. At mentioned temperatures concentrations were measured at five minute time intervals. The data of concentration versus time were plotted at each temperature.

As expected, the juice that separates from the frozen block is more concentrated at the beginning of the thawing step and decreases as thawing proceeds as in Figures 3.1– 3.12. These figures show that the degree of separation was observed to be dependent upon initial concentrations of the juice. The degree of separation decreased with increasing initial concentration of the juice. Tables 7– 18 indicate that equation coefficient decreases with increasing temperature. Temperature effect on the separation of concentrated juice is seen clearly. This is shown that lower temperatures exhibit higher degree of separation.



(a) (b) (c) (d)

Figure 3.1. Variation of concentration with time for sumac concentrates at different temperatures: (a) initial concentration 1 ºBrix, (b) initial concentration 2 ºBrix, (c) initial concentration 3 ºBrix, (d) initial concentration 4 ºBrix

Table 3.7. Regression analyses for sumac concentrates (initial concentration 1, 2, 3 and 4 ºBrix) at different temperatures

Initial Concentration (ºBrix)	**Temperature (ºC)**	**Equation**	**R^2**
1	**10**	y= 23.39*exp(-0.044*x)	0.916
	15	y= 22.12*exp(-0.050*x)	0.913
	20	y= 20.38*exp(-0.051*x)	0.908
	25	y= 19.23*exp(-0.053*x)	0.912
2	**10**	y= 24.012*exp(-0.035*x)	0.926
	15	y= 21.625*exp(-0.036*x)	0.926
	20	y= 20.29*exp(-0.036*x)	0.930
	25	y= 19.63*exp(-0.038*x)	0.929
3	**10**	y= 28.68*exp(-0.040*x)	0.912
	15	y= 27.25*exp(-0.042*x)	0.904
	20	y= 26.22*exp(-0.045*x)	0.918
	25	y= 24.89*exp(-0.047*x)	0.940
4	**10**	y= 27.98*exp(-0.037*x)	0.907
	15	y= 27.94*exp(-0.041*x)	0.909
	20	y= 27.05*exp(-0.047*x)	0.923
	25	y= 25.32*exp(-0.049*x)	0.929

* x= Time (min)
* y= Concentration (°Brix)

Table 3.7 shows the data fitted by non-linear regression analysis at different temperatures for lower sumac concentrates. The determination of coefficient (R^2) values changed between 0.904 and 0.940. The higher R^2 values were obtained by using exponential decay model. This model was observed to be the best fitted model for all data. In the model equation, y-axis shows that the concentration (ºBrix) decays with x-axis (time). Negative exponent indicates exponential decay.

Figure 3.2 illustrates the change in ºBrix as a function of time at different temperatures for initial concentration between 5 and 20 ºBrix of sumac concentrates.

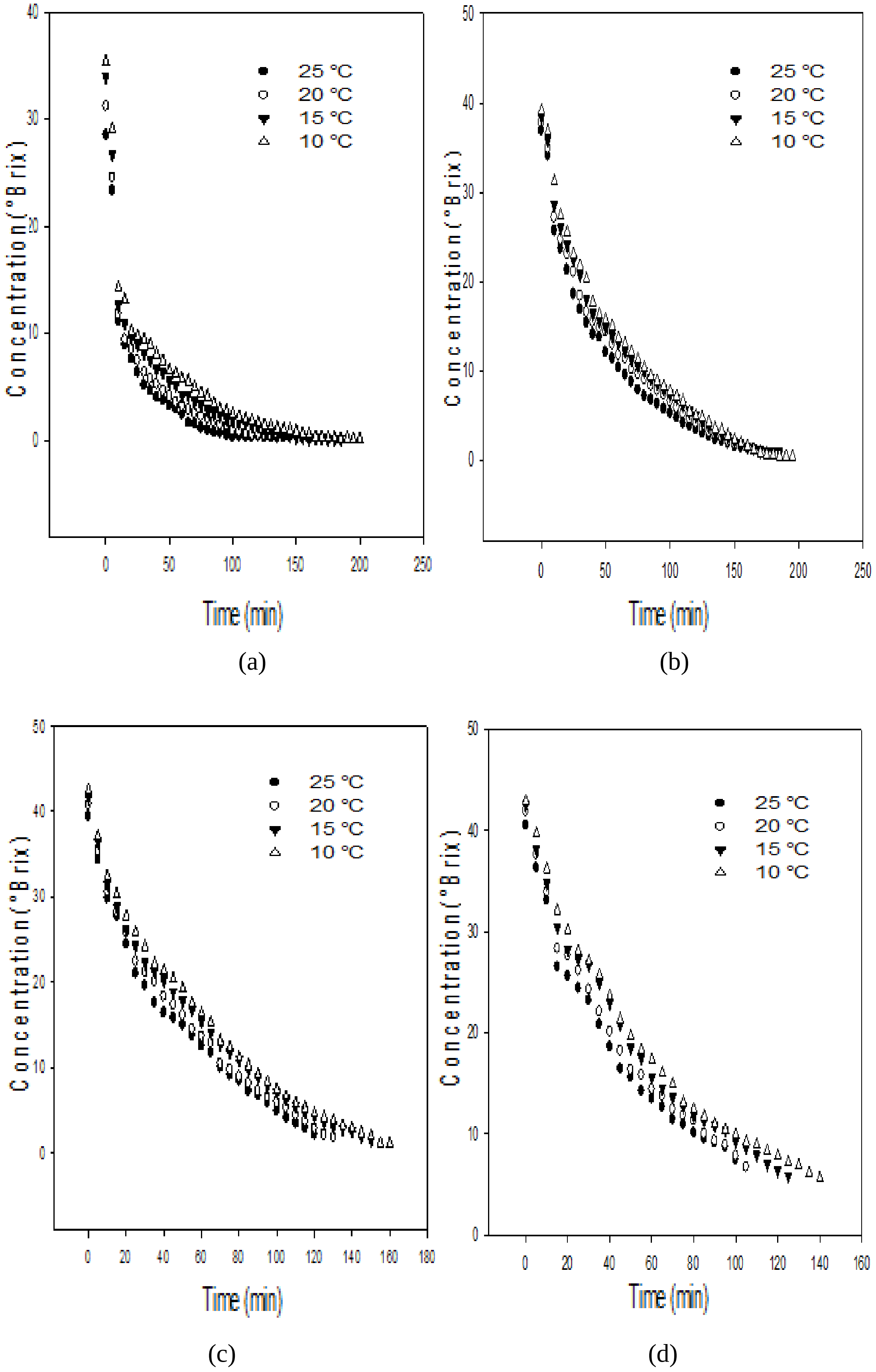


Figure 3.2. Variation of concentration with time for sumac concentrates at different temperatures: (a) initial concentration 5 ºBrix, (b) initial concentration 10 ºBrix, (c) initial concentration 15 ºBrix, (d) initial concentration 20 ºBrix

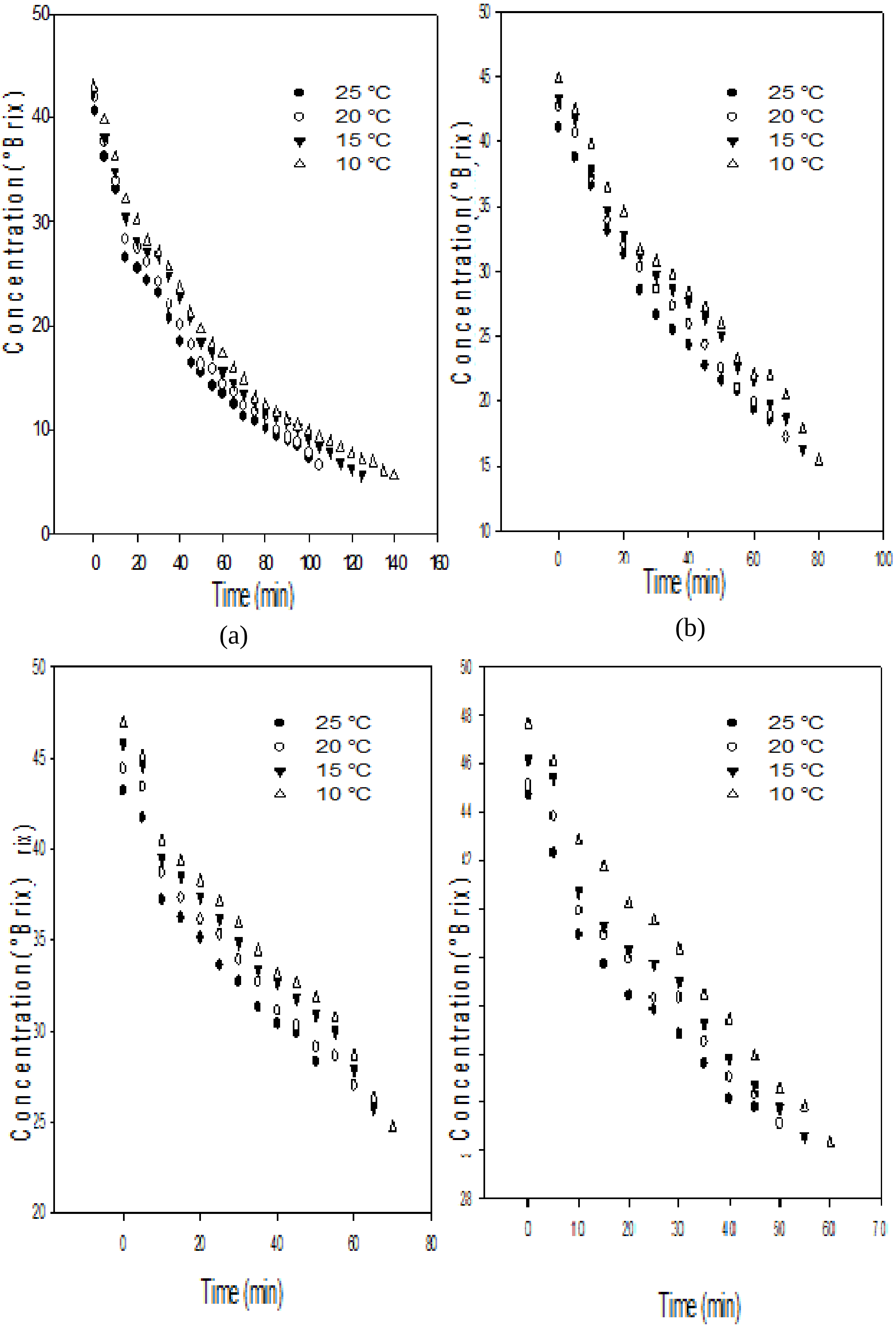
Table 3.8. Regression analyses for sumac concentrates (initial concentration 5, 10, 15 and 20 ºBrix) at different temperatures

Initial Concentration (ºBrix)	**Temperature (ºC)**	**Equation**	**R^2**
5	**10**	y= 29.86*exp(-0.0350*x)	0.906
	15	y= 29.46*exp(-0.0424*x)	0.912
	20	y= 28.88*exp(-0.0530*x)	0.937
	25	y= 27.66*exp(-0.0592*x)	0.958
10	**10**	y= 37.73*exp(-0.017*x)	0.992
	15	y= 36.07*exp(-0.017*x)	0.989
	20	y= 35.04*exp(-0.018*x)	0.985
	25	y= 34.27*exp(-0.021*x)	0.984
15	**10**	y= 40.66*exp(-0.017*x)	0.990
	15	y= 39.22*exp(-0.017*x)	0.989
	20	y= 38.75*exp(-0.019*x)	0.992
	25	y= 37.56*exp(-0.020*x)	0.991
20	**10**	y= 41.77*exp(-0.015*x)	0.997
	15	y= 40.78*exp(-0.015*x)	0.994
	20	y= 40.02*exp(-0.017*x)	0.992
	25	y= 38.51*exp(-0.016*x)	0.986

* x= Time (min)
* y= Concentration (°Brix)

According to regression analyses (Table 3.8), the higher determination coefficient (R^2) values were obtained for sumac concentrates by exponential decay model. R^2 values changed between 0.906 and 0.997. In the model equation, y-axis shows that the concentration (ºBrix) decays with x-axis (time).

The change in ºBrix as a function of time at different temperatures for higher sumac concentrates with initial concentration between 25 and 40 ºBrix are shown in Figure 3.3.



(a) (b)

(c) (d)

Figure 3.3. Variation of concentration with time for sumac concentrates at different temperatures: (a) initial concentration 25 ºBrix, (b) initial concentration 30 ºBrix, (c) initial concentration 35 ºBrix, (d) initial concentration 40 ºBrix

Table 3.9. Regression analyses for sumac concentrates (initial concentration 25, 30, 35 and 40 ºBrix) at different temperatures

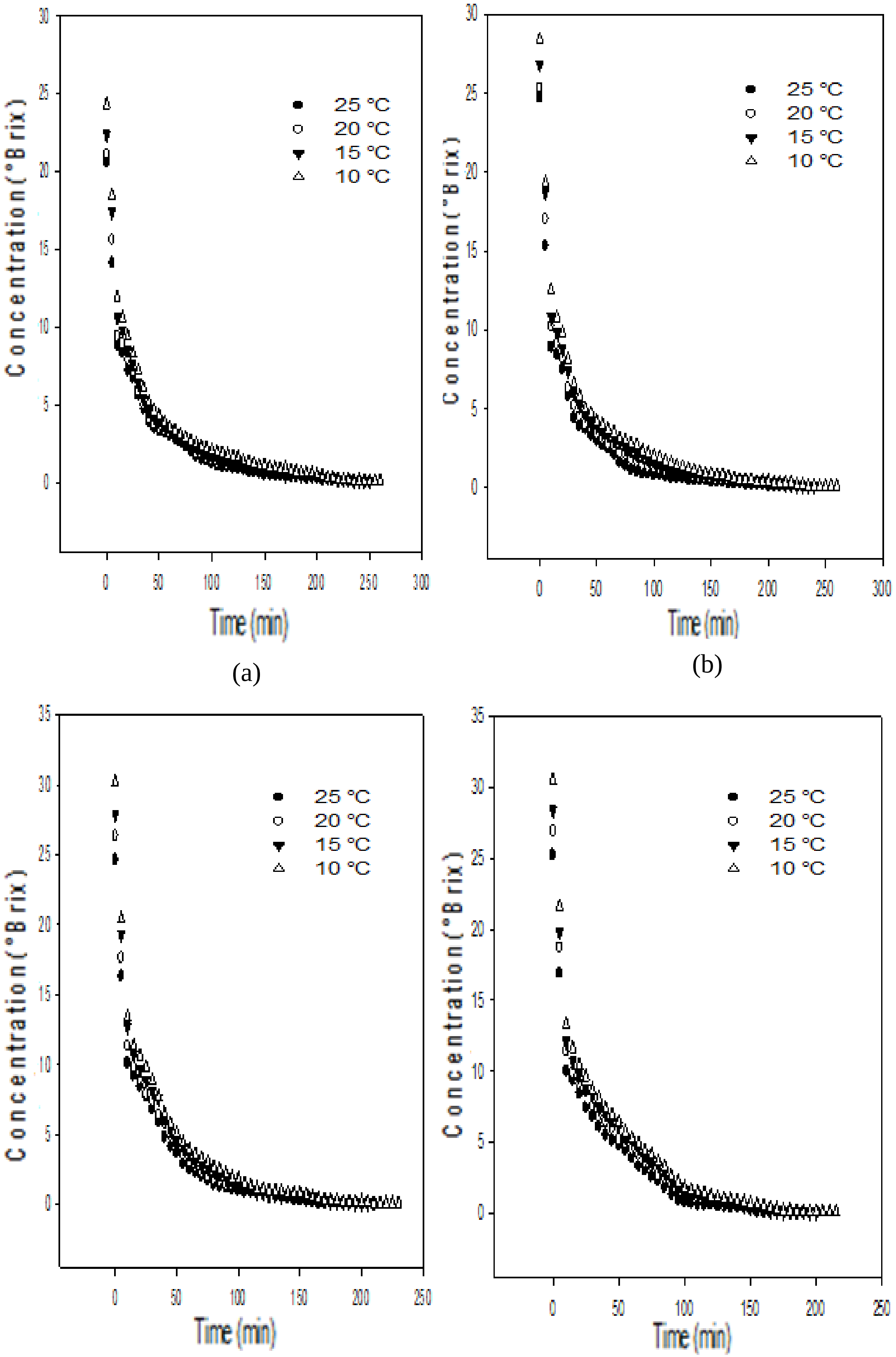
Initial Concentration (ºBrix)	Temperature (ºC)	Equation	R^2
25	**10**	y= 44.81*exp(-0.016*x)	0.998
	15	y= 43.16*exp(-0.016*x)	0.997
	20	y= 42.28*exp(-0.017*x)	0.994
	25	y= 41.40*exp(-0.018*x)	0.992
30	**10**	y= 44.38*exp(-0.012*x)	0.989
	15	y= 42.95*exp(-0.012*x)	0.988
	20	y= 42.29*exp(-0.013*x)	0.996
	25	y= 40.75*exp(-0.013*x)	0.993
35	**10**	y= 45.72*exp(-0.008*x)	0.975
	15	y= 44.65*exp(-0.008*x)	0.972
	20	y= 43.45*exp(-0.008*x)	0.976
	25	y= 42.09*exp(-0.008*x)	0.964
40	**10**	y= 47.12*exp(-0.007*x)	0.993
	15	y= 45.36*exp(-0.007*x)	0.968
	20	y= 44.31*exp(-0.007*x)	0.973
	25	y= 43.31*exp(-0.008*x)	0.959

* x= Time (min)
* y= Concentration (°Brix)

Table 3.9 shows the data fitted by non-linear regression analysis at different temperatures for higher sumac concentrates. The determination of coefficient (R^2) values changed between 0.959 and 0.998. This model was observed to be the best fitted model for all data.

3.5. Effect of Temperature on the Concentration of Apple Concentrates

The change in ºBrix as a function of time at different temperatures for lower apple concentrates with a constant initial concentration illustrates Figure 3.4.



(a) (b)

(c) (d)

Figure 3.4. Variation of concentration with time for apple concentrates at different temperatures: (a) initial concentration 1 ºBrix, (b) initial concentration 2 ºBrix, (c) initial concentration 3 ºBrix, (d) initial concentration 4 ºBrix

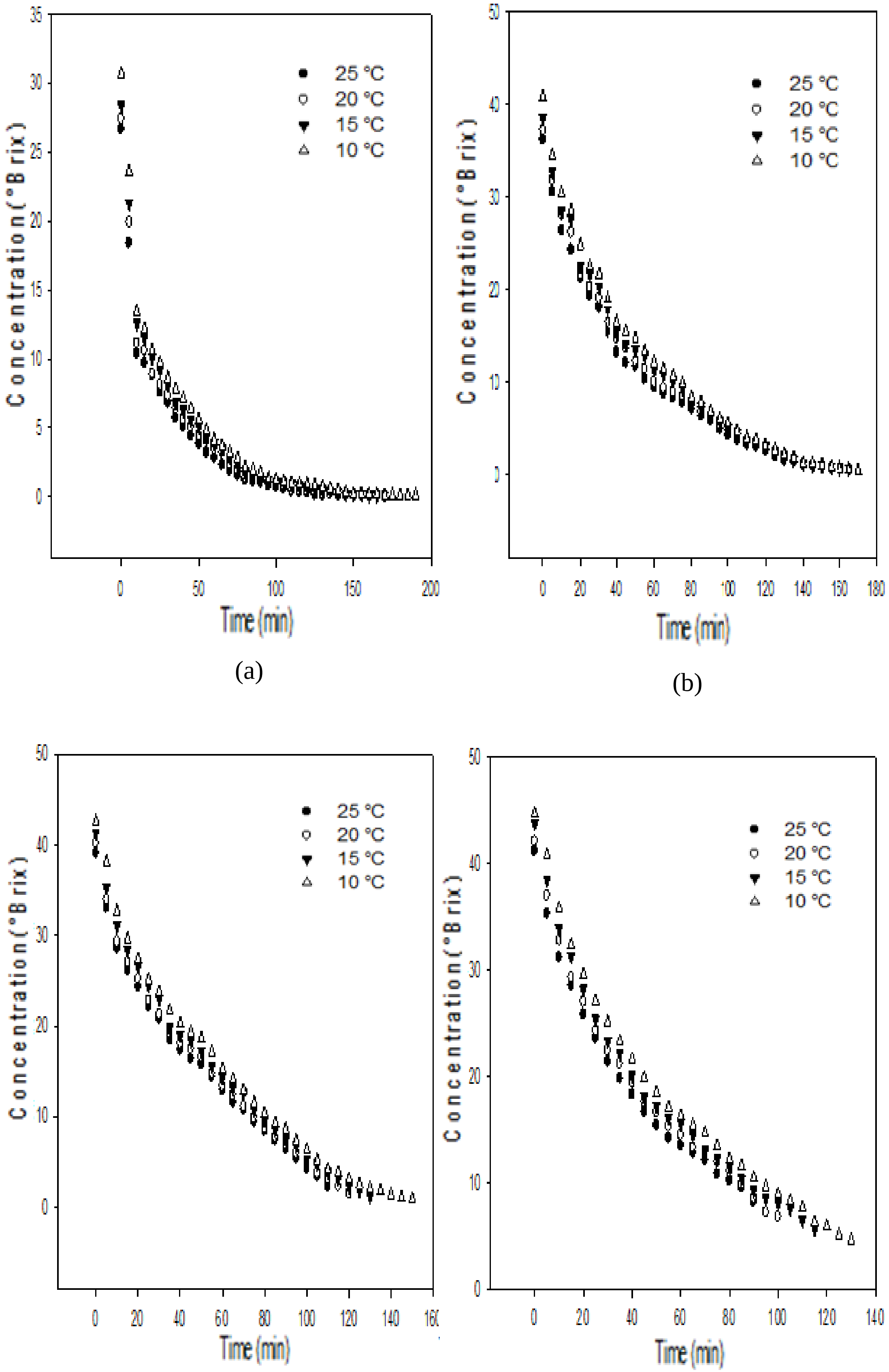
Table 3.10. Regression analyses for apple concentrates (initial concentration 1, 2, 3 and 4 ºBrix) at different temperatures

Initial Concentration (ºBrix)	**Temperature (ºC)**	**Equation**	**R^2**
1	**10**	y= 20.61*exp(-0.032*x)	0.945
	15	y= 19.26*exp(-0.033*x)	0.950
	20	y= 17.84*exp(-0.034*x)	0.947
	25	y= 17.03*exp(-0.035*x)	0.941
2	**10**	y= 23.85*exp(-0.038*x)	0.937
	15	y= 22.93*exp(-0.042*x)	0.935
	20	y= 22.02*exp(-0.046*x)	0.945
	25	y= 21.52*exp(-0.053*x)	0.946
3	**10**	y= 24.91*exp(-0.035*x)	0.949
	15	y= 23.42*exp(-0.036*x)	0.954
	20	y= 22.06*exp(-0.038*x)	0.950
	25	y= 20.83*exp(-0.040*x)	0.952
4	**10**	y= 24.31*exp(-0.030*x)	0.931
	15	y= 22.48*exp(-0.030*x)	0.927
	20	y= 21.66*exp(-0.032*x)	0.929
	25	y= 20.47*exp(-0.035*x)	0.928

* x= Time (min)
* y= Concentration (°Brix)

By statistical analyses of the results (Table 3.10), the best fit was obtained by exponential decay model and of R^2 values were obtained between 0.928−0.954. Results indicated that equation coefficient decreases with increasing temperature. This is clearly shown that lower temperatures exhibit higher degree of separation.

Figure 3.5 illustrates the change in ºBrix as a function of time at different temperatures for apple concentrates with initial concentration between 5 and 20 ºBrix.



(a)

(b)

(c)

(d)

Figure 3.5. Variation of concentration with time for apple concentrates at different temperatures: (a) initial concentration 5 ºBrix, (b) initial concentration 10 ºBrix, (c) initial concentration 15 ºBrix, (d) initial concentration 20 ºBrix

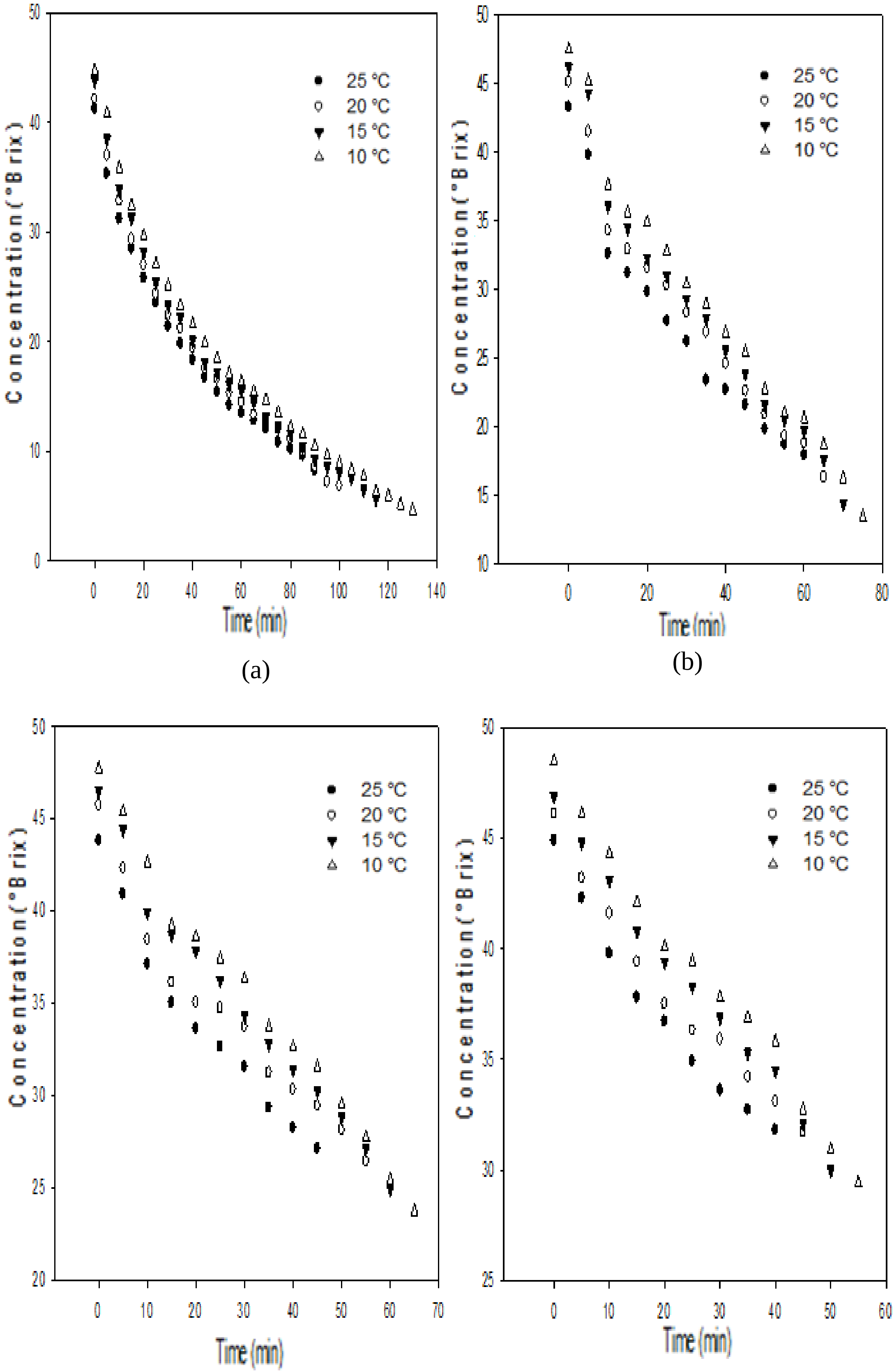
Table 3.11. Regression analyses for apple concentrates (initial concentration 5, 10s, 15 and 20 ºBrix) at different temperatures

Initial Concentration (ºBrix)	**Temperature (ºC)**	**Equation**	**R^2**
5	**10**	y= 26.66*exp(-0.037*x)	0.954
	15	y= 24.73*exp(-0.037*x)	0.959
	20	y= 23.71*exp(-0.040*x)	0.947
	25	y= 23.19*exp(-0.044*x)	0.949
10	**10**	y= 38.79*exp(-0.020*x)	0.994
	15	y= 36.57*exp(-0.020*x)	0.993
	20	y= 35.46*exp(-0.021*x)	0.995
	25	y= 34.04*exp(-0.021*x)	0.993
15	**10**	y= 41.34*exp(-0.018*x)	0.987
	15	y= 39.43*exp(-0.018*x)	0.986
	20	y= 37.86*exp(-0.019*x)	0.984
	25	y= 36.74*exp(-0.019*x)	0.986
20	**10**	y= 42.68*exp(-0.016*x)	0.994
	15	y= 41.11*exp(-0.017*x)	0.992
	20	y= 39.65*exp(-0.017*x)	0.990
	25	y= 38.38*exp(-0.018*x)	0.988

* x= Time (min)
* y= Concentration (°Brix)

Table 3.11 shows that the higher determination coefficient (R^2) values were obtained for apple concentrates by exponential decay model. R^2 values changed between 0.947 and 0.995. In the model equation, y-axis shows that the concentration (ºBrix) decays with x-axis (time).

Temperature effect on the separation of concentrated juice is seen clearly in Figure 3.6. Frozen concentrates thawed at lower temperatures and concentrations were observed to exhibit higher degree of separation.



(a) (b)

(c) (d)

Figure 3.6. Variation of concentration with time for apple concentrates at different temperatures: (a) initial concentration 25 ºBrix, (b) initial concentration 30 ºBrix, (c) initial concentration 35 ºBrix, (d) initial concentration 40 ºBrix

Table 3.12. Regression analyses for apple concentrates (initial concentration 25, 30, 35 and 40 ºBrix) at different temperatures

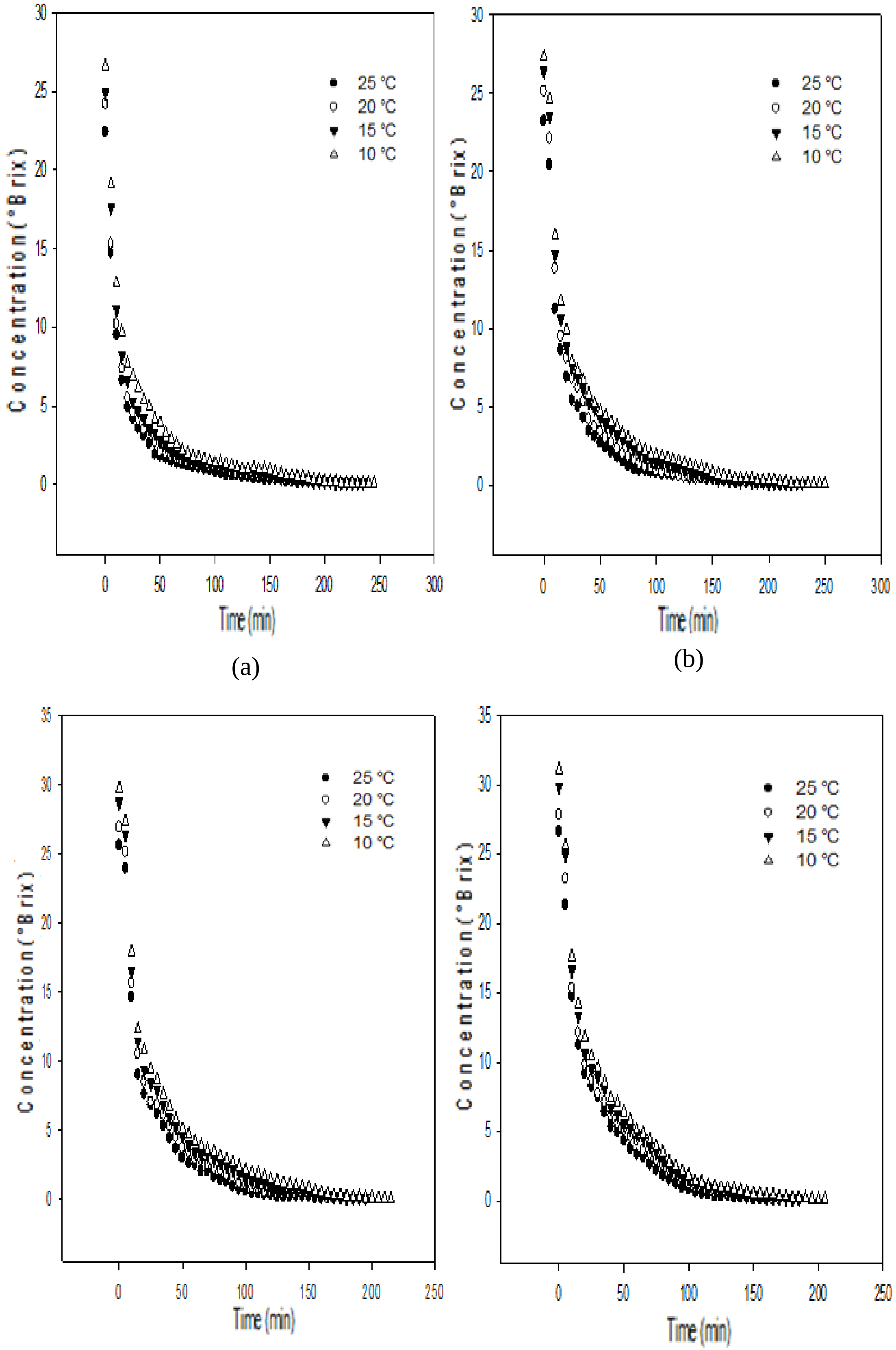
Initial Concentration (ºBrix)	**Temperature (ºC)**	**Equation**	**R^2**
25	**10**	y= 46.82*exp(-0.017*x)	0.994
	15	y= 44.95*exp(-0.017*x)	0.996
	20	y= 42.95*exp(-0.018*x)	0.995
	25	y= 41.53*exp(-0.018*x)	0.997
30	**10**	y= 46.72*exp(-0.015*x)	0.983
	15	y= 45.11*exp(-0.015*x)	0.979
	20	y= 43.20*exp(-0.015*x)	0.978
	25	y= 41.13*exp(-0.015*x)	0.971
35	**10**	y= 47.41*exp(-0.009*x)	0.987
	15	y= 45.74*exp(-0.009*x)	0.988
	20	y= 43.65*exp(-0.009*x)	0.964
	25	y= 42.51*exp(-0.011*x)	0.976
40	**10**	y= 48.33*exp(-0.008*x)	0.987
	15	y= 46.79*exp(-0.008*x)	0.992
	20	y= 45.13*exp(-0.008*x)	0.985
	25	y= 44.02*exp(-0.009*x)	0.983

* x= Time (min)
* y= Concentration (°Brix)

Table 3.12 shows the data fitted by non-linear regression analysis at different temperatures for higher apple concentrates. The determination of coefficient (R^2) values changed between 0.964 and 0.997.

3.6. Effect of Temperature on the Concentration of Grape Concentrates

Figure 3.7 illustrates the change in ºBrix as a function of time at different temperatures for lower grape concentrates with a constant initial concentration.The observed effect of initial concentration was similar to other concentrates.



(a) (b) (c) (d)

Figure 3.7. Variation of concentration with time for grape concentrates at different temperatures: (a) initial concentration 1 ºBrix, (b) initial concentration 2 ºBrix, (c) initial concentration 3 ºBrix, (d) initial concentration 4 ºBrix

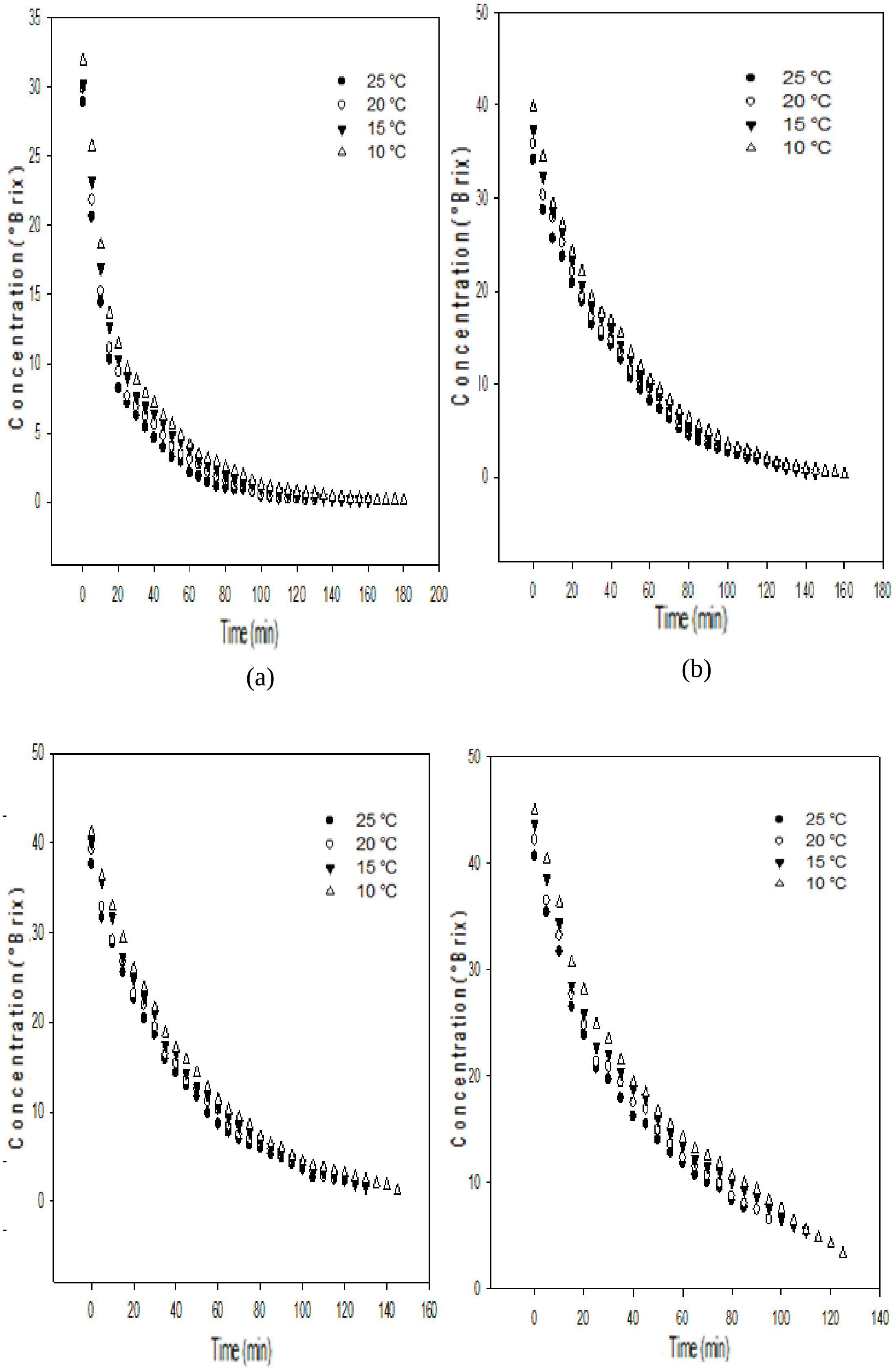
Table 3.13. Regression analyses for grape concentrates (initial concentration 1, 2, 3 and 4 ºBrix) at different temperatures

Initial Concentration (ºBrix)	Temperature (ºC)	Equation	R^2
1	**10**	y= 23.68*exp(-0.044*x)	0.954
	15	y= 23.00*exp(-0.055*x)	0.958
	20	y= 22.26*exp(-0.062*x)	0.959
	25	y= 21.10*exp(-0.066*x)	0.968
2	**10**	y= 25.73*exp(-0.037*x)	0.957
	15	y= 25.04*exp(-0.040*x)	0.960
	20	y= 24.56*exp(-0.046*x)	0.972
	25	y= 22.97*exp(-0.052*x)	0.969
3	**10**	y= 28.15*exp(-0.036*x)	0.957
	15	y= 27.71*exp(-0.041*x)	0.958
	20	y= 26.74*exp(-0.050*x)	0.964
	25	y= 25.93*exp(-0.050*x)	0.967
4	**10**	y= 27.84*exp(-0.033*x)	0.969
	15	y= 27.02*exp(-0.035*x)	0.966
	20	y= 25.50*exp(-0.037*x)	0.967
	25	y= 24.69*exp(-0.040*x)	0.977

* x= Time (min)
* y= Concentration (°Brix)

Table 3.13 shows that the higher (R^2) values were obtained for apple concentrates by exponential decay model. R^2 values changed between 0.954 and 0.977. In the model equation, y-axis shows that the concentration (ºBrix) decays with x-axis (time).

Temperature effect on the separation of concentrated juice is seen in Figure 3.8. The degree of separation was observed to be dependent upon initial concentrations of the juice, also.



(a)

(b)

(c)

(d)

Figure 3.8. Variation of concentration with time for grape concentrates at different temperatures: (a) initial concentration 5 ºBrix, (b) initial concentration 10 ºBrix, (c) initial concentration 15 ºBrix, (d) initial concentration 20 ºBrix

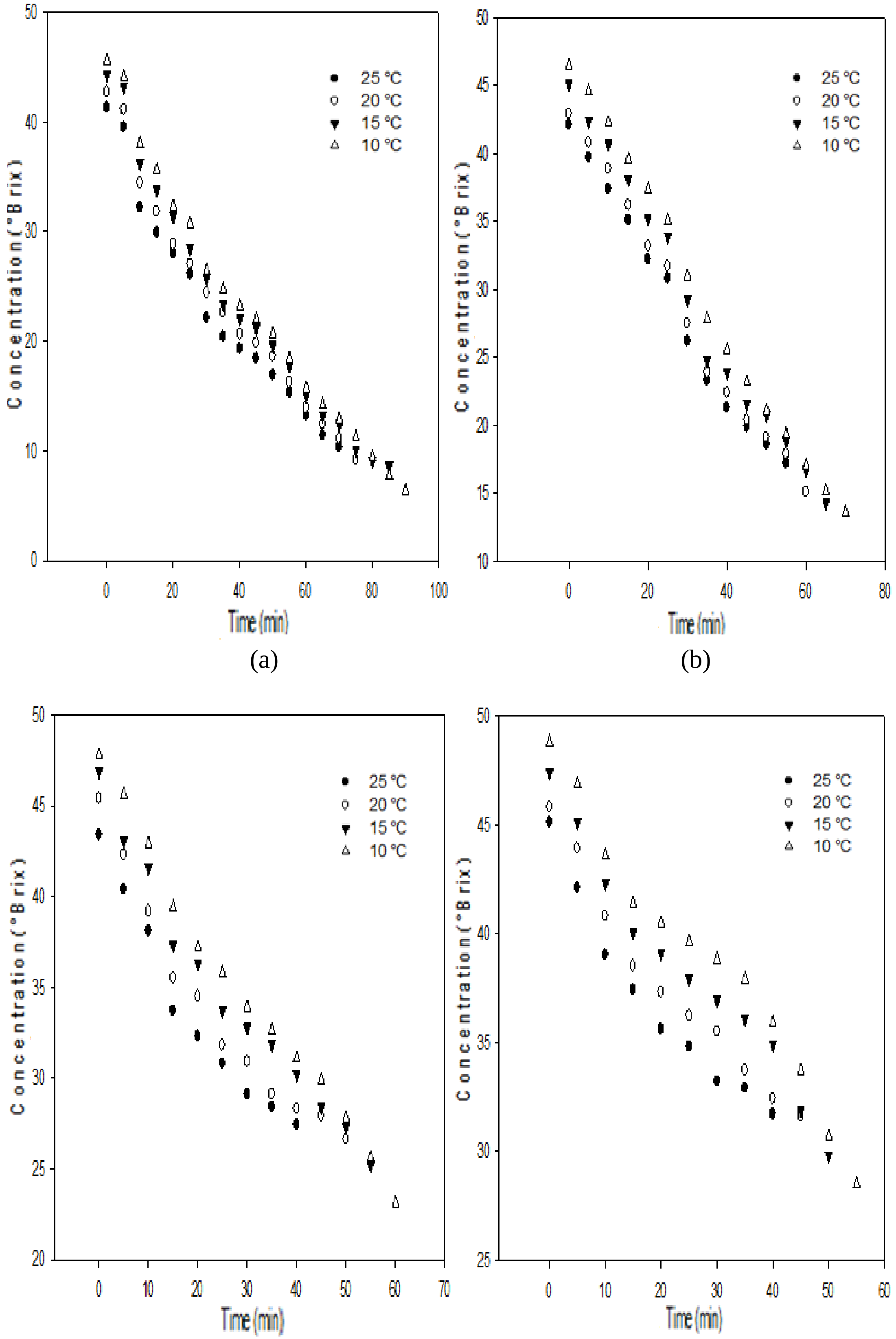
Table 3.14 shows that the best fit was obtained for grape concentrates between initial concentrations 10 and 20 ºBrix due to their higher R^2 values ranging from 0.973 to 0.999. Results indicated that, the higher determination coefficients are obtained from grape concentrates

Table 3.14. Regression analyses for grape concentrates (initial concentration 5, 10, 15 and 20 ºBrix) at different temperatures

Initial Concentration (ºBrix)	**Temperature (ºC)**	**Equation**	**R^2**
5	**10**	y= 29.58*exp(-0.039*x)	0.978
	15	y= 27.76*exp(-0.040*x)	0.978
	20	y= 27.44*exp(-0.046*x)	0.973
	25	y= 26.97*exp(-0.052*x)	0.980
10	**10**	y= 38.80*exp(-0.023*x)	0.996
	15	y= 37.08*exp(-0.023*x)	0.996
	20	y= 35.32*exp(-0.023*x)	0.997
	25	y= 33.50*exp(-0.024*x)	0.996
15	**10**	y= 40.76*exp(-0.022*x)	0.999
	15	y= 39.64*exp(-0.022*x)	0.998
	20	y= 37.73*exp(-0.023*x)	0.997
	25	y= 36.62*exp(-0.024*x)	0.998
20	**10**	y= 42.88*exp(-0.018*x)	0.992
	15	y= 40.80*exp(-0.019*x)	0.986
	20	y= 39.62*exp(-0.020*x)	0.986
	25	y= 38.39*exp(-0.021*x)	0.986

* x= Time (min)
* y= Concentration (°Brix)

It was obvious in the Figure 3.9 that the higher the initial concentration of the juice, the lower degree of separation was achieved. This method is, therefore, not feasible for samples having an initial concentration higher than 20 ºBrix.



(a) (b)

(c) (d)

Figure 3.9. Variation of concentration with time for grape concentrates at different temperatures: (a) initial concentration 25 ºBrix, (b) initial concentration 30 ºBrix, (c) initial concentration 35 ºBrix, (d) initial concentration 40 ºBrix

Table 3.15. Regression analyses for grape concentrates (initial concentration 25, 30, 35 and 40 ºBrix) at different temperatures

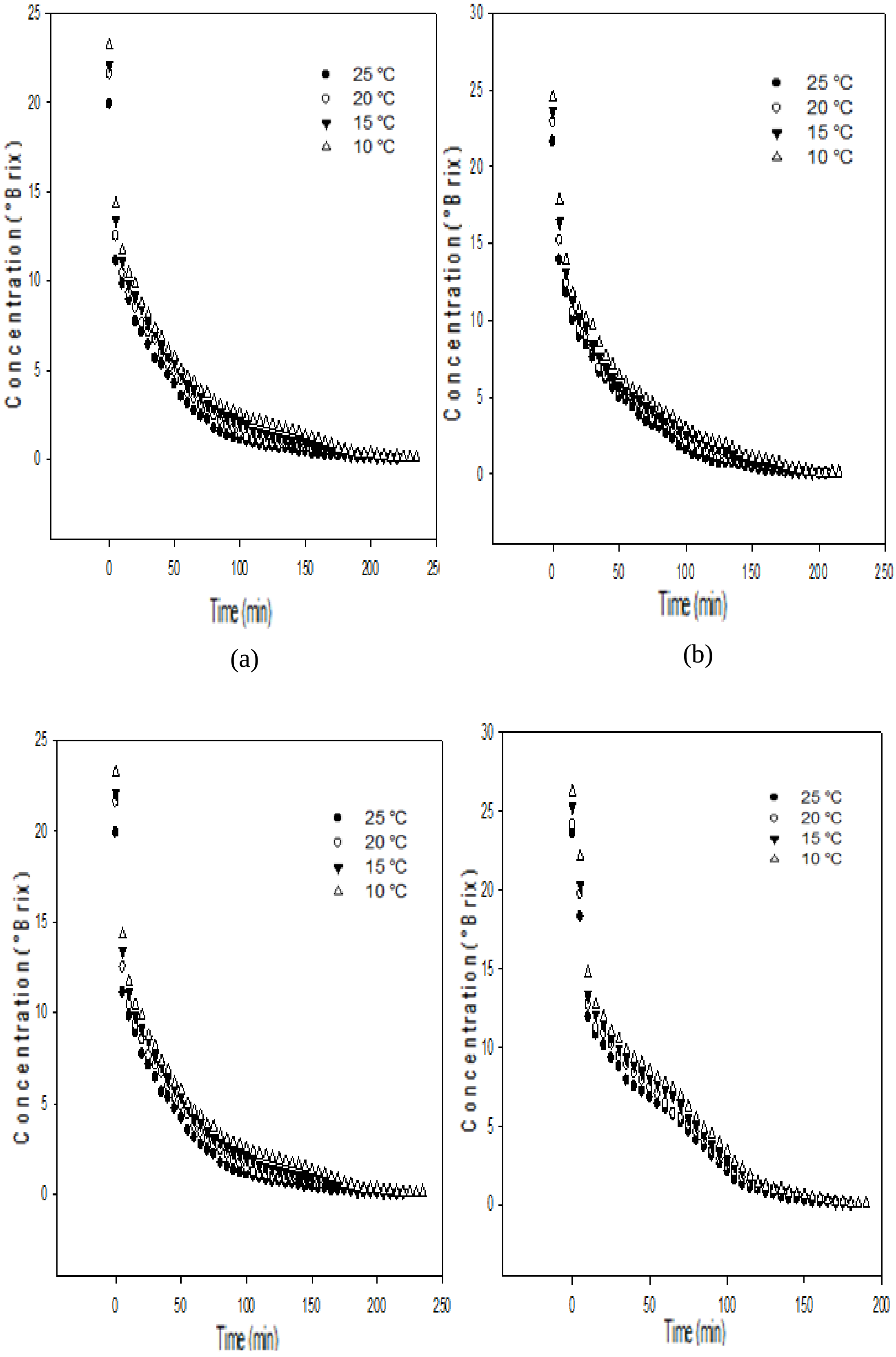
Initial Concentration (ºBrix)	Temperature (ºC)	Equation	R^2
25	10	y= 47.01*exp(-0.018*x)	0.989
	15	y= 45.19*exp(-0.018*x)	0.991
	20	y= 42.99*exp(-0.019*x)	0.991
	25	y= 41.16*exp(-0.019*x)	0.989
30	10	y= 49.34*exp(-0.017*x)	0.983
	15	y= 47.15*exp(-0.017*x)	0.982
	20	y= 44.92*exp(-0.017*x)	0.984
	25	y= 43.59*exp(-0.017*x)	0.986
35	10	y= 47.68*exp(-0.011*x)	0.992
	15	y= 45.67*exp(-0.011*x)	0.986
	20	y= 43.94*exp(-0.011*x)	0.968
	25	y= 42.565*exp(-0.012*x)	0.970
40	10	y= 48.55*exp(-0.008*x)	0.963
	15	y= 46.69*exp(-0.008*x)	0.974
	20	y= 44.98*exp(-0.008*x)	0.978
	25	y= 43.69*exp(-0.009*x)	0.958

* x= Time (min)
* y= Concentration (°Brix)

Table 3.15 shows that the higher (R^2) values were obtained for apple concentrates by exponential decay model. R^2 values changed between 0.958 and 0.992. In the model equation, y-axis shows that the concentration (ºBrix) decays with x-axis (time).

3.7. Effect of Temperature on the Concentration of Carrot Concentrates

Figures (3.10−3.12) illustrate the change in ºBrix as a function of time at different temperatures for carrot concentrates with a constant initial concentration.



(a) (b)

(c) (d)

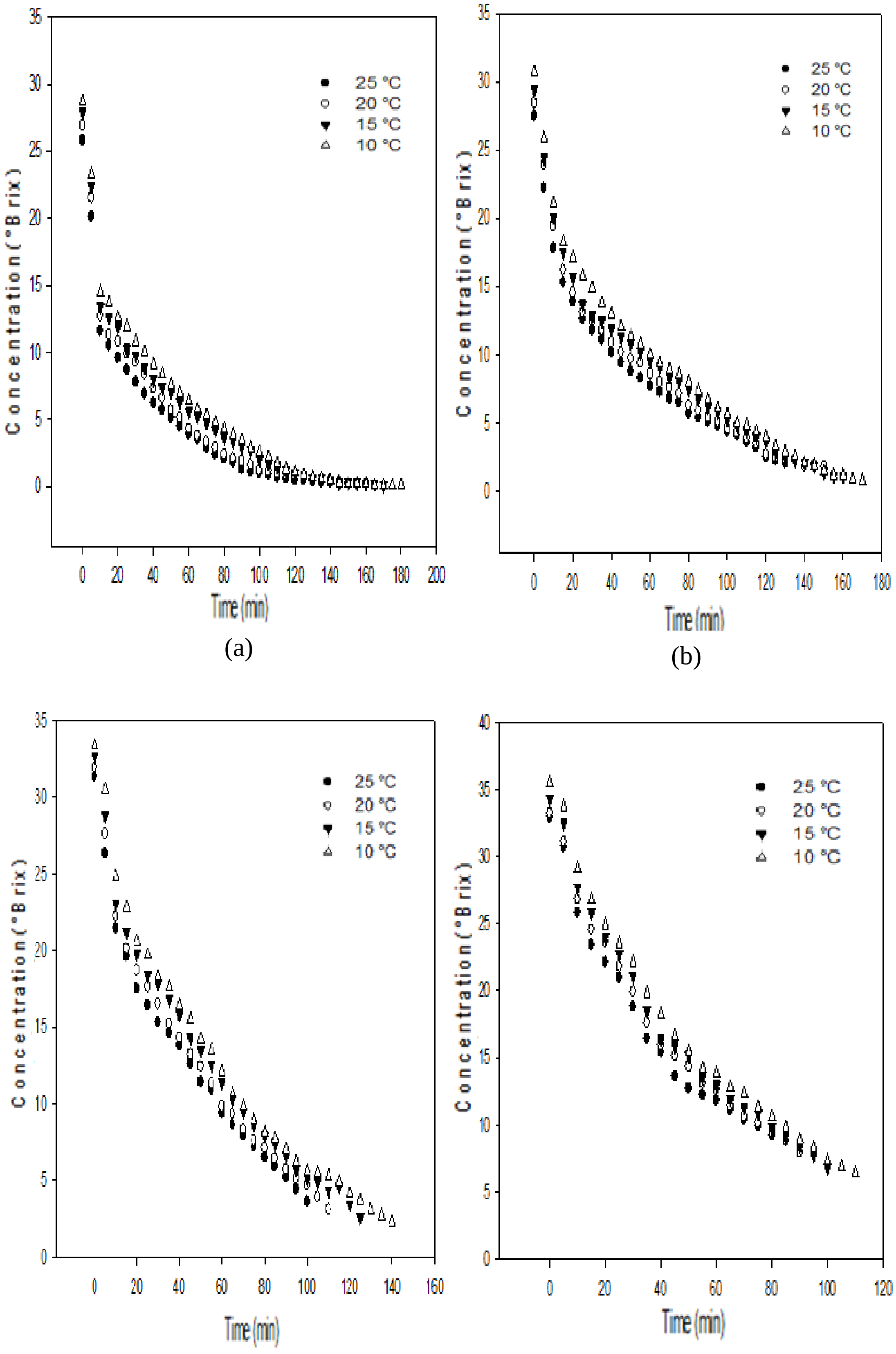
Figure 3.10. Variation of concentration with time for carrot concentrates at different temperatures: (a) initial concentration 1 ºBrix, (b) initial concentration 2 ºBrix, (c) initial concentration 3 ºBrix, (d) initial concentration 4 ºBrix

Table 3.16. Regression analyses for carrot concentrates (initial concentration 1, 2, 3 and 4 ºBrix) at different temperatures

Initial Concentration (ºBrix)	**Temperature (ºC)**	**Equation**	**R^2**
1	**10**	y= 17.41*exp(-0.022*x)	0.939
	15	y= 16.94*exp(-0.024*x)	0.947
	20	y= 16.61*exp(-0.027*x)	0.943
	25	y= 15.67*exp(-0.029*x)	0.950
2	**10**	y= 19.58*exp(-0.022*x)	0.958
	15	y= 18.73*exp(-0.023*x)	0.954
	20	y= 18.20*exp(-0.025*x)	0.954
	25	y= 17.40*exp(-0.026*x)	0.960
3	**10**	y= 20.41*exp(-0.022*x)	0.938
	15	y= 19.27*exp(-0.022*x)	0.928
	20	y= 18.95*exp(-0.025*x)	0.939
	25	y= 18.80*exp(-0.028*x)	0.956
4	**10**	y= 21.81*exp(-0.020*x)	0.945
	15	y= 20.67*exp(-0.021*x)	0.943
	20	y= 19.98*exp(-0.022*x)	0.944
	25	y= 19.15*exp(-0.023*x)	0.936

* x= Time (min)
* y= Concentration (°Brix)

Table 3.16 shows the data fitted by non-linear regression analysis at different temperatures for lower carrot concentrates. The determination of coefficient (R^2) values changed between 0.928 and 0.960. The higher R^2 values were obtained by using exponential decay model. This model was observed to be the best fitted model for all data. In the model equation, y-axis shows that the concentration (ºBrix) decays with x-axis (time). Negative exponent indicates exponential decay.



(a) (b)

(c) (d)

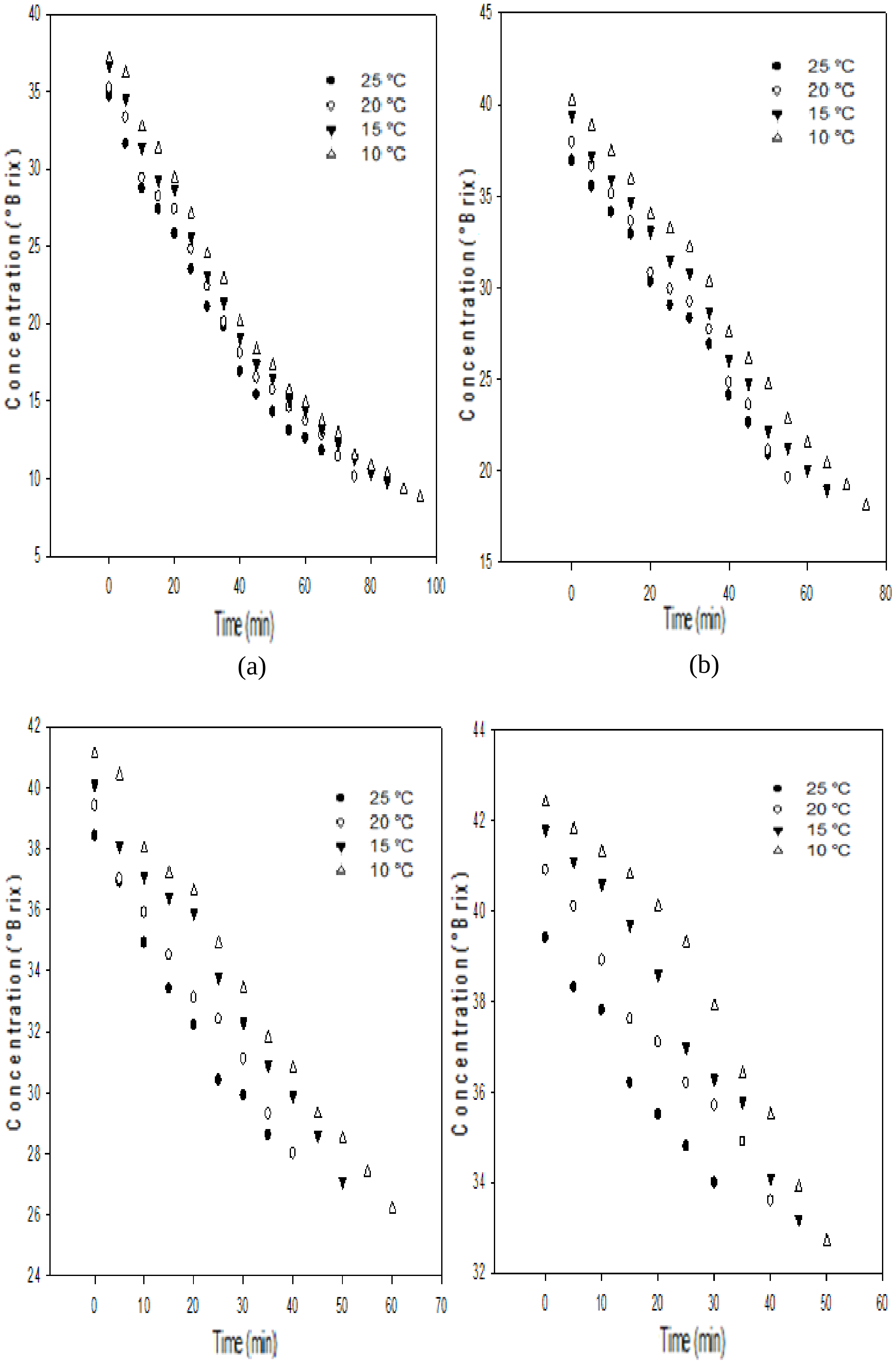
Figure 3.11. Variation of concentration with time for carrot concentrates at different temperatures: (a) initial concentration 5 ºBrix, (b) initial concentration 10 ºBrix, (c) initial concentration 15 ºBrix, (d) initial concentration 20 ºBrix

Table 3.17. Regression analyses for carrot concentrates (initial concentration 5, 10, 15 and 20 ºBrix) at different temperatures

Initial Concentration (ºBrix)	Temperature (ºC)	Equation	R^2
5	10	y= 24.27*exp(-0.025*x)	0.957
	15	y= 23.43*exp(-0.027*x)	0.949
	20	y= 23.29*exp(-0.031*x)	0.956
	25	y= 22.36*exp(-0.035*x)	0.952
10	10	y= 26.72*exp(-0.017*x)	0.975
	15	y= 25.07*exp(-0.017*x)	0.964
	20	y= 24.35*exp(-0.018*x)	0.964
	25	y= 23.18*exp(-0.019*x)	0.958
15	10	y= 31.47*exp(-0.017*x)	0.990
	15	y= 30.03*exp(-0.017*x)	0.984
	20	y= 29.20*exp(-0.019*x)	0.983
	25	y= 28.28*exp(-0.019*x)	0.977
20	10	y= 34.85*exp(-0.016*x)	0.996
	15	y= 33.64*exp(-0.016*x)	0.994
	20	y= 32.49*exp(-0.016*x)	0.994
	25	y= 31.85*exp(-0.017*x)	0.985

* x= Time (min)
* y= Concentration (°Brix)

According to regression analyses (Table 3.17), the lower determination coefficients are obtained from carrot concentrates. The degree of separation was observed to be influenced also by the nature of the juice being concentrated.



(a)

(b)

(c)

(d)

Figure 3.12. Variation of concentration with time for carrot concentrates at different temperatures: (a) initial concentration 25 ºBrix, (b) initial concentration 30 ºBrix, (c) initial concentration 35 ºBrix, (d) initial concentration 40 ºBrix

Table 3.18 shows the data fitted by non-linear regression analysis at different temperatures for higher carrot concentrates. The determination of coefficient (R^2) values changed between 0.952 and 0.996.

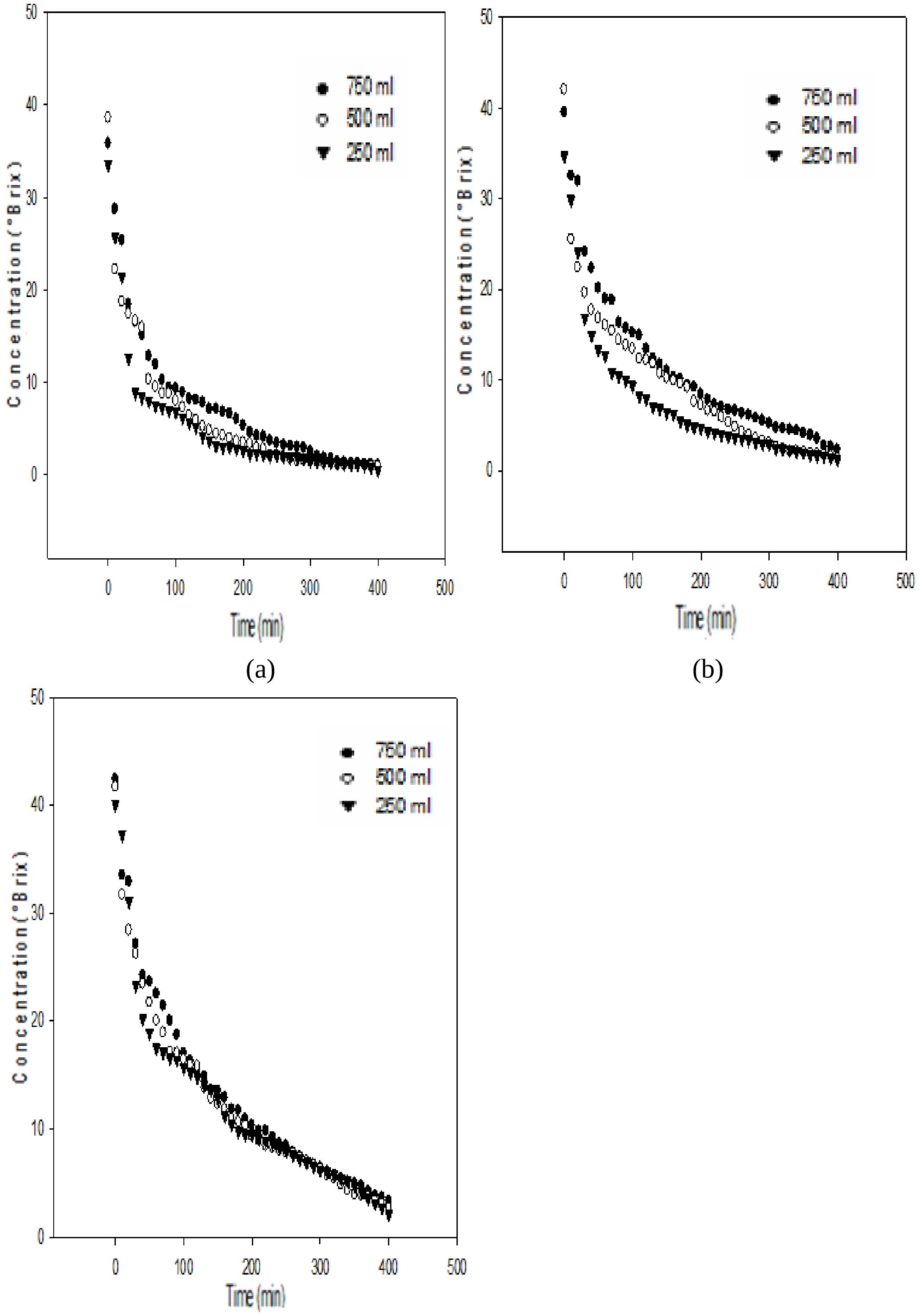
Table 3.18. Regression analyses for carrot concentrates (initial concentration 25, 30, 35 and 40 ºBrix) at different temperatures

Initial Concentration (ºBrix)	Temperature (ºC)	Equation	R^2
25	10	y= 38.69*exp(-0.016*x)	0.995
	15	y= 37.28*exp(-0.016*x)	0.996
	20	y= 35.80*exp(-0.016*x)	0.993
	25	y= 34.87*exp(-0.017*x)	0.994
30	10	y= 41.66*exp(-0.011*x)	0.985
	15	y= 40.35*exp(-0.011*x)	0.981
	20	y= 38.99*exp(-0.011*x)	0.977
	25	y= 37.74*exp(-0.011*x)	0.981
35	10	y= 41.62*exp(-0.008*x)	0.994
	15	y= 40.29*exp(-0.008*x)	0.984
	20	y= 39.02*exp(-0.008*x)	0.991
	25	y= 38.26*exp(-0.009*x)	0.993
40	10	y= 43.42*exp(-0.005*x)	0.952
	15	y= 42.37*exp(-0.005*x)	0.983
	20	y= 40.83*exp(-0.005*x)	0.990
	25	y= 39.36*exp(-0.005*x)	0.989

* x= Time (min)
* y= Concentration (°Brix)

3.8. Effect of the Size of Frozen Samples on the Degree of Separation

Three different sizes of various concentrations were for different juices. Concentration was plotted against time each volume separately. Figure 3.13 indicates the variation of concentration with time for sumac concentrates at different sizes. For each experiment, concentration decreased by time so exponential decay model was selected.



(a)

(b)

(c)

Figure 3.13. Variation of concentration with time for sumac concentrates at different sizes: (a) initial concentration 1 ºBrix, (b) initial concentration 5 ºBrix, (c) initial concentration 10 ºBrix

Table 3.19. Regression analyses for sumac concentrates (initial concentration 1, 5 and °Brix) at different sizes

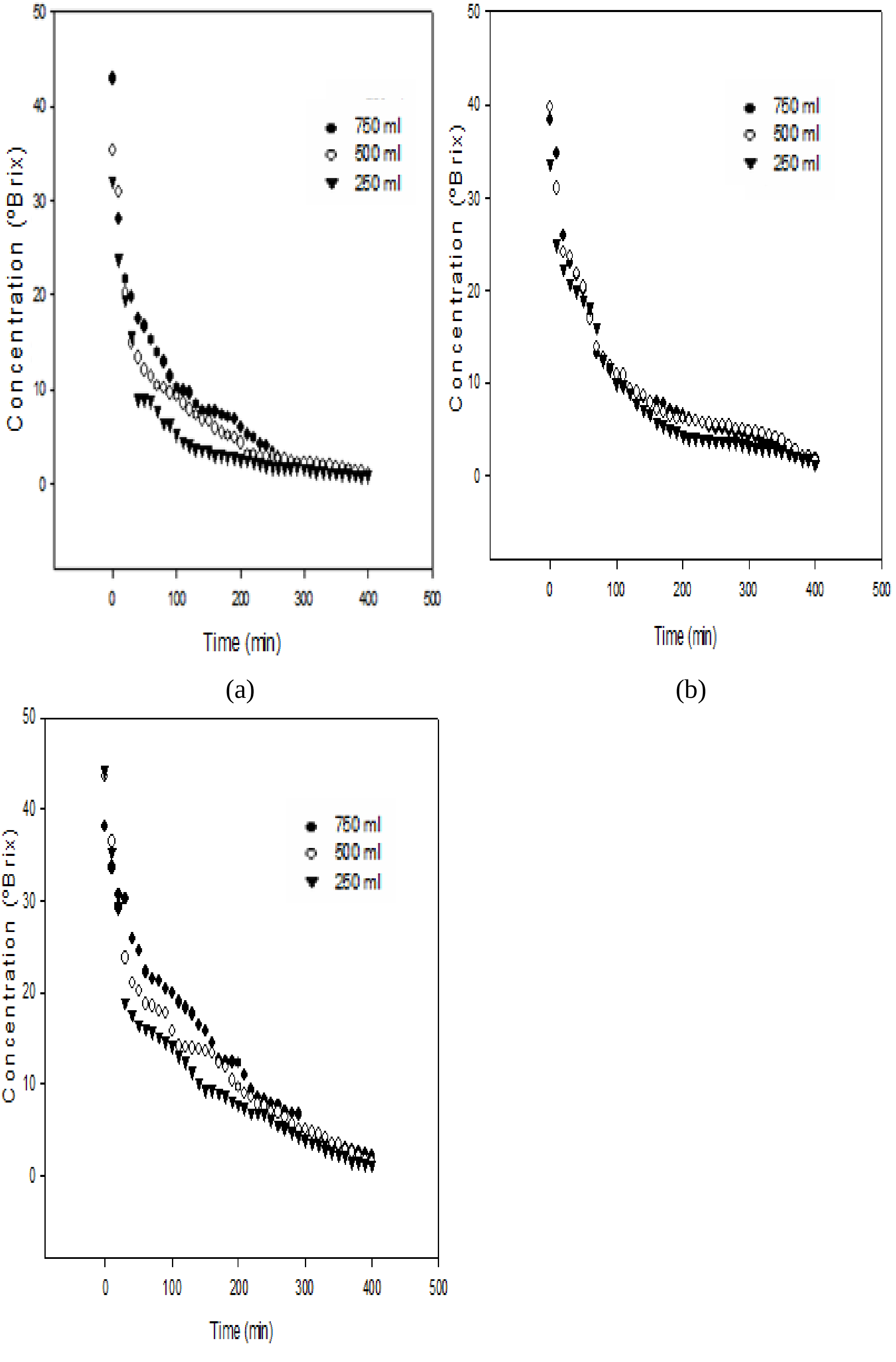
Initial Concentration (°Brix)	**mL**	**Equation**	**R^2**
1	**250**	y= 29.36*exp(-0.018*x)	0.911
	500	y= 29.77*exp(-0.014*x)	0.930
	750	y= 29.88*exp(-0.011*x)	0.944
5	**250**	y= 29.22*exp(-0.011*x)	0.928
	500	y= 29.53*exp(-0.008*x)	0.912
	750	y= 33.26*exp(-0.007*x)	0.961
10	**250**	y= 32.61*exp(-0.007*x)	0.917
	500	y= 33.11*exp(-0.006*x)	0.958
	750	y= 35.16*exp(-0.006*x)	0.968

* x= Time (min)
* y= Concentration (°Brix)

Table 3.19 presents the regression analysis at different sizes for sumac concentrates. The determination coefficient (R^2) values changed between 0.911 and 0.968.

Figures 3.14 illustrates the variation of concentration with time for apple concentrates at different sizes. The size of samples being thawed was observed to affect the degree of separation. The rate of melting increased with increasing surface area of sample. Because a larger surface area contacts with the surrounding air. It can absorb more heat, so more melting occurs. Even though larger surface area melts fast, it may take more time to melt. Because more ice is present during the melting, its surface area decreases so more time requires to melt.

Table 3.20 shows that the regression analysis at different sizes for apple concentrates. The determination coefficient (R^2) values changed between 0.900 and 0.986. By statistical analyses of the results, the most effective degree of separation of juice from ice was observed at lower temperatures regardless sample size.



(a)

(b)

(c)

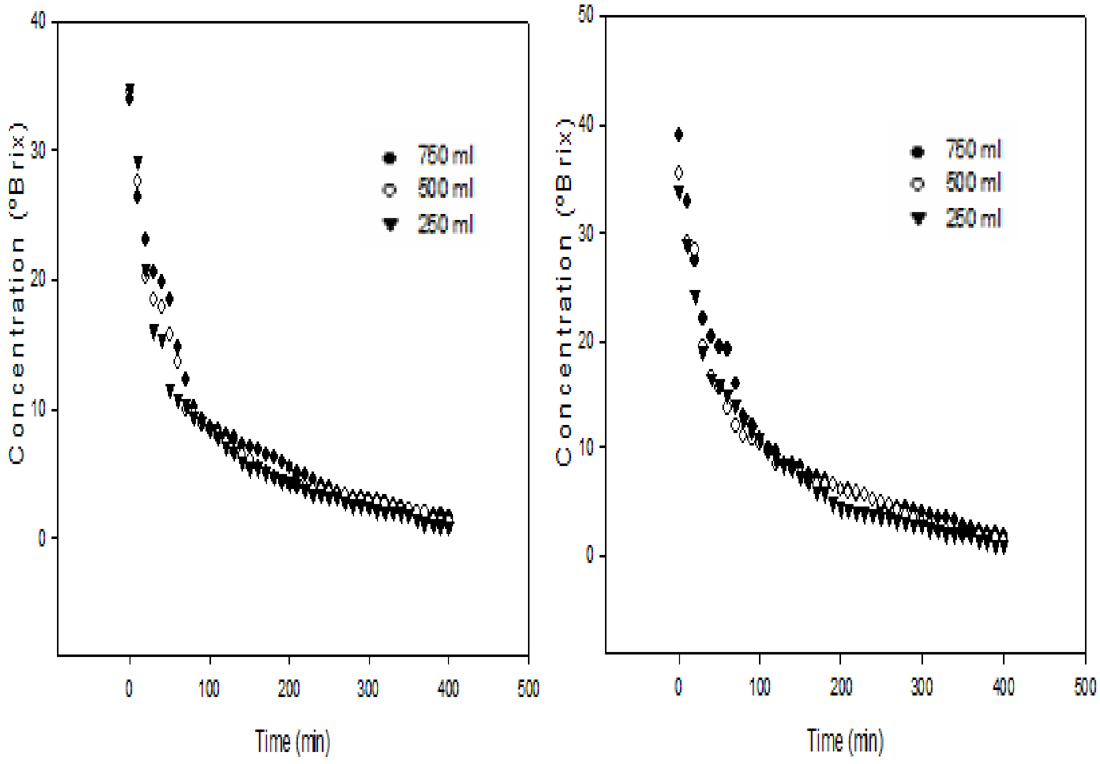
Figure 3.14. Variation of concentration with time for apple concentrates at different sizes: (a) initial concentration 1 ºBrix, (b) initial concentration 5 ºBrix, (c) initial concentration 10 ºBrix

Table 3.20. Regression analyses for apple concentrates (initial concentration 1, 5 and ºBrix) at different sizes

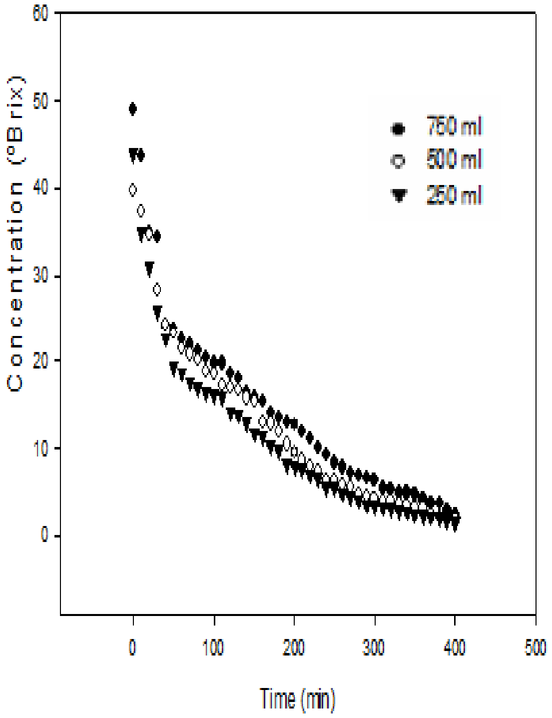
Initial Concentration (ºBrix)	mL	Equation	R^2
1	**250**	y= 28.57*exp(-0.018*x)	0.940
	500	y= 28.80*exp(-0.012*x)	0.908
	750	y= 31.86*exp(-0.010*x)	0.924
5	**250**	y= 29.22*exp(-0.009*x)	0.971
	500	y= 32.20*exp(-0.009*x)	0.931
	750	y= 33.19*exp(-0.009*x)	0.937
10	**250**	y= 33.52*exp(-0.008*x)	0.900
	500	y= 34.27*exp(-0.007*x)	0.935
	750	y= 35.50*exp(-0.006*x)	0.986

* x= Time (min)
* y= Concentration (°Brix)

Figures 3.15 illustrates the variation of concentration with time for grape concentrates at different sizes. Concentration decreased by time so exponential decay model was selected.



(a) (b)



(c)

Figure 3.15. Variation of concentration with time for grape concentrates at different sizes: (a) initial concentration 1 ºBrix, (b) initial concentration 5 ºBrix, (c) initial concentration 10 ºBrix

Table 3.21. Regression analyses for grape concentrates (initial concentration 1, 5 and ºBrix) at different sizes

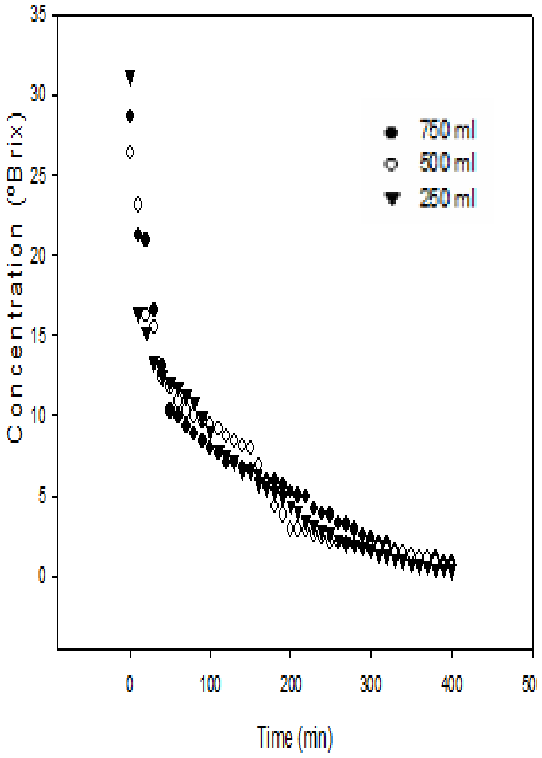
Initial Concentration (ºBrix)	**mL**	**Equation**	**R^2**
1	**250**	y= 28.86*exp(-0.012*x)	0.921
	500	y= 28.89*exp(-0.011*x)	0.942
	750	y= 28.90*exp(-0.010*x)	0.953
5	**250**	y= 29.41*exp(-0.010*x)	0.969
	500	y= 29.82*exp(-0.010*x)	0.931
	750	y= 33.34*exp(-0.009*x)	0.955
10	**250**	y= 36.13*exp(-0.008*x)	0.961
	500	y= 37.19*exp(-0.007*x)	0.981
	750	y= 40.75*exp(-0.007*x)	0.947

* x= Time (min)
* y= Concentration (°Brix)

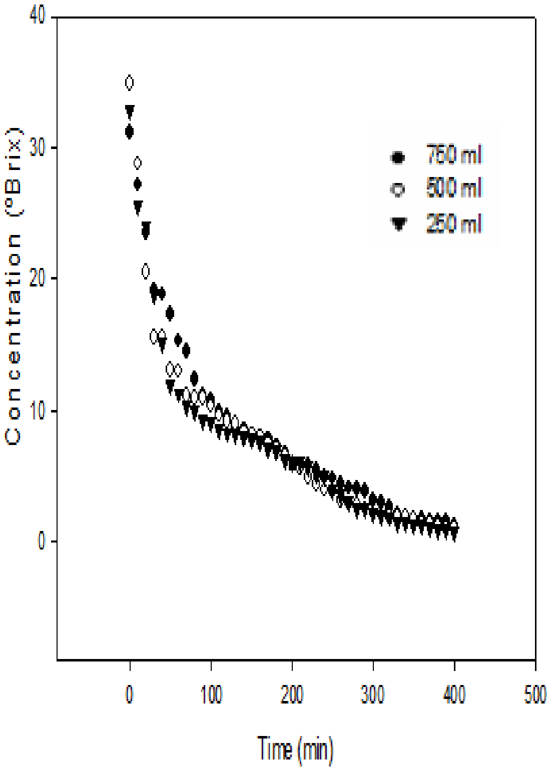
Table 3.21 shows that the regression analysis at different sizes for grape concentrates. The determination coefficient (R^2) values changed between 0.921 and 0.981. The regression analysis shows that when volume size increased, higher ºBrix value was obtained.

This is due to the decrease in (surface area/volume)$_{\text{SAMPLES}}$ as the size increases, which causes a relatively less heat transfer and consequently slower rate of thawing, resulting in a more concentrated juice leaving the ice front.

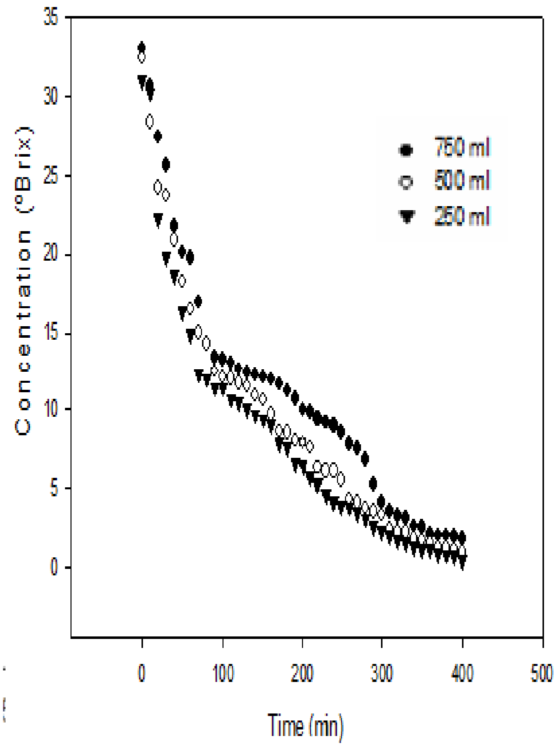
Figures 3.16 illustrates the variation of concentration with time for carrot concentrates at different sizes.



(a)



(b)



(c)

Figure 3.16. Variation of concentration with time for carrot concentrates at different sizes: (a) initial concentration 1 ºBrix, (b) initial concentration 5 ºBrix, (c) initial concentration 10 ºBrix

Table 3.22. Regression analyses for carrot concentrates (initial concentration 1, 5 and ºBrix) at different sizes

Initial Concentration (ºBrix)	**mL**	**Equation**	**R^2**
1	**250**	y= 21.67*exp(-0.009*x)	0.907
	500	y= 22.29*exp(-0.009*x)	0.950
	750	y= 22.62*exp(-0.009*x)	0.918
5	**250**	y= 26.32*exp(-0.009*x)	0.918
	500	y= 26.90*exp(-0.009*x)	0.913
	750	y= 27.23*exp(-0.008*x)	0.972
10	**250**	y= 27.97*exp(-0.008*x)	0.965
	500	y= 29.05*exp(-0.007*x)	0.978
	750	y= 29.78*exp(-0.006*x)	0.953

* x= Time (min)
* y= Concentration (°Brix)

Equation coefficient are shown in Table 3.22. Equation coefficient increases, increasing sample size. According to regression analyses, sample size affects the degree of separation.

3.9. Effect of Time on the Concentration

According to data, generally concentration (ºBrix) decreased at 10−15 minutes instantaneously for lower concentrated juices. After these times, concentration decreased slowly. Figures (3.17−3.21) show the variation of concentration with temperature for 10 ºBrix grape concentrate at different time intervals.

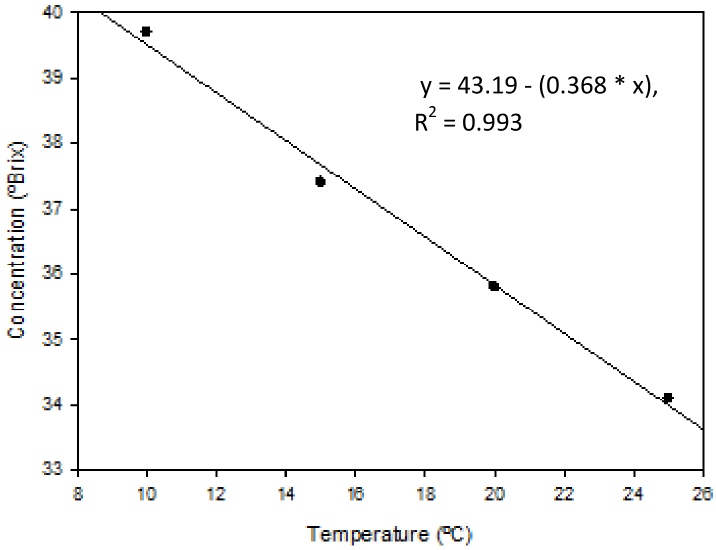


Figure 3.17. Variation of concentration versus temperature for 10 ºBrix grape concentrate at 0 min

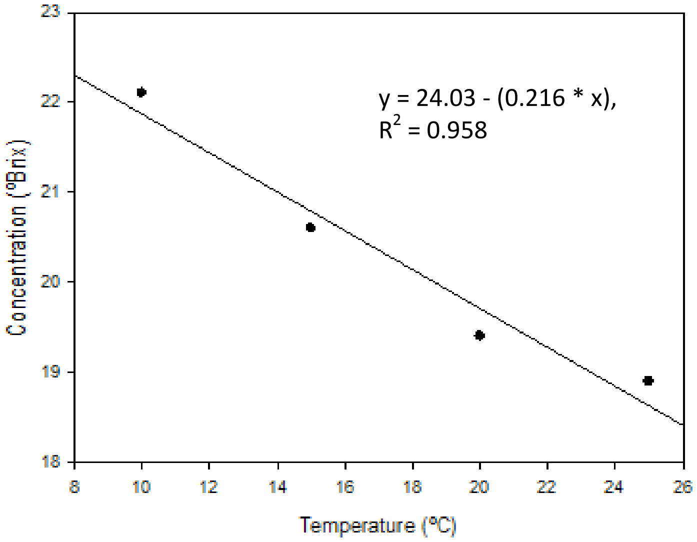


Figure 3.18. Variation of concentration versus temperature for 10 Brix grape concentrate at 25 min

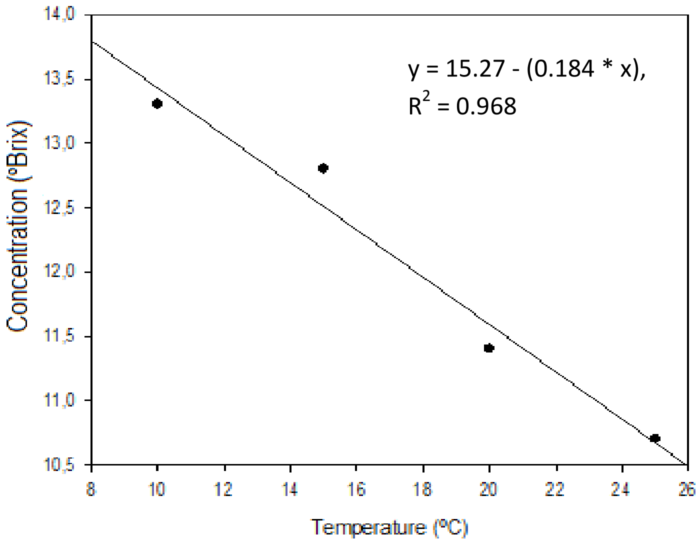


Figure 3.19. Variation of concentration versus temperature for 10 ºBrix grape concentrate at 50 min

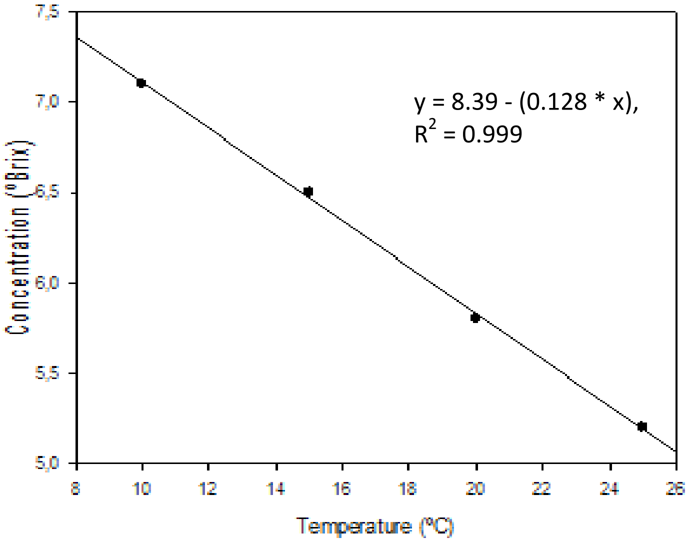


Figure 3.20. Variation of concentration versus temperature for 10 ºBrix grape concentrate at 75 min

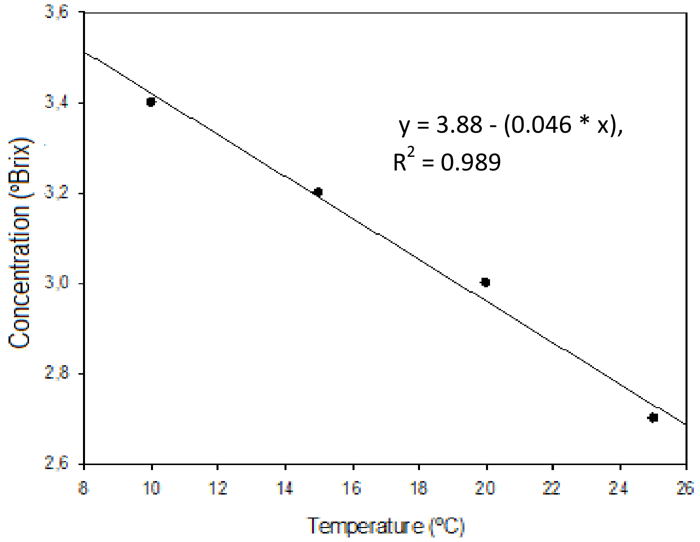


Figure 3.21. Variation of concentration versus temperature for 10 ºBrix grape concentrate at 100 min

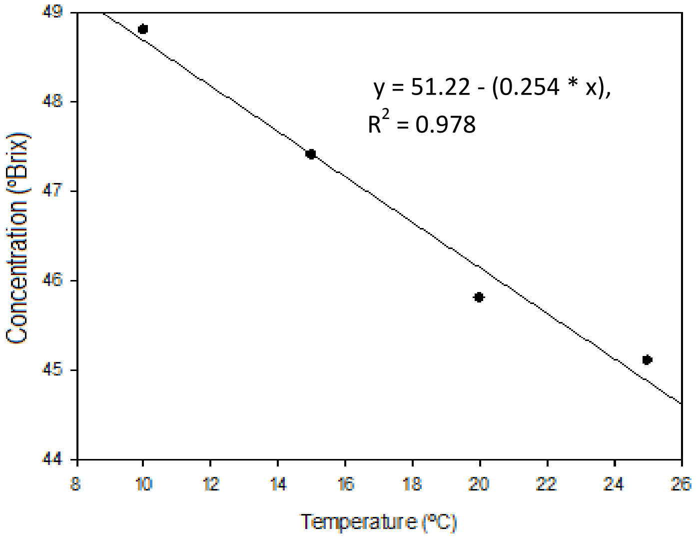


Figure 3.22. Variation of concentration versus temperature for 40 ºBrix grape concentrate at 0 min

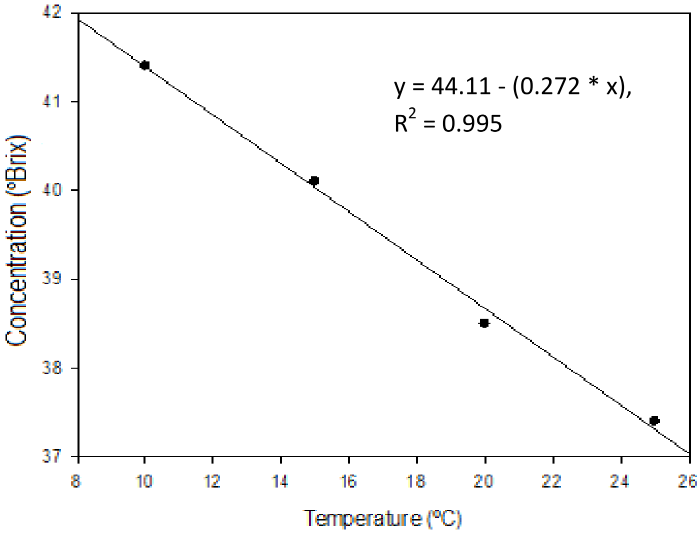


Figure 3.23. Variation of concentration versus temperature for 40 ºBrix grape concentrate at 15 min

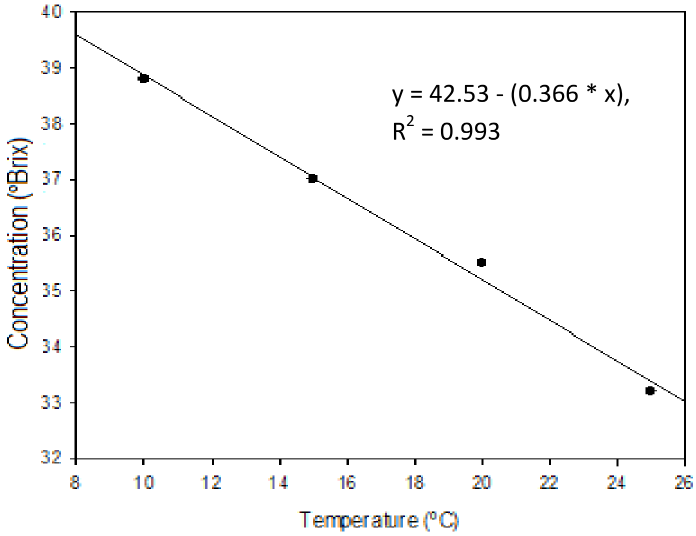


Figure 3.24. Variation of concentration versus temperature for 40 ºBrix grape concentrate at 30 min

The separation of higher concentrated juices was slowly at each time interval. Figures 3.22−3.24 illustrate the change of concentration with temperature for 40 ºBrix grape concentrate at different time intervals.

Figures (3.25−3.30) show the variation of concentration with temperature for 10 ºBrix carrot concentrate at different time intervals. These plots show that freeze concentration is suitable to lower concentrated juices.

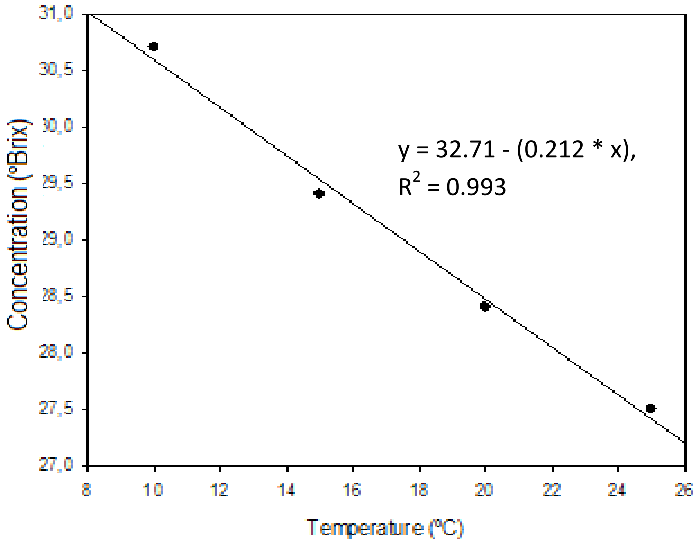


Figure 3.25. Variation of concentration versus temperature for 10 ºBrix carrot concentrate at 0 min

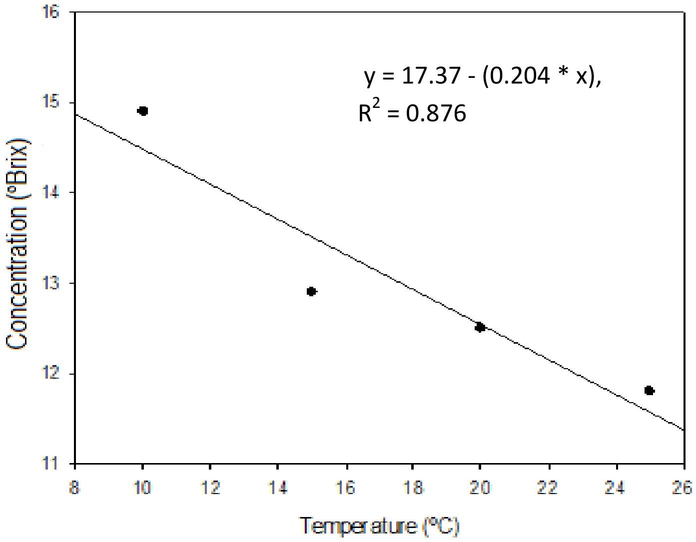


Figure 3.26. Variation of concentration versus temperature for 10 ºBrix carrot concentrate at 25 min

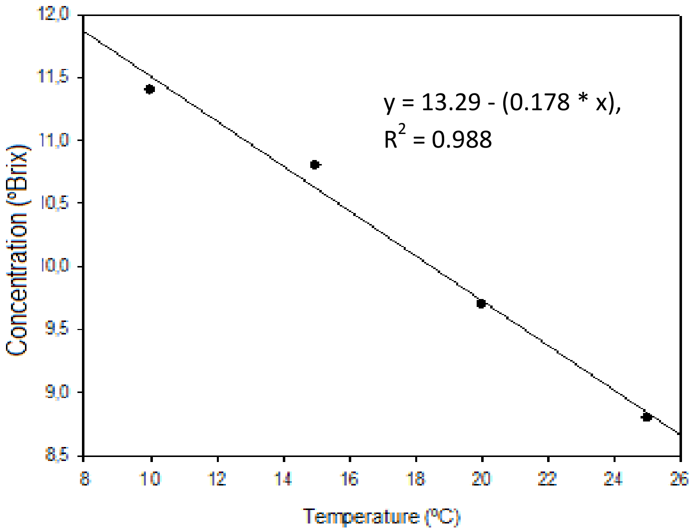


Figure 3.27. Variation of concentration versus temperature for 10 ºBrix carrot concentrate at 50 min

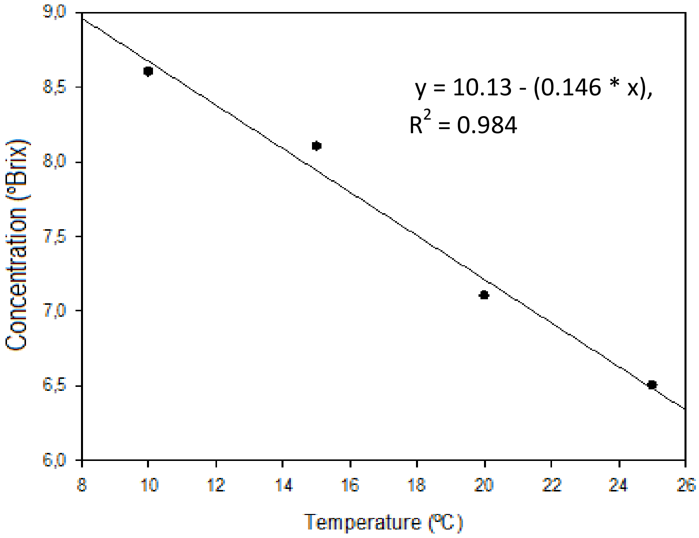


Figure 3.28. Variation of concentration versus temperature for 10 ºBrix carrot concentrate at 75 min

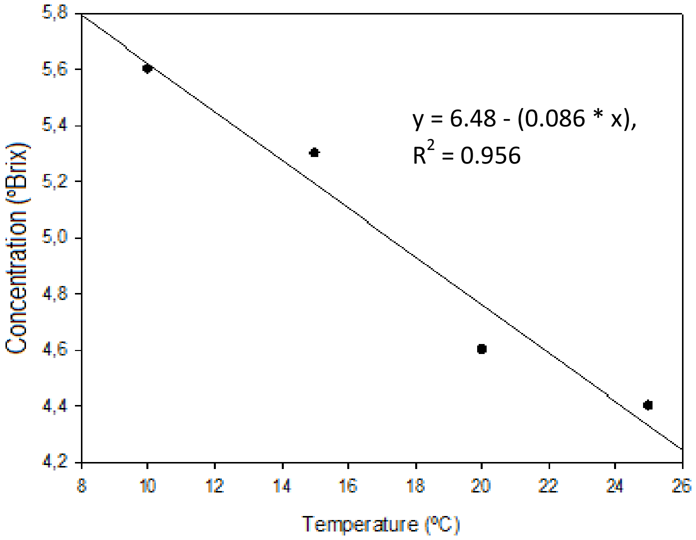


Figure 3.29. Variation of concentration versus temperature for 10 ºBrix carrot concentrate at 100 min

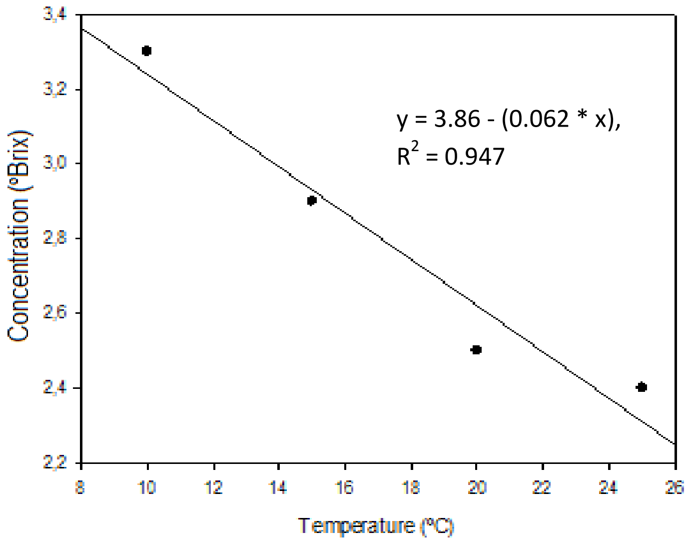


Figure 3.30. Variation of concentration versus temperature for 10 ºBrix carrot concentrate at 125 min

The separation of higher concentrated juices was slowly at each time interval. Figures 3.31−3.33 illustrate the change of concentration with temperature for 40 ºBrix carrot concentrate at different time intervals. The degree of separation is very low for higher concentrated carrot juices. Therefore, the degree of separation was slower at each time interval for higher concentrated juices.

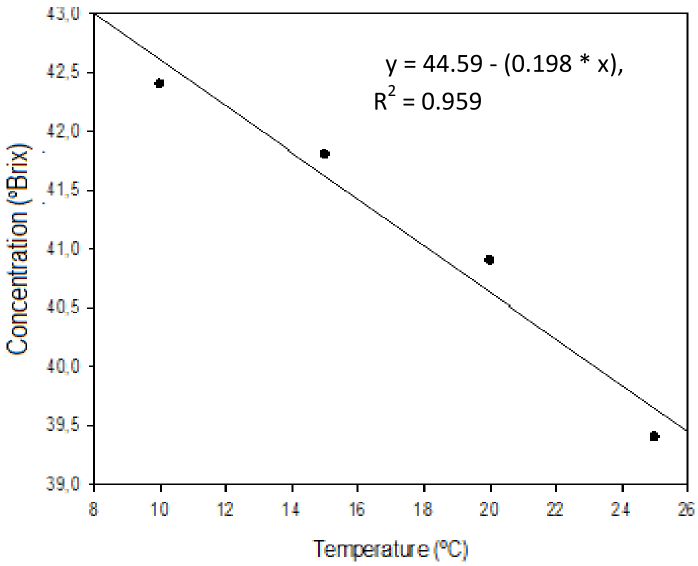


Figure 3.31. Variation of concentration versus temperature for 40 ºBrix carrot concentrate at 0 min

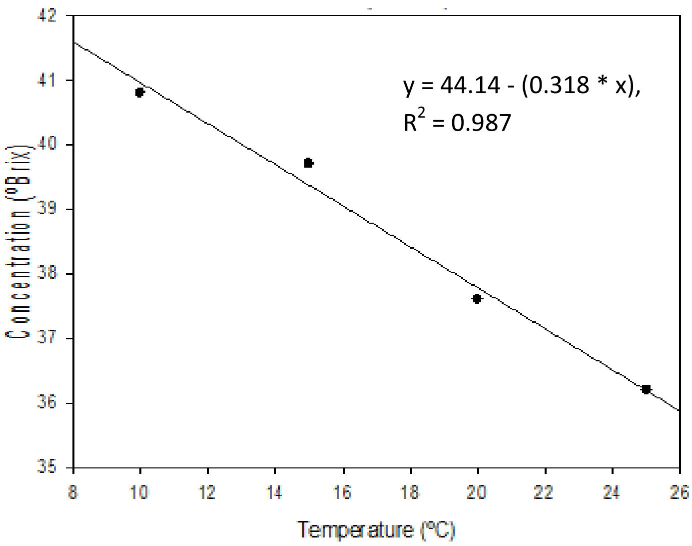


Figure 3.32. Variation of concentration versus temperature for 40 °Brix carrot concentrate at 15 min

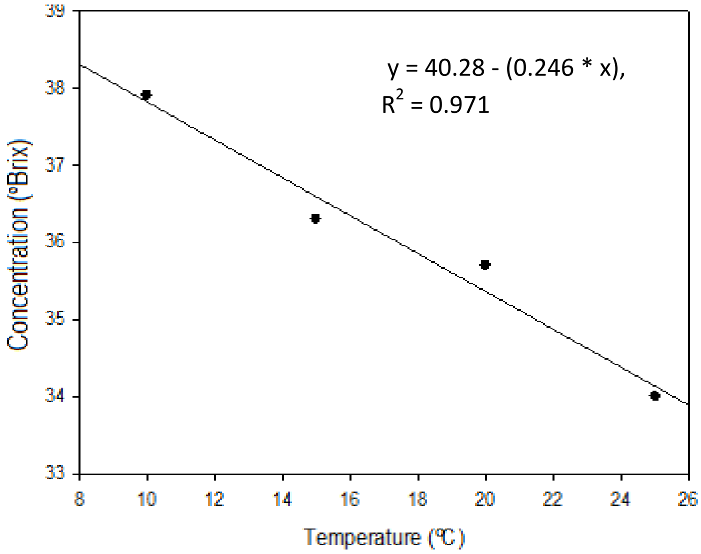


Figure 3.33. Variation of concentration versus temperature for 40 °Brix carrot concentrate at 30 min

Although the degree of separation is improved with the size of the samples, the time of separation, increases in parallel. This necessitates optimizing the size of the samples to achieve the highest degree of separation in shortest time. The degree of separation did not change appreciably with sample size in the first 60-90 minutes, after this time degree of separation was observed to be different for each size. After 60-90 minutes, the separation degree was decreased slowly.

3.10. Effect of Temperature

The influence of temperature on the rheological parameters of fruit juices have been studied in many articles. Temperature influence on viscosity has been found to be related to soluble solids content, and experimental data for fixed concentrations can be related to the temperature using the Arrhenius-Guzman equation. Therefore, the variation in concentration with temperature on the flow behavior of fluid foods can be described by the exponential type Arrhenius relationship.

E_a is defined as the energy that must be overcome in order for a chemical reaction to occur. Activation energy may also be defined as the minimum energy required starting a chemical reaction.

The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds.

The measured concentration results were used to calculate the values of parameter (flow activation energy E_a) in Arrhenius equation. Figure 3.34 shows that these results are suitable to first order reaction. This figure illustrates first order reaction for 35 ºBrix carrot concentrate. First order reaction was observed to be the best fitted model for all data. From the Arrhenius equation, the activation energy can be expressed as:

$$k = A\,e^{-Ea/RT} \qquad (1)$$

where A is pre-exponential factor, R is the universal gas constant (8.314 J/mol K), T is the temperature (in Kelvin) and k is the reaction rate coefficient. This equation suggests that the activation energy is dependent on temperature. E_a (kJ/mol K) can be evaluated from the reaction rate coefficient at any temperature.

Take the natural log of both side in equation (1):

$$ln\ k = ln\ A - E_a / Rt \qquad (2)$$

Equation (2) has the form of a straight line as in Figure 3.35. It shows that temperature effect on concentration of 20 ºBrix sumac concentrate. The slope of this graph gives $- E_a / R$.

A linear plot is obtained between rate constant and inverse of temperature. The slope of the straight line gives the activation energy.

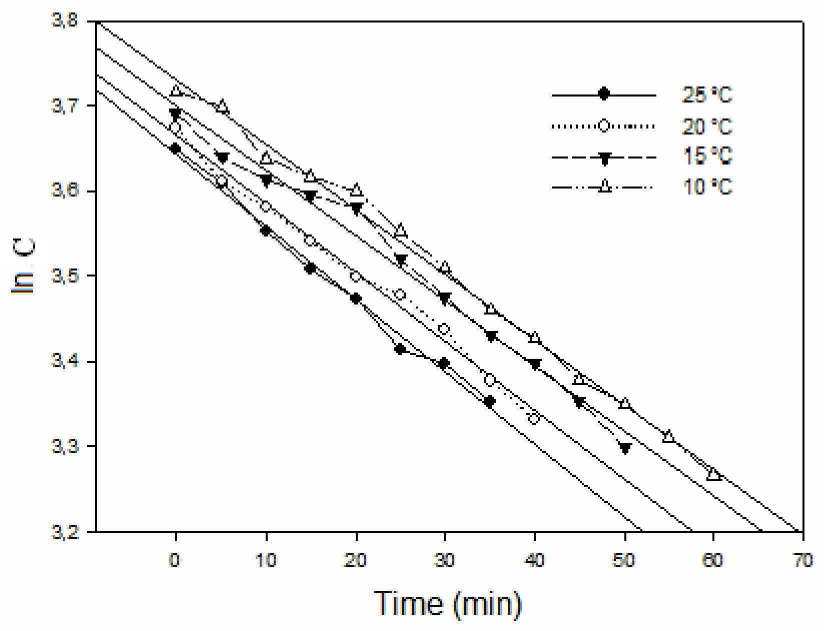


Figure 3.34. First order reaction for 35 ºBrix carrot concentrate

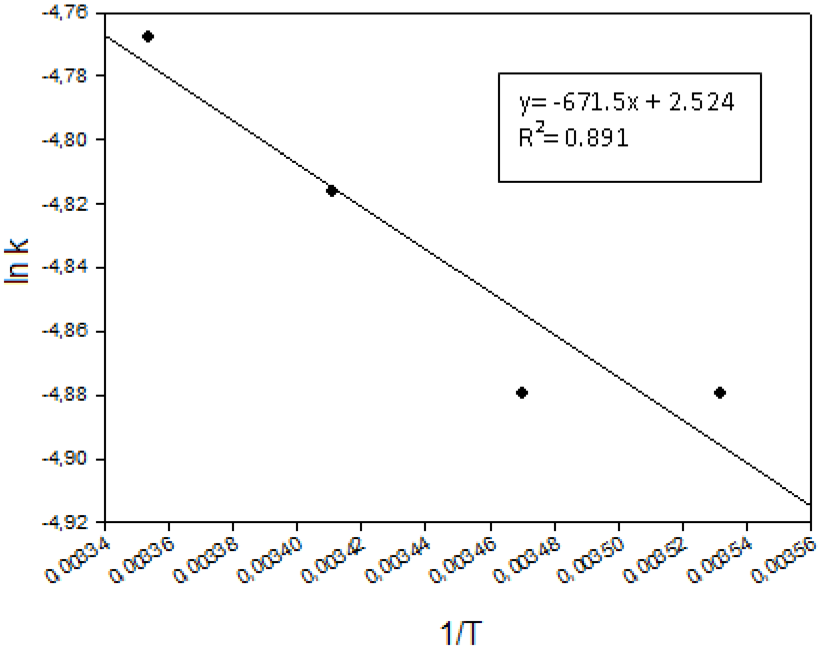


Figure 3.35. Arrhenius plot for 35 ºBrix carrot concentrate

Table 3.23. Activation energy for different concentrated juices

Fruit Juices	**Initial Concentration (°Brix)**	**Activation Energy (E_a) (kJ/mol K)**	**R^2**
Sumac	10	5.57	0.699
	15	5.54	0.922
	20	4.46	0.892
	25	5.23	0.884
	30	6.09	0.826
	35	1.23	0.882
	40	1.93	0.824
Apple	10	6.81	0.986
	15	6.94	0.982
	20	3.28	0.916
	25	2.89	0.892
	30	2.79	0.941
	35	4.61	0.656
	40	5.71	0.895
Grape	10	1.85	0.963
	15	3.32	0.921
	20	3.44	0.963
	25	3.25	0.893
	30	1.67	0.894
	35	5.05	0.896
	40	6.37	0.996
Carrot	10	5.62	0.920
	15	4.18	0.934
	20	2.26	0.947
	25	3.97	0.993
	30	6.73	0.983
	35	5.59	0.963
	40	5.40	0.952

Table 3.23 shows E_a values for sumac, apple, grape, and carrot concentrates. The value of E_a did not change significantly for concentrated juices. However, E_a values changed significiantly for 35 and 40 ºBrix grape concentrate. E_a values decreased for 35 and 40 ºBrix sumac concentrate. According to Wang (2007), the general tendency is for the activation energy to increase with the soluble solids concentration. This observation indicates that the effect of temperature on concentration of fruit juice concentrates is not pronounced for this study.

CHAPTER 4

CONCLUSION

In this study, the application of a modified version of freeze concentration, called differential freeze concentration, was applied to concentrate sumac, apple, grapes, and carrot juices.

The outcomes of this work can be summarized as follows:

1. When all juices were thawed, the more concentrated portion was always observed to separate from the ice front at the beginning of thawing. The concentration of the juice leaving the ice phase was observed to decrease with time.

2. The concentration of the juice leaving the ice phase was seen to be strongly dependent on the initial concentration of the frozen juice. The lower the initial concentration of the juice, the higher degree of separation was achieved. This method is, therefore, not feasible for samples having an initial concentration higher than 20 ^{o}Brix.

3. The more concentrated region of the frozen samples was visually observed to be near their centers. This is in agreement with the fact that, mass transfer occurs from high to low concentration regions.

4. The decay exponential model fitted best to the data obtained from the differential freeze concentration experiments for all juices.

5. The size of samples being thawed was observed to affect the degree of separation. The larger the size of samples, the higher the degree of separation realized. This is due to the decrease in (surface area/volume)$_{\text{SAMPLES}}$ as the size increases, which causes a relatively less heat transfer and consequently slower rate of thawing, resulting in a more concentrated juice leaving the ice front.

6.Although the degree of separation is improved with the size of the samples, the time of separation, increases in parallel. This necessitates optimizing the size of the samples to achieve the highest degree of separation in shortest time.

7. The degree of separation was observed to be influenced also by the nature of the juice being concentrated. In general, more acidic samples resulted in a higher degree of separation. Thus the less acidic carrot juice exhibited lower degree of separation than that of sumac juice.

4.1. Suggestion for Future Work

Freeze concentration presents new opportunities in a wide variety of applications. Freeze concentration can be supported with the other methods to get higher concentrated samples. However, it has some problems like cost which prevent commercial application. The technique is easier and cheaper to use and adapt to small scale batch proseses. A mathematical model, from which the transport properties of the present systems are determined, can be developed for the future work.

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