Evaluation of the Quality Parameters of Sumac Berries and Sumac Concentrate

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ABSTRACT

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When sumac (*Rhus coriaria*) berries were leached in water, the juice obtained had a bright red color with a characteristic sour taste. To prevent microbial and chemical deteriorations, this juice was concentrated using a batch-type rotary, and a rising film evaporator. The quality parameters, such as color, composition, and moisture sorption of both sumac berries and the resulting concentrate were then evaluated with respect to age, storing conditions, leaching temperature, and geographical type of berries. The variation of the rheological characteristics and the density of the concentrate with temperature, and total soluble solids (TSS) were also evaluated. The composition, and thus the color, and sorption properties of both the berries and the concentrate were observed to be highly temperature-dependent. As expected, the rate of extraction of TSS of sumac berries increased while the density and viscosity decreased with temperature. At relatively low TSS ($X \leq 60$ brix), sumac concentrate showed Newtonian behavior, while samples with higher TSS ($X \geq 70$ brix) exhibited a slight yield stress (σ_0=3.05 pa) with shear-thinning behavior (n=0.85) at the lowest temperature (20 ^{o}C) studied.

Zero and first order kinetics were applied to Hunter-Lab color parameters of the concentrate. The activation energy of the change of L value for 10% TSS was found to be 26.97 kj/mol whereas for 37% TSS it was 36.67 kj/mol.

Total phenolic content (TPC) of the concentrate were determined as a function of the type, age, and processing of the berries. Samples prepared from one year old and two years old berries were observed to contain 0.28, and 0.25 mg gallic acid /L respectively. Non-processed new crop sumac extract had the highest quantity of anthocyanin (614 mg/l) as compared with 342 mg/L for the processed (concentrated in a rising film evaporator) sample. The polymeric color of the concentrate was observed to increase with the age of berries. This means that, on standing under ambient conditions, sumac berries undergo some reactions leading to the intensification of the polymeric color. The main organic acids found in sumac concentrate were identified as malic and gallic acids. Although a slight variation with respect to the geographic origin was observed, on average, malic and gallic acids, constitute 42.7 % and 10.2 % of the whole organic acids present in sumac berries respectively.

Key words: Sumac berries, sumac concentrate, quality parameters, *Rhus coriaria*.

ÖZET

SUMAK TANELERİNİN VE SUMAK KONSANTRESİNİN KALİTE PARAMETRELERİNİN DEĞERLENDİRİLMESİ

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Sumak (*Rhus coriariaria*) su ile ıslatıldığında elde edilen sıvı kendine özgü ekşi tadıyla birlikte parlak kırmızı bir renge sahiptir. Mikrobiyal ve kimyasal bozulmaları engellemek için, elde edilen bu sıvı batch-tip dönerli evaporatörde ve yükselen filmli evaporatörde yoğunlaştırılmış hale getirildi. Sumak tanelerinin ve bunlardan elde edilen konsantrenin kalite parametreleri; örneğin, renk, kompozisyon ve su soğurma izotermleri; hasat zamanına, depolama şartlarına, ekstraksiyon sıcaklığına ve sumak tanelerinin coğrafik tipine göre değerlendirildi. Ayrıca, sumak konsantresinin akışkanlık özelliklerindeki ve yoğunluktaki değişimleri, sıcaklığa ve suda çözünen katı madde miktarına göre değerlendirildi. Sumak tanelerinin ve konsantresinin içerik, renk ve su soğurma özelliklerinin belirgin olarak sıcaklığa bağlı olduğu gözlendi. Beklenildiği gibi, sumak tanelerinin toplam katı maddesinin ekstraksiyon hızı, sıcaklık artarken yoğunluk ve viskozite değerleri düşmüştür. Çalışılan en düşük sıcaklıkta (20^oC), yüksek toplam katı madde ($X \leq 60$ brix) kayma-incelmesi davranışla ($n=0.85$) birlikte bir akım-gerilimi ($\sigma_0=3.05$ pa) özelliği gösterirken, daha düşük toplam katı madde değerlerinde sumac konsantreleri Newtonsu davranış gösterdi. Sumak konsantresinin Hunter-Lab renk parametrelerine, sıfır ve birinci derece kinetik uygulandı.%10 toplam katı maddede, L değerindeki değişimlere ait aktivasyon enerjisi 26,97 kj/mol bulunurken, bu değer %37'deki sumak konsantresi için 36.67 kj/mol olarak bulundu. Toplam fenolik madde içeriği; tip, yaş ve işlem şekillerinin fonksiyonu olarak belirlendi. Bir ve iki yıllık sumak tanelerinden hazırlanan numunelerin, sırasıyla 0,28 ve 0,25 mg gallik asit /L fenolik madde

içerdiği gözlenmiştir. Yükselen filmli evaporatörde işlenmiş numune 342 g/l antosiyanin içerirken, işlem görmemiş yeni mahsul sumak özütünün en fazla miktarda antosiyanine (614 mg/l) sahip olduğu gözlendi. Konsantredeki polimerik rengin, sumak tanelerinin yaşı ile birlikte arttığı gözlenmiştir. Bu, saklama şartlar altında kalırken, sumak tanelerinin polimerik rengi kuvvetlendiren bazı reaksiyonlara uğraması demektir. Sumak konsantrelerinde bulunan belli başlı organik asitler malik asit ve gallik asit olarak belirlenmiştir. Coğrafik orijine bağlı az derecede değişimler gözlenmesine rağmen, sumak tanelerinde bulunan toplam organik asitlerin %42,7'sinin malik, %10,2'sinin gallik asit olduğu saptandı.

Anahtar kelimeler: Sumak taneleri, sumak konsantresi, kalite parametreleri, *Rhus coriaria*.

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CHAPTER 1

1. INTRODUCTION

1.1. Definition and Properties of Sumac

Sumach or Sumac is the name given to numerous shrubs and small trees of the botanical genus *Rhus* (family Anacardiaceae), which comprises about 150 species, natives chiefly in warm regions. The genus is found in subtropical and warm temperate regions throughout the world (Zalacain et al., 2003; Koşar, et al., 2006; Özcan, M., 2003; Arslan, 2000). They have a milky or resinous juice, simple or compound leaves; small flowers, with the parts in fours and sixes, and small, dry, one-seeded, often hairy, sometimes highly colored fruits, usually in dense clusters. (Figure 1.1).

Figure 1.1. A sumac cluster with leaves

A bushy shrub of the *Anacardiaceae* family can reach up to 3m (10 ft). It has light gray or reddish stems which exude a resin when cut. Young branches are hairy. The

leaves are pinnate with up to eleven serrated elliptic leaflets, hairy on the underside. In autumn the leaves turn to a bright red. White flowers are followed by conical clusters of fruit, each enclosed in a reddish brown hairy covering. Easily propagated by seed, sumac grows best in poor soils (Zalacain et al., 2003).

The name sumac is given also to the commercial preparation of the dried and ground leaves of the Sicilian or tanners' sumac (*R.coriaria*) of southern Europe, long used in making leather.

Sumac is known as any shrub or tree of the genus Rhus. Some species are poisonous to the touch. One of the most common innocent eastern species of America, and the largest, is Rhushirta, the staghorn sumac, so called because its young, short branches are covered with down, in color and texture not unlike a deer's antlers "in the velvet". The trees are not more than 30 feet high, but are up to grow in clumps and have a tropical appearance, with their long pinnate leaves turning to vivid yellow and crimson in autumn. The fragnant, or sweet-scented sumac (*Rhus crenata*), is a low shrub with aromatic leaves and large panicles of greenish, honey-scented flowers which bloom in spring and are a famous food for bees. In the fall the leaves turn to a bright red. Flowers bloom in June and July. They are dense in panicles of greenish-red small flowers. The edible fruit is a large erect cluster of small bright red berries (www.natures.herbal.com). In this study, from now on, the term sumac will refer to *Rhus coriaria*.

The active constituents in sumac are being studied for use in many diseases. Some possible applications are in the treatment of diabetes, and some cancers. Sumac berries contain free malic acid and calcium maleate coexisting with tannic acid, gallic acids, fixed oil, extractive red coloring matter and little volatile oil.

The plant contains calcium maleate, dihydrofisetein, fisetin, iodine, gallic acid methyl esters, tannic acid and gallic acids, selenium, tartaric acid and many beneficial minerals (www.natures.herbal.com).

Sumac is a very popular condiment in Turkey, and in the Middle East and in some European countries where the ground fruits are liberally sprinkled over rice. Mixed

with freshly cut onions, it is frequently eaten as an appetizer. The fruits of sumac are cooked with water to a thick, very sour essence, which is then, added to meat and vegetable dishes. The berries can be dried, ground and sprinkled into the cooking, or macerated in hot water and mashed to release their juice, the resulting liquid being used as one might use lemon juice. Ground sumac keeps well if kept away from light and air. The juice extracted from sumac is popular in salad dressings and marinades and the powdered form is used in stews and vegetable and chicken casseroles (Perry and Chilton, 1973).

1.2. Production of the Sumac Concentrate

A concentrate is a form of substance which has had the majority of its base component (in the case of a liquid: the solvent) removed. Typically this will be the removal of water from a solution or suspension such as the removal of water from fruit juice. One benefit of producing a concentrate is that of a reduction in weight and volume for transportation as the concentrate can be re-constituted at the time of usage by the addition of the solvent (Ribeiro, et al., 2007; Jiao et al., 2004).

Concentrated juice was developed during World War II to provide nourishment for the armed forces.

To concentrate a solution, one must add more solute, or reduce the amount of solvent (for instance, by selective evaporation). By contrast, to dilute a solution, one must add more solvent, or reduce the amount of solute.

1.2.1. Solid-Liquid Extraction (Leaching)

Extraction is a method of separating the constituents of a mixture utilizing preferential solubility of one or more components in a second phase. Commonly, this added second phase is a liquid, while the mixture to be separated may be either solid or liquid.

Liquid/solid extraction may be considered as the dissolving of one or more components in a solid matrix by simple solution, or by the formation of a soluble form by chemical reaction. (McGraw Hill Professional Science and Technology Encyclopedia, 2000).

The extraction and purification of bioactive compounds from natural sources has become very important for the utilization of phytochemicals in the preparation of dietary supplements, functional food ingredients, and additives to food, pharmaceutical and cosmetic products. The extraction yield of bio-active compounds from plant materials is influenced mainly by the process of extraction with aqueous and/or organic solvent. Solid-liquid extraction uses a solvent to remove a soluble fraction from an insoluble, permeable solid. The concentration of each compound within the plant tissue reaches equilibrium with the concentration dissolved in the solvent (Cacace and Mazza, 2003).

There are different types of equipment used for leaching. Most of these fall into one of two categories:

a. Percolation (liquid added to solids): The solvent is contacted with the solids in a continuous or batch method.
b. Dispersed solids (solids added to liquid): The solids are usually crushed into small pieces before being contacted with solvents.

Whether the leaching is taking place via percolation or by dispersed solids there are three important factors that aid in leaching: temperature, contact time/area, and solvent selection. Temperature is adjusted to optimize the solubility and thus mass transfer.

Liquid-to-solid contact is essential for the extraction to take place and maximizing the contact area per unit volume reduces equipment size. Solvent selection plays an important role in solubility's as well as the separation steps that follow leaching. Nearly all leaching equipment employs some type of agitation to aid in mass transfer and to ensure proper mixing.

1.2.2. Clarification (Fining)

Fining agents are used to achieve clarity and to improve color, flavor and physical stability (Morris and Main, 1995).

Clarification is an important step in the processing of fruit juice and is often achieved through microfiltration, enzymic treatment or by using common clarifying aids like gelatin, bentonite, silica sol, polyvinyl pyrolidone or a combination of these compounds (Chatterjee et al., 2004).

Fining agents are of two kinds: some are positively charged and others negatively. Just like with magnets where north is attracted to south, positive attracts negative and they form agglomerates which eventually drop to the bottom of the vessel. (http://www.meadmadecomplicated.org)

Gelatin is an amphoteric protein whose isoionic point is between 5 and 9 depending on raw material and method of manufacture. In fining applications, gelatin reacts with polyphenols and proteins in fruit juices forming a precipitate which settles leaving a supernatant which is stable to further cloud formation with storage time (http://www.gelatin.co.za).

1.2.3. Evaporation

Evaporation is one of the most important unit operations in food processing. Large quantities of fruit and vegetable juices, sugar and syrups are concentrated in several types of commercial evaporators (Saravacos et al., 1970).

At the beginning of the industrialization of food technology, batch processes were widely used. In batch evaporation, the process liquid was boiled in a vessel until enough water was evaporated, and the product had the required consistency.

Because of the sensitivity of foods to heat, the liquid content of an evaporator should be as small as possible relative to the heating surfaces, so as to minimize residence time. In order to fulfill this requirement, tubular evaporators were improved (Hulbert et al., 1998; Nindo et al., 2007; Vaillant et al., 2001).

Evaporation is an operation used to remove a liquid from a solution, suspension, or emulsion by boiling off some of the liquid. It is thus a thermal separation, or thermal concentration process. Evaporation is a process as one that starts with a liquid

product and ends up with a more concentrated, but still pumpable concentrate as the main product from the process (Lee and Lee, 1999; Ribeiro, et al., 2007).

In most cases it is essential that the product is subject to minimal thermal degradation during the evaporation process, requiring that the temperature and time exposure must be minimized.

For economic reasons (reduced transport and storage costs), fruit juices are routinely concentrated. This is especially true in the case of tropical fruit juice for which centers of production and consumption are normally far apart geographically. Classical thermal concentration techniques lead to subsequent losses of aromatic compounds and vitamins.

Additionally, technological improvements to thermal concentration methods, while lessening the damage they cause, have more or less reached their peak. Despite improvements, thermal processing is continued to lead to an inevitable loss of nutrients, and the resulting concentrates tend towards the low-quality end of the market. Meanwhile, a demand for juices with better conserved nutritional and sensory qualities is increasing.

Concentration reduces weight and volume and results in immediate economic advantages. Foods are also concentrated because the concentrated forms have become desirable components of diet in their own right. The level of water in virtually all concentrated foods is in itself more than enough to permit microbial growth.

Obviously concentration that exposes food to 100°C or higher temperatures for prolonged periods can cause major changes in organoleptic and nutritional properties. Cooked foods and darkening of color are two of the more common heat induced results which must be kept under control during a well designed process with an efficient evaporator which is still safe.

Microbial destruction is another type of a change that may occur during concentration and will be largely dependent upon temperature. Concentration at a

temperature of 100°C or slightly above will kill many microorganisms but cannot be dependent on to destroy bacterial spores. When the food contains acid, the kill will be greater but again sterility is unlikely.

1.2.2.1. Rising Film Evaporator

The evaporator is essentially a vertical single tube in shell arrangement in which the product to be evaporated is on the tube side and the heating medium, steam, on the shell side. Schematic diagram of the used rising film evaporator in this study is shown in Fig.1.2. The process liquid feed is by gravity from a stainless steel feed tank through a flow meter and manually operated control valve. Vapor, produced by boiling in the tube, rises and carries a 'film' of more concentrated liquid up the tube and into a cyclone separator where the vapor and liquid are separated. The vapor enters water cooled condenser where it condenses and flows out into a condensate collecting tank. The liquid concentrate can be recycled back through evaporator tube or collected as product in the product collecting tank. The evaporator ducting, cyclone and condenser are all constructed from stainless steel, and a glass 'elbow' at the top of the evaporator allows the vapor/liquid film mechanism to be seen before and condensate collecting tanks are borosilicate glass to allow the condition and quantity of the products to be observed (http://www.armfield.co.uk).

A clean-in-place pump is included which allows efficient cleaning by re-circulation of the system and also utilizes the industrial spray nozzle technique to clean the glass collecting tanks. Vacuum can be applied to the system by a diaphragm type vacuum pump, giving suitable reduced boiling temperatures for the evaporation of milk and other heat sensitive food products. All important temperatures in the system are detected by sensors which are connected to digital read-out display with selector switch. The temperatures can also be monitored on any appropriate instrumentation such as a chart recorder or computer data logger.

Operation of the rising film is straightforward. Liquor is fed into the bottom liquor chamber and than into tubes. There it is heated with condensing steam or any other suitable heat transfer medium, such as Dowtherm or hot liquor. If the vapor pressure of the feed equals or exceeds the system pressure at the bottom tube sheet, vaporization will occur immediately. For colder feed, the lower portion of the tubes is used to preheat the liquor to its boiling point. Vaporization then begins at that

height within the tubes where the vapor pressure of the feed liquor equals the system pressure. As the liquor climbs up the inside of the tubes, additional vapor is generated and the velocity of the liquid-vapor mixture increases to a maximum at the tube exit. The outlet mixture impinges upon a deflector, mounted above the top tube sheet of the heat exchanger, where gross, initial separation of the liquid from the vapor occurs.

Additional liquor is separated from the vapor by gravity as the vapor body. AQ mesh-type or centrifugal entrainment separator can be installed near the top of the vapor body to remove most of the remaining traces of liquid from the vapor. The exit vapor is conducted to the next effect of a multiple-effect evaporator, to a compressor or to condenser. The concentrated liquor is discharged from a connection near the bottom of the vapor body. Heat transfer rates are enhanced in the non boiling section by surface or local boiling zone are several times greater than those in the non-boiling zone, so it is important to reduce the non-boiling zone to a maximum.

1.2.2.2. Rotary Vacuum Evaporator

A rotary evaporator is a device used in chemical and biochemical laboratories for the efficient and gentle evaporation of solvents. The main components of a rotary evaporator are a vacuum system, consisting of a vacuum pump and a controller, a rotating evaporation flask which can be heated in a heated fluid bath, and a condenser with a condensate collecting flask. The system works because lowering the pressure lowers the boiling point of liquids, including that of the solvent. This allows the solvent to be removed without excessive heating.

Evaporation under vacuum can be performed in a standard distillation rig. However, the rotary evaporator has a key advantage. As the evaporating flask rotates, the liquids are forced to the outside of the flask with the centrifugal motion. This creates a larger surface area of the liquids and hence allows for quick, gentle evaporation.

Rotary evaporators are highly effective at removing the majority of organic solvents during the extraction process. The remainder of the solvents is usually removed using a high-vacuum line. Rotary evaporators are usually not recommended for removing aqueous solvent due to water's high boiling point.

Some rotary evaporators are also fitted with a 'descending condenser' glassware assembly that aids evaporations with bumping tendencies. Scientists who have many samples to evaporate often prefer to use a modern centrifugal evaporator which safely dries samples in parallel and also prevents "bumping" episodes.

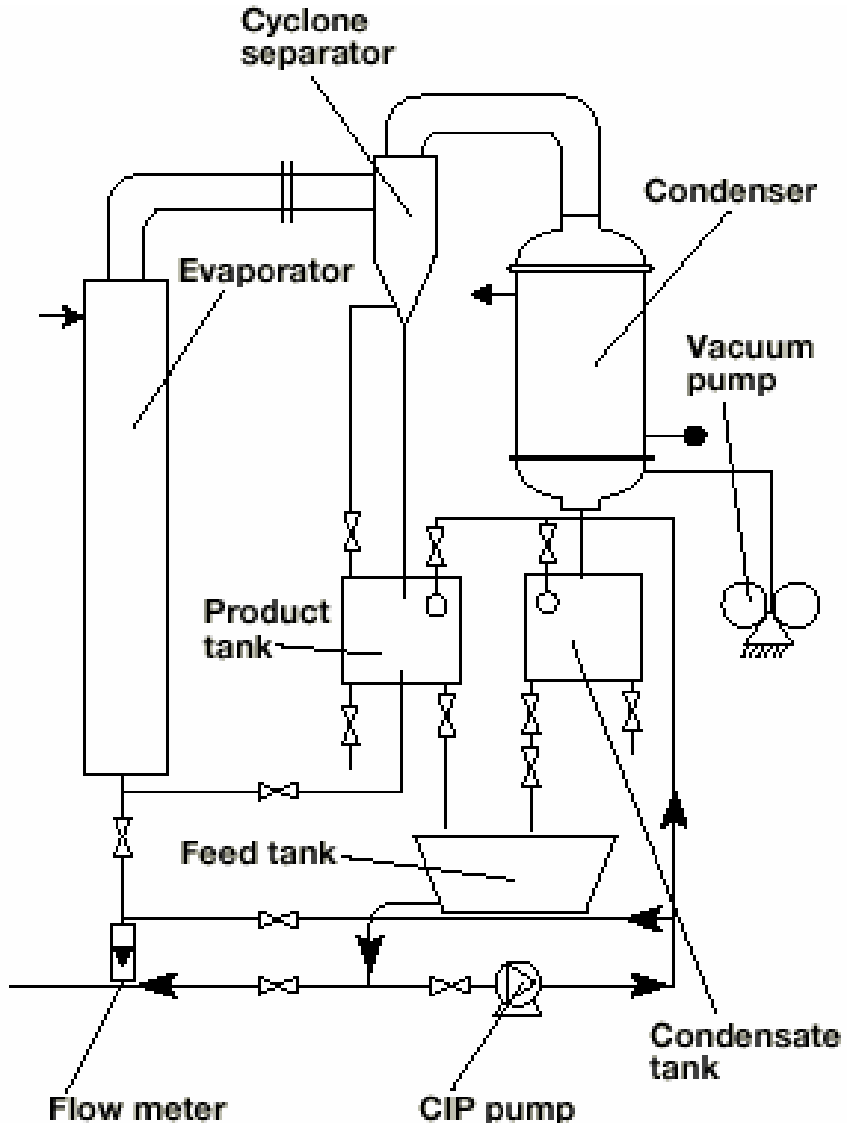

Figure 1.2. Schematic diagram of rising film evaporator

1.3. Quality Parameters of Sumac Concentrate

1.3.1. Water Sorption Isotherms

Water is a constituent of food, which affects food safety, stability, quality and with a fraction of a percent and reaches even more than 98%. Fresh products and liquid

foods contain usually large amounts of water while baked and dry products are poor in water (Lewicki, 2004).

Control of moisture content during the processing of foods is an ancient method of preservation, and probably humankind's first technology for extending the stability of foods. This is achieved by either removing, or binding water such that the food becomes stable to microbial and chemical deterioration.

State of water in a solution or a solid is expressed by the activity coefficient- a thermodynamic measure of chemical potential of water in the system proposed to express water activity as the ratio of vapor pressure of water in food (p) to the vapor pressure of pure water (p_0) at some temperature and total pressure;

$$a_w = [p/p_0]_{P,T} \qquad (1.1)$$

The state of water in food results from the structure of the water molecule and its interactions with remaining food constituents.

Water sorption isotherm is useful for predicting water sorption properties of foods, although they provide little insight into the interaction of water and food components (Lewicki, 2004; Stend, 2003)

1.3.2. Phenolic Composition of Sumac

Plants accumulate a wide variety of "secondary" compounds, including alkoloids, terpenes and phenolics. Although these compounds apparently do not function in "primary" metabolism such as biosynthesis, biodegradation and other energy conversions of intermediary metabolism, they do have diverse biological activities ranging from toxicity of hormonal mimicry, and may play a role in protecting plants from herbivory and disease (http://www.ansci.cornell.edu.plants)

Phenolic metabolism in plants is complex, and yields a wide array of compounds ranging from the familiar flower pigments (anthocyanidins) to the complex phenolics of the plant cell wall (lignin). However, the group of phenolic compounds known as

tannins is clearly distinguished from other plant secondary phenolics in their chemical reactivities and biological activities.
Sumac contains a certain amount of phenolic matter. Therefore, phenolic matter content of sumac concentrate will be investigated in details.
One of the most satisfactory definition of tannins was given by Horvath (1981): 'Any phenolic compound of sufficiently high molecular weight containing sufficient hydroxyls and other suitable groups (i.e. carboxyls) to form effectively strong complexes with protein and other macromolecules under the particular environmental conditions being studied' (http://tannindefinition.htm; FAO/IAEA Working Document, 2000).

Tannins are complex organic materials, and frequently have very large molecules and high molecular weights, on the order of 2,000 or greater, although it is still not certain whether they might better be considered macro-molecular substances. i.e., those with very large molecules and high molecular weights which break down into smaller fragments.

Vegetable tannins for the most part are uncrystallizable colloidal substances with pronounced astringent properties. They have the ability to precipitate gelatin from solution and to form insoluble compounds with gelatin yielding tissues which is the property which enables them to convert raw hide into and skin into leather, consolidating the dermal network of the hide into firmer and drier structures of improved thermal stability, durability, and water resistance (http://palimpsest.stanford.edu/don/dt/dt3686.html).

Traditional use of tannins as agents for converting animal hides to leather ("tanning") is one manifestation of the most obvious activity of the tannins: their ability to interact with and precipitate proteins, including the proteins found in animal skins. The term "tannin" comes from the ancient Celtic word for oak, a typical source for tannins for leather making (http://www.ansci.cornell.edu/plants).

Because they are extremely complex substances, vegetable tannins are difficult to classify; however, they are usually considered to consist of polyphenolic systems of two types: the hydrolyzed tannins (the pyrogallol class), the main constituents of

which are esters of glucose with acids such as chebulic, ellagic, gallic and m-didallic: and the condensed (catechol) tannins (http://palimpsest.stanford.edu/don/dt/).

1.3.2.1. Classification of Tannins

Bate-Smith (1954) defined the plant tannins as water soluble phenolic compounds with a molar mass between 300 and 3000, showing the usual phenol reactions (e.g. blue color with iron (III) chloride), and precipitating alkaloids, gelatins and other proteins. However, this definition does not include all tannins, since, more recently, molecules with a molar mass of up to 20000 D have been isolated that should also be classified as tannins on the basis of their molecular structures. Griffith defined tannins as "macromolecular phenolic substances" and divided them in two major groups, the 'hydrolysable' and 'condensed' tannins. (Khanbabaee and van Ree, 2001).

Due to the enormous structural diversity of the tannins a systematic classification system based on specific structural characteristics and chemical properties would provide a convenient framework for further study. The observation that many tannins can be fractionated hydrolytically into their components, for example by treatment with hot water or with tannases, led to the classification of such tannins as 'hydrolysable tannins'. Non-hydrolysable oligomeric and polymeric proanthocyanidins were classified as condensed tannins. Therefore, the term 'hydrolysable tannins' includes both the gallotannins and the ellagitannins. This classification is shown Figure in 1.3.

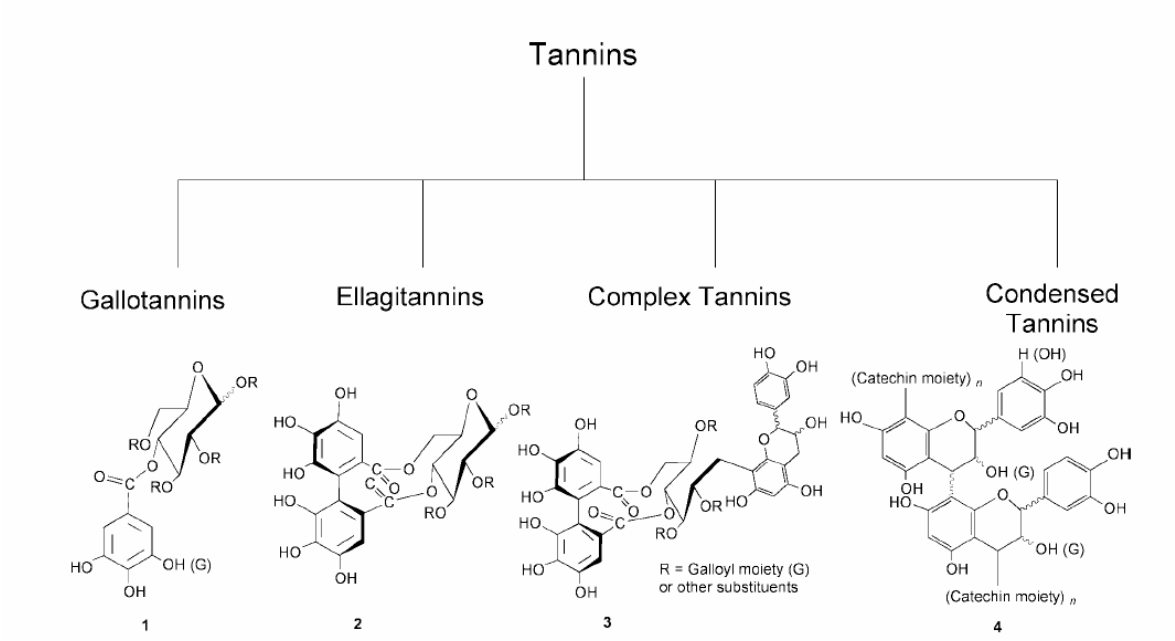

Figure 1.3. Classification of the tannins

1.3.2.2. Hydrolysable Tannins

The core of hydrolysable tannin consists of a polyhydric alcohol such as glucose. Linked to this alcohol via ester linkages are the molecules of gallic or hexahydroxydiphenic acid (Figure1.4.b, 1.4.d). These ester bonds are readily hydrolyzed by acids, bases, and gastrointestinal esterases. Hydrolysis reaction usually yields polyhydric alcohol and gallic acid, or phenolic acids related to it **(**Wroblewski, 2000).

Depending on the identity of the polyphenolic acid released during hydrolysis these tannins are divided into two groups. Gallotannins give rise to gallic acid molecules upon hydrolysis. Chinese tannin extracted from nutgall (Figure l.4.a), and Turkish tannin extracted from *Qzwczrs irfectora are* representative tannins of this group. They are widely used to test the biological effects of tannins. Hydrolysis of ellagitannins results in the release of hexahydroxydiphenic acid which then lactonizes to form ellagic acid (Figure 1.4.e). Corilagin (Figure 1.4.c) is the simplest form of ellagitannin present in *Caesalpina, Coriaria. Terminalia chebrrla,* and *Eucalyptus siberiana.*

1.3.2.3. Condensed Tannins

Condensed tannins are structurally more complex than hydrolysable tannins. They are mostly polymers of flavan-3-ols or flavan-3, 4-diols (Figure 1.5.a, 1.5.b), or a

mixture of both. The structure of typical condensed tannin from sorghum grain has been determined by Gupta and Haslarn (1978) (Figure 1.5.c). In hot, strong minera1 acids condensed tannins can be depolymerized to yield products such as anthocyanidins as well as some other less well characterized compounds. This is the reason why condensed tannins are often referred to as proanthocyanidins. Depending on the source of the tannin, its polymerization state might range anywhere from two to hundreds of flavanol units. Most of the condensed tannins have between four and forty flavanol units. The condensed tannins which are most widely used for the testing of biological effects include quebracho, sorgfium and wattle tannins. Epigallocatechin (EGC) and epigallocatechin gallate (EGCG) are representative monomeric condensed tannins (Figure 1.5.e, 1.5.f) and they are the major polyphenolic components of green tea These molecules which are snails by tannin standards are very useful in the study of protein-tannin interactions at the molecular level.

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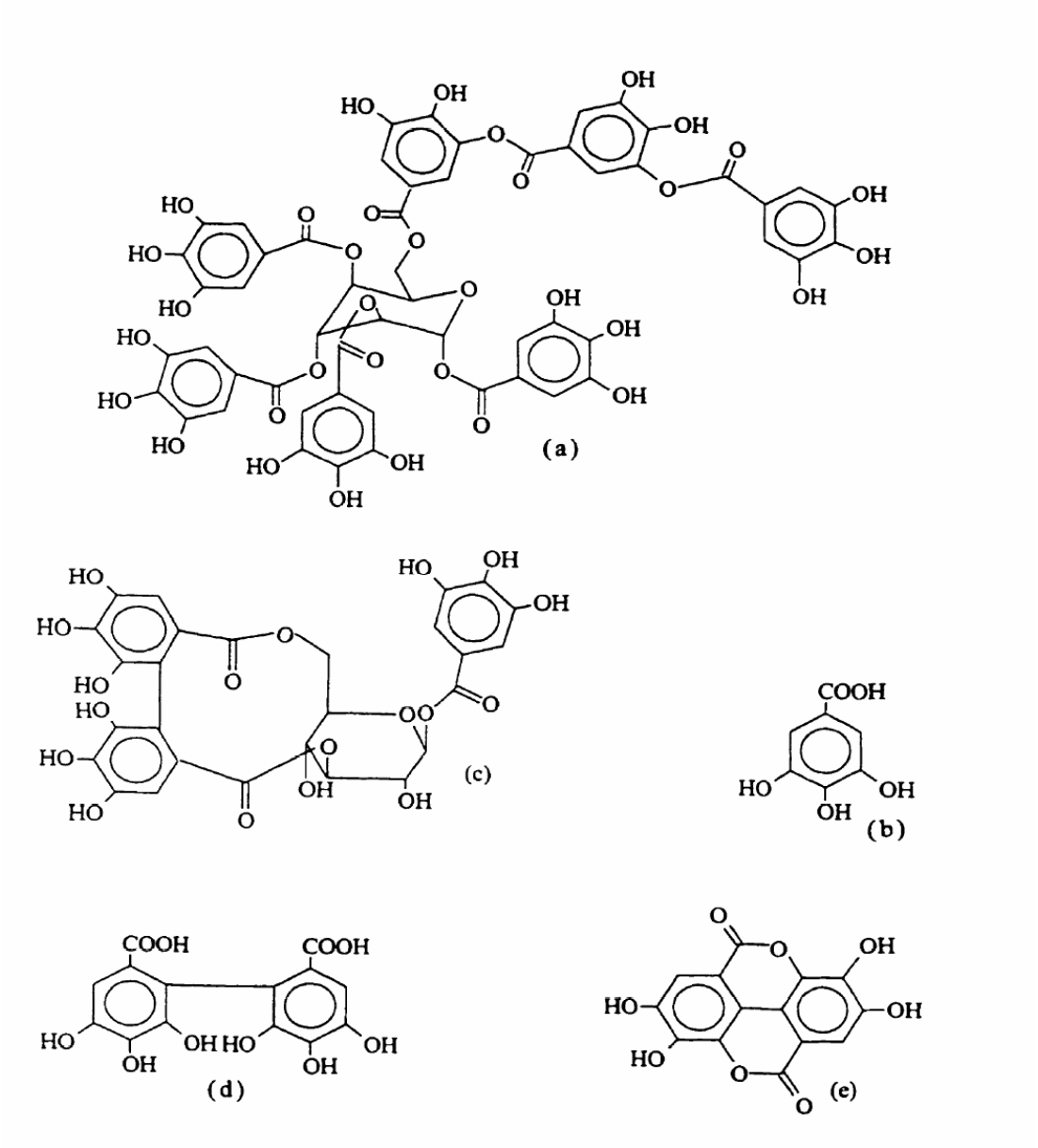

Figure 1.4. Structures of typical hydrolysable tannins: a) Chinese tannin, b) gallic acid, c) eliagitannin, d) hexahydroxydiphenic acid, *e)* ellagic acid.

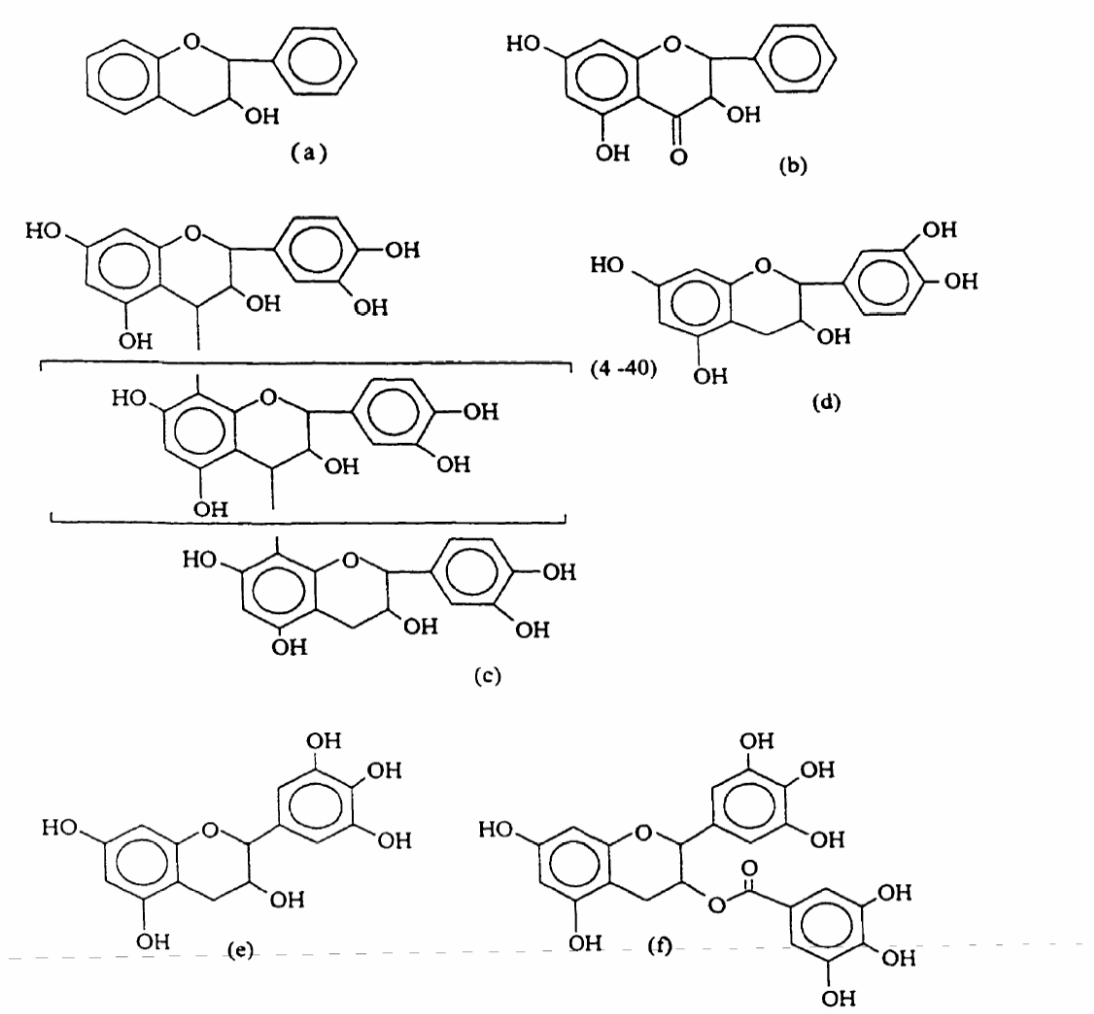

Figure 1.5. Structures of typical condensed tannins: a) flavan-3-ol, b) flavan-3,4-diol, c) condensed tannin from sorghum grain, d) cyanidin, one of many anthocyanidins, e) epigallocatechin, f) epigallocatechin gallate.

1.3.3. Rheological Properties

In consideration to the limitations of the multicomponent analysis based exclusively on the chemical index parameters, further attributes were studied with respect to quality control of fruit derived products, such as characterization of their rheological behavior (Fügel, et. al, 2005). In addition to chemical and physical properties in the food industry, rheological characteristics of concentrated fruit juices are important. Moreover, rheological characteristics depend on both the chemical composition of fruits and processing conditions (Sengül, et. al, 2005).

Processing of juices from fruits is a complex operation with many variables that influence the final product quality. In addition to chemical and physical properties, the rheological behavior of fruit juices is important for the design of processing

equipment, quality control during processing, consumer acceptance, and understanding of the structure of food and raw agricultural materials. The viscosity of food products cannot be predicted theoretically, due to complicated physical and chemical structures. Therefore experimental measurements of viscosity are necessary for the characterization of fluid foods. In practice, rheology stands for viscosity measurements, characterization of flow behavior and determination of material structure. Basic knowledge of this subject is essential process design and product quality evaluation (Juszczak and Fortuna, 2003; Kaya and Sözer, 2005).

Rheological measurements have also been considered as an analytical tool to provide fundamental insights on the structural organization of food. Numerous studies have been conducted on the rheological properties of fruit and vegetable products. **(**Rao, 1977; Khalil, Ramakrishna, Nanjundaswamy and Patwardhan, 1989; Truong and Walter, 1994; Godfrey, Bourne and Rao, 1995; Bhattacharya, 1999; Ahmed, Shivhare and Sandhu, 2002; concentrates include temperature, (Saravacos, 1970; Holdworth, 1971; Vitali and Rao,1984) total soluble solids (TSS), (Rao, 1977; Harper and ElSahrigi; Ilicali, 1985; Hernandez, Chen, Johnson and Carted, 1995) particle size, (Tanglertpaibul and Rao, 1987, Ahmed, Shivhare and Singh, 2000), addition of enzyme, (Khalil et al.) and pH (Dik and Ozilgen, 1994). Various rheological models have been used to represent the flow behavior of fluid food foods. The power law model is one most commonly used to describe the flow of food products without yield stress, while Casson and Herschel-Bulkley models have been employed for foods with definite yield stress. Fruit juices are mostly Newtonian in nature and commonly represented by power law model (flow behavior index=1.0). Fruit juice concentrates and purees with higher total soluble solids have been well described by Herschel-Bulkley model.

The present study was undertaken to accomplish the task of "characterization of rheological behavior of sumac concentrate" **(**Juszczak and Fortuna, 2004).

1.3.4. Color as Quality Parameter

The thermal processing of food is primarily intended to inactivate pathogens and other deteriorative microorganisms capable of making it unsuitable for consumption.

At the same time it has an inactivation effect on enzymatic systems, nutrients, and organoleptic properties, including texture and color (Barreiro et al., 1997).

Color measurement is a critical objective quality parameter that can be used for the following applications: as quality index measurements of raw and processed foods for use in quality control documentation and communication; for determinations of conformity of food quality specifications; and for analyses of quality changes as a result of food processing, storage, and other factors (Giese, 2000).

Color may be observed as the light transmitted through a solution containing substances extracted from the food in a transparent medium or as the light reflected from a surface of an opaque food.

Any color is uniquely specified by a set of three imaginary red (X), green (Y) and blue (Z) primaries. These are the International Commission on Illumination (CIE) tristimulus values. To make color data more intuitive and easier to interpret, these tristimulus values are usually converted to other color scales, all of which are mathematical transforms of the tristimulus X, Y and Z. Similarly, color indexes and differences can be calculated from these values (Silva et. al, 1999).

The L, a, b scale is recognized to show a better discrimination between small color space, providing good discrimination for saturated colors (Barreiro et al., 1997; Lozano and Ibarz, 1997).

The L value represents a nonlinear mathematical approximation of the white-black response of the eye, ranging from 100 for a perfect white to 0 for perfect black, measures the luminosity of the sample. A positive value of a" indicates redness, and a negative value greenness. A plus value of "b" indicates a yellowness and minus values blueness. There are other parameters derived from other the Hunter-chroma that indicates "L", "a", "b" scale the total color difference (ΔE), the saturation index (SI), chroma that indicates color saturation and is proportional to its intensity, "a／b" ratio.

Manufacturers of colored products are expected to supply them at a level of color quality sufficient to satisfy their customers. Since customer requirements are often not easy to satisfy, management of the color acceptability process can prove to be difficult.

Color measuring instruments and industry accepted color difference systems are widely utilized in industrial color acceptability applications. Colorimetry is used to supplement the visual evaluation process, as it provides a way to consistently quantify color differences, and thus facilitate the management of product color tolerance.

The CIE L, a, b system describes and orders based on the opponent theory of color vision. The opponent theory is that colors cannot be perceived as both red and green at the same time, or yellow or blue at the same time. However, colors can be perceived as combinations of: red and yellow, red and blue, green and yellow, and green and blue.

Most of the quality factors, including color can be described by degradation kinetics of zero or first order, with the effect of temperature in velocity constant taken into account by the Arrhenius equation.

1.3. 5. Characterization and Measurement of Anthocyanins

Anthocyanin pigments are responsible for the attractive red to purple blue colors of many fruits and vegetables. Anthocyanins are relatively unstable and often undergo degradative reactions during processing and storage. Measurement of total anthocyanin pigment content along with indices for the degradation of these pigments is very useful in assessing the color quality of these foods. Interest in the anthocyanin content of foods and nutraceutical preparations has intensified because of their possible health benefits. They may play a role in the reduction or coronary heart disease and increased visual acuity, and also have antioxidant and anticancer properties. Anthocyanins have also found considerable potential in the food industry as safe and effective food colorants; interest in this application has increased in recent years. Quantitative and qualitative anthocyanin compositions are important

factors in determining the feasibility of the use of new plant materials as anthocyanin-based colorant sources (Giusti and Wrolstad, 2001).

The total anthocyanin content in crude extracts containing other phenolic materials has been determined by measuring absorptivity of the solution at a single wavelength. This is possible because anthocyanins have a typical absorption band in the 490 to 550 nm region of the visible spectra. This band is far from the absorption bands of other phenolics, which have spectral maxima in the UV range.

The differential method measures the absorbance at two different pH values, and relies on the structural transformations of the anthocyanin chromophore as a function of pH (Giusti and Wrolstad, 2001).

1.3.6. Identification of Organic Acids in Sumac Concentrate

Organic acids are widely distributed in fruits and vegetables. They are also used extensively as food acidulants in the manufacturing of beverages, fruit and vegetable drinks or juices. The principal acids used to enhance beverage flavors are citric, tartaric, fumaric and phosphoric acids. Citric acid is the most widely used acid while malic and tartaric acid are important natural compounds of fruits that are used along with fumaric acid in fruit-flavored drinks (Shui and Leong, 2002).

The content of organic acids in fruit juices not only influences their flavor but also their stability, nutrition, acceptability and keeping quality. Separation, identification and quantification of the major organic acids present in fruit juice is of considerable importance, since these compounds influence the organoleptic properties of the product under examination and provide useful information regarding not only its authenticity but also microbiological alterations that may have occurred previously. (Cunha, et al., 2002). The organic acid composition of fruits and is also of its important influence on the sensory properties of fruits and fruit juices (Karadeniz, 2004).

Organic acids are important in characterizing the flavor of fruit juices. The presence and concentration determine tartness and other flavor attributes. In some cases, it is necessary to determine organic acids to assess whether an expensive juice has been

illegally adulterated with a cheaper juice. Because organic acid profiles are distinct to each type of fruit juice, evidence of tampering can be evaluated by comparing the known juice fingerprint to that of the suspected adulterated juice (Dionex, Application Note 143). Therefore, organic acid composition of sumac concentrate was determined in order to indicate a profile for further studies.

1.4. The aim of the present study

Knowledge of the physical and chemical properties of foods is fundamental in analyzing the unit operations present in the food industry. The study of these properties and their responses to process conditions are necessary because they influence the treatment received during the processing and also because they are good indicators of other properties and qualities of food.

In Mediterranean, diet is particularly rich in spices. Sumac (*Rhus coriaria*) is one example, which is widely used in Turkey and Middle East. The fruits are red colored and contain one seed. Its dried and ground leaves have been used as a tanning agent due to their high tannin content. There are several studies about the phytochemical properties of sumac including tannin content, antimicrobial activity, antioxidant property etc. However, there is a lack in information about the physical and chemical properties of sumac berries and quality parameters of concentrated juice obtained from sumac berries. Because both sumac berries and juice extracted from them are used to give sour taste in diets and their quality parameters according to several conditions were important.

The objectives of this study were to:

1. Determine the physico-chemical properties of sumac berries.
2. Determine the sorption isotherms of sumac berries and sumac concentrate.
3. Evaluate the rheological behavior of sumac concentrate.
4. Apply the color kinetics to observe the changes at different temperatures.
5. Determine the organic acid composition and phenolic compound.

CHAPTER 2

2. MATERIALS and METHODS

2.1. Materials

2.1.1. Sumac

The required sumac berries were supplied from sumac trees grown in the campus of University of Gaziantep. They were first destemmed and screened to separate the unripened, flower residues. These residues were utilized later and called 'second crop' in this thesis.

2.1.2. Chemicals

Water used for all extraction processes in this thesis was supplied from the Food Engineering Department, General Chemistry Laboratory, water-distilling unit.

NaOH, $MgCl_2$, $NaNO_3$, $(NH_4)_2SO_4$, KCl and $Sr(NO_3)_2$ which were used for sorption isotherms of sumac berries were supplied from Merck Company (Germany). Standard organic acids; tartaric, gallic, malic, succinic, citric and Folin-Ciocalteu reagent were supplied from Sigma Co. (USA).

2.2. Properties of sumac berries

Physical properties of sumac berries were determined as follows: Dimensions of berries were measured with a caliper (Mitotoyo, No.505-633). The average weight of sumac berry was determined as the average weight of randomly selected 100 berries. Protein content, moisture content, fat/oil content, ash content were determined according to AOAC 1990.

2.3. Solubility properties of sumac berries

The amount of solvent was chosen as 3 times the mass of sumac berries in solubility determinations. Thus 50 grams of sumac berries were soaked into 150 g of the solvent in which the solubility is to be determined. After equilibration for 24 hrs at

constant temperature water bath, the juice was filtered for the determination of the soluble solids.

2.4. Sorption isotherms of sumac berries

Two kinds of sumac samples were used mainly. These were 1-year old and new crop sumacs. In this study, four types of samples were prepared. First sample, 1-year old whole sumac berry; second sample, new (cultivated at July) crop whole sumac berry; third sample 1-year old crop sumac skin; and fourth sample was new crop sumac skin.

Several saturated salt solutions were utilized to maintain constant relative humidity (RH) environment. Saturated salt solutions such as NaOH, $MgCl_2$, $NaNO_3$, $(NH_4)_2SO_4$, KCl and $Sr(NO_3)_2$ corresponding to different constant RH values were prepared (Göğüş et al., 1998).

The dishes for placing samples were prepared by using a specific metal die. The dishes were prepared from aluminum foil in this specific die. Each sample was placed into a separate dish. All dishes -containing 0.5-0.6 gram samples- were placed in sealed jars containing saturated salt solutions of different relative humidity's and stored in controlled temperature incubators at 15, 25 and 35°C respectively. The saturated salt solutions and their corresponding water activities at different temperatures are given in the Table 2.1:

Table 2.1. Saturated salt solutions and their water activities at different temperatures

SALTS	a_w values		
	15°C	25°C	35°C
NaOH	0.0957	0.0824	0.0692
$MgCl_2$	0.3330	0.3278	0.3205
$NaNo_3$	0.7646	0.7425	0.7206
$(NH_4)_2So_4$	0.8170	0.8099	0.8027
KCl	0.8592	0.8434	0.8295
$Sr(NO_3)_2$	0.8872	0.8506	-

The dishes containing the samples were weighed at some time intervals depending on whether they approached a constant mass. Weight changes between measurements were evaluated carefully. The equilibrium was considered to have been reached when the moisture content did not change by more than 0.1% during consecutive weighing. When the samples reached constant weight, their moisture contents were determined by oven method (at 105°C for 24 h) (AOAC, 1990).

2.5. Sorption isotherms of sumac berries and concentrate by water activity display instrument

Sorption isotherms of sumac berries and sumac concentrate were determined by using Rotronic Hygropalm AW1 (Germany), water activity display unit. Measurements were carried out at 25^{o}C until the moisture content approached the equilibrium. Samples were 1-year old Siirt sumac, 1, 2 and 3-years old Gaziantep sumac. Sorption isotherms of sumac concentrate were measured separately.

2.6. Preparation of sumac concentrate

Flow diagram for preparation of sumac concentrate is shown in Fig.2.1. After harvesting the sumac berries in clusters, they were destemmed, and then screened to separate the inorganic impurities and unripe flower residues. The screened berries were then soaked and leached in distilled water in the leaching unit as shown in Fig. 2.2. The suspended insoluble matter in the juice was removed by filtration. Clarified juice was then concentrated separately in a rising film evaporator (Armfield FT 22, UK) and a rotary evaporator (Bibby, RE 100) under vacuum. All brix measurements were carried out by two hand-refractometers (ATAGO), 0-52 ^{o}Brix and 53-99 ^{o}Brix.

2.7. Variation of pH value of sumac concentrates with total soluble solids

pH value of sumac concentrates were measured by a pH meter (pH315i/SET WTW, Germany), at room temperature (23^{o}C).

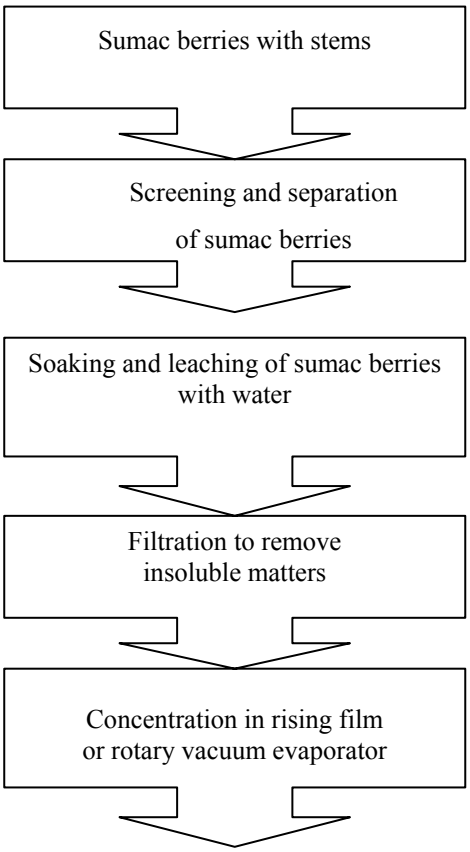

Figure 2.1. Flow diagram for preparation of sumac concentrate.

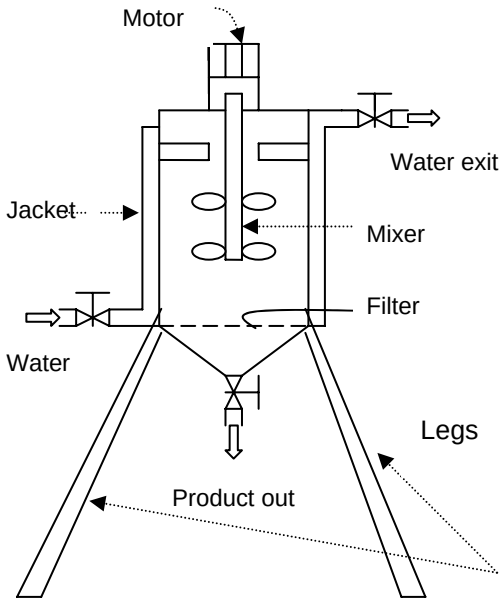

Figure 2.2. Schematic diagram of extraction unit

2.8. Effect of soaking temperature on the extraction of sumac berries

Temperature is an important parameter that affects the properties of leached materials. This parameter was then studied in order to determine these affects.

Sumac berries were soaked in water berries/water ratio of 1:3. Sumac berries were held in water at different temperatures, 25, 40, 50, and 70^{o}C.

Water was added to soak all berries. Water-soaked berries in beakers were placed into fixed temperature water bath firstly at 40^{o}C. This assay was performed for again at 50 and 70^{o}C.

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2.9. Density measurements

Density is an important quality parameter for especially liquid foods, including fruit concentrates, milk, oils etc.

Density of sumac concentrates was measured by using densometers (Eichschein, Germany) ranging from 1 to 1.3. Four different sumac concentrate samples were used; 30, 50, 55 and 69 ^{o}Brix.

A wide brix range was used for the measurement of density at different concentrations; ranging from 2 to 69 ^{o}Brix. These measurements were repeated for concentrate obtained from sumac berries and also concentrate obtained from sumac with shoots (or 'second crop sumac').

2.10. Rheological properties of sumac concentrate

The sumac extract was concentrated to 69 ^{o}Brix using rotary vacuum evaporator (Biby, RE 100), samples with lower soluble solids contents were obtained by diluting the concentrated juice with distilled water.

The rheological measurements were carried out by using a RheoStress RSI (Haake, Karlsruhe, Germany) controlled stress rheometer. The temperature of the bottom plate was controlled with TCP/P peltier unit and a thermostat. Vegetable oil was

applied to the exposed surfaces of the sample to prevent evaporation. The measuring system was a cone and plate sensor with a 3.5 cm diameter and an angle of 2°. Shear rate range was 0-600 s^{-1}. The rheological behavior of the samples with total soluble solids concentration of 69, 60, 55.5 and 50.6 °Brix were studied at 20, 30, 40 and 50°C.

Experimental results were analyzed by using a Rheowin Pro Data Manager, Version 2.64 (Rheowin, Haake, Karlruhe, Germany).

2.11. Color analysis

Color measurements are very important for food materials which contain phenolic matters, since the phenolic contents change the color properties. Since sumac concentrate has a certain phenolic content, color analysis evaluation became important.

In this study, two concentrations were chosen 10 ^{o}Brix and 37 ^{o}Brix. Color measurements were performed with a HunterLAB ColorFlex (Model A60-1010-615) (Hunter Associates Lab. Inc. Reston VA, USA).

After careful stirring, the color parameters of the sumac samples were determined with “L”, “a”, “b” scales. Hunter lab color standard of white tile of which has L= 93.01, a = -1.11, b=1.30 was used. The parameters “L”, “a” and “b” of the samples were read and the variation in these parameters were plotted against time. (Barreiro et al, 1997; Lozano and Ibarz, 1997; Camelo and Gozez, 2004; Moussaid et al, 2004).

For the effect of temperature on the color parameters, measurements were carried out at three different temperatures (40, 60, 80^{o}C). Changes in color parameters of; L, a, and b values were measured and recorded. Sumac concentrates were placed into test tubes and plugged. They were placed into ovens at three different temperatures and color values were measured at 30 min time intervals for 240 min.

2.12. Total phenolic matter

Folin-Ciocalteu method was used for the determination of total phenolic matter of sumac concentrates (Makkar, 2003; Kraus, et al, 2003). Major chemical reagents used in this method were prepared as in follows:

- **Gallic acid stock solution**: 0.500 g of dry gallic acid in 10 ml of ethanol in a 100 ml volumetric flask and diluted to volume with water.
- **Sodium Carbonate solution;** 200 g of anhydrous sodium carbonate was dissolved in 800 ml water and brought to boil. After cooling, a few crystal of sodium carbonate was added, and after 24 hr, filtered and water was added to make up1 liter.
- **Calibration curve;** To prepare calibration curve, 0, 1, 2, 3, 5 and 10 ml of the gallic acid stock were added into 100 ml volumetric flasks, and diluted to volume with water. The solutions will have phenol concentrations of 0, 50, 100, 150, 250, and 500 mg gallic acid/liter of solution.

From each calibration solution, sample or blank, 20 µL was pipetted and 1.58 ml of water was added to each, and then 100 µL of the Folin-Ciocalteu reagent was added. Solutions were maintained at 20^{o}C for 2 hr. After that, absorbance of each solution at 765 nm was determined against the blank (the 0 ml gallic acid) and absorbance vs. concentration (Makkar, 2003; http: //waterhouse.ucdavis.edu/phenol/folinmicro.htm) by using spectrophotometer (Perkinelmer, UV-VIS spectrophotometer Lambda, 25 1.24).

2.13. Total monomeric anthocyanin by the pH-Differential method

Anthocyanin pigments undergo reversible structural transformations with a change in pH manifested by strikingly different absorbance spectra. The colored oxonium form predominates at pH 1.0 and the colorless hemiketal form at pH 4.5. The pH-differential method is based on this reaction, and permits accurate and rapid measurement of the total anthocyanins, even in the presence of polymerized degraded pigments and other interfering compounds (Giusti and Wrolstad, 2001).

Materials of this experiment were prepared as follows:

- **Potassium chloride buffer, 0.025 M, pH 1.0**

  1.86 g KCl and 980 ml of distilled water were mixed in a beaker. The pH was measured and adjusted to 1.0 with concentrated HCl. Then, it was transferred to a 1 liter volumetric flask and filled to 1 liter with distilled water.

- **Sodium acetate buffer, 0.4 M, pH 4.5**

  54.43 g $CH_3CO_2Na.3H_2O$ and 960 ml distilled water were mixed in a beaker. The pH was measured adjusted to 4.5 with concentrated HCl. Then, it was transferred to a 1 liter volumetric flask and filled to 1 liter with distilled water.

After turning on the spectrophotometer, it was allowed to warm up at least 30 min before taking measurements. The appropriate dilution factor was determined for each sample by diluting with potassium chloride buffer, pH 1.0, until the absorbance of the sample at the $\lambda_{vis\text{-}max}$ was within the linear range of the spectrophotometer (Perkin Elmer, USA). In this trial, $\lambda_{vis\text{-}max}$ was determined as '523 nm'. Final volume of the sample is divided by the initial volume to obtain the dilution factor. After obtaining dilution factor, the spectrophotometer was made zero with distilled water at all wavelengths that will be used ($\lambda_{vis\text{-}max}$ and 700 nm).

Two dilutions of the sample were prepared, one with potassium chloride buffer, pH 1.0, and the other with sodium acetate buffer, pH 4.5, diluting each by the previously determined dilution factor. These solutions were equilibrated for 15 min. The absorbance of each dilution were measured at the 523 and at 700 nm (to correct for haze), against a blank cell filled with distilled water.

Finally the results were recorded and absorbance of the diluted sample and monomeric anthocyanin pigment concentration in the original sample were calculated.

Monomeric anthocyanin in the sumac concentrate samples were calculated as follows:

Absorbance of the diluted sample (A):

$A = (A_{\lambda vis\text{-}max} - A_{700})_{pH\ 1.0} - (A_{\lambda vis\text{-}max} - A_{700})_{pH\ 4.5}$

Monomeric anthocyanin pigment concentration in the original sample:

Monomeric anthocyanin pigment (mg/liter) = (A×MW×DF×1000)/ (ε) (2.1)

where MW is the molecular weight, DF is the dilution factor, ε is the molar absorptivity.

The MW and ε used in this formula correspond to the predominant anthocyanin in the sample. The ε of the major pigment is not available, because the sample composition is unknown than, pigment content was calculated as cyanidin-3-glucoside, where MW is 449.2 and ε is 26,900.

2.14. Indices for pigment degradation, polymeric color, and browning

1 g of potassium metabisulfite ($K_2S_2O_5$) was dissolved in 5 ml of distilled water. Sumac samples were diluted with distilled water. 2.8 ml of the diluted sample was transferred to each of glass spectrophotometer cuvettes. 0.2 ml of bisulfite solution was added to one cuvette and 0.2 ml distilled water to the other. After that, they were equilibrated for 15 min. Absorbance of both samples at 420 nm, $\lambda_{vis\text{-}max}$ (which was 523 nm for sumac concentrates), and 700 nm, against a blank cell filled with distilled water in UV-VIS spectrophotometer (PelkinElmer, Lambda 25:1.24) by using the software of UV-WinLab 32 Version 5.1.1.

Color density of the control sample (treated with water) was calculated as follows:

Color density = $[(A_{420\ nm}\text{-}A_{700\ nm}) + (A_{\lambda vis\text{-}max}\text{-}\ A_{700\ nm})] \times$ DF (for control sample (treated with water))

Polymeric color = $[(A_{420\ nm}\text{-}A_{700\ nm}) + (A_{\lambda vis\text{-}max}\text{-}\ A_{700\ nm})] \times$ DF (for bisulfite bleached sample)

Percent polymeric color = (polymeric color/color density) × 100 (2.2)

2.15. Identification of Organic Acids in Sumac Concentrate by HPLC

Standard solutions and sumac concentrate samples were filtered through a 0.45 μm Millipore membrane filter and 25 μl aliquots of samples or standards were injected into HPLC. Organic acids were identified and determined from retention times of standard acids.

The standard solutions of organic acids (tartaric, malic , citric, succinic and gallic) were prepared individually in 1% concentration with double distilled water.

Intelligent HPLC pump (Jasco Co.) with HP UV-VIS detector was used. Integration and data storage were performed with Chemstation for LC software. The organic acids were eluted isocratically using a Supelco C-18 column (25cm×4.6mm, 5 μm). Organic acids were detected at 210 nm and 40^{o}C. The mobile phase was water containing 0.1% phosphoric acid. Mobile phase was used at a flow rate of 1.0 ml/min.

2.16. Identification of organic acids in sumac powder and sumac concentrate by FT-IR.

Two samples were mentioned by using PerkinElmer FT-IR Spectroscopy. Solid sumac was ground to a fine powder and it is dispersed in a matrix. KBr was used as a matrix material. 2 mg of ground sumac was mixed thoroughly with about 350 mg of ground KBr. The mixture was transferred to a die that has a barrel diameter of 13mm. That was then placed in a suitable press and pressed at around 12,000 psi for one to two minutes. Re-crystallization of the KBr resulted in a clear glassy disk about 1 mm thick. Then, this disk was ready to be analyzed by transmission.

Sumac concentrate was analyzed as thin film in cell, a cell consisting of two IR transparent windows. A Teflon spacer was used to produce a film of the desired thickness.

Principle of the spectroscopy as follows: An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared

beam comes into contact with the sample. An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystals.

Diamond crystal was used for the measurements. After the crystal has been cleaned and infrared background has been collected, the sumac concentrate was simply poured onto the crystal. The whole crystal was covered. The crystal was recessed into the metal plate plate to retain the sample.

After the crystal area has been cleaned and the background collected, the sumac powder was placed onto the small crystal area. Force was applied to the sample, pushing it onto the diamond surface. Then, spectrums were collected.

2.17. Statistical Analysis

Statistical analyze were performed using the SPSS 8.0 system software. Experimental results were subjected to one-way and two-way analysis of variance (ANOVA) according to the General Linear Model (GLM) procedure with least-square means effects.

The parameters of the models were calculated by the NLIN (non-linear) procedure of the Sigma Plot (Scientific Graph System, version 8.00).

CHAPTER 3

3. RESULTS and DISCUSSION

3.1. Properties of sumac berries

Several properties related with the appearance of sumac berries were determined as shown in Table 3.1.

Table 3.1. Properties of sumac berries

Property	
Color	pale yellow to light brownish when dry, purple when soaked in water
Shape	ellipsoidal
Apparent density	0.378 g/cc
Size (three axis of the ellipsoid)	5.91 ± 0.02 mm 5.10 ± 0.02 mm 2.95 ± 0.02 mm
Average spherical diameter	4.65 ± 0.02 mm

Sumac berries were observed to compose of 50% skin and 50% seeds. The seed is made up of a hard shell, and the seed meal in which the nutrients are contained. The hairy skin, on the other hand, covers the seed and contains the water soluble solids, mostly organic acids and poly-phenols. The seeds are ellipsoidal in shape with an average spherical diameter of 3.33 mm. The shell, which is very tough, constitutes 65% of the seed, the remaining being the seed meal.

Table 3.2 illustrates some physical and chemical properties of sumac seeds. As seen, the percentage of protein and oil are high in the seed meal. Therefore, this part of sumac berries may be considered for a further study for alternate uses.

Table 3.2. Properties of sumac seeds

Property		
Density of whole seed	1.20 g/ml	
Composition of seed meal(% by mass)	protein oil moisture ash carbohydrates	:18.0 :33.4 :2.5 :8.8 :45.3
Oil in the seed	appearance refractive index (20^oC) density (20^oC)	: pale yellow : 1.4705 : 0.912 g/ml

Table 3.3 shows the properties of hairy skin of sumac berries. It was observed to contain 34% water soluble solids, remaining being the water-insoluble inerts mostly fibrous materials. When compared with the seed, protein content was lower.

Table 3.3. Properties of hairy skin of sumac berries

Property		
Average thickness	0.32 mm	
Soluble solids (%)	34	
Water-insoluble inerts (%)	66	
Composition of hairy skin (%)	protein	: 2.15
	ash	: 0.52
	others	: (cellulosic materials)

The solubility of constituents of sumac berries in various solvents was also determined. In Table 3.4 solubility properties of sumac berry and hairy skin are shown.

Table 3.4. Solubility properties of sumac in various solvents

Solvent	Solubility (%)
Hexane	0.52
Ether	7.30 (whole sumac berry)
	23.50 (hairy skin)
Methylene chloride	2.00
Methanol	20
Ethanol	22

3.2. Evaluation of Sorption Isotherms of Sumac Berries

In this study, adsorption characteristics of old crop sumac and new crop sumac were investigated at 15, 25 and 35 ^{o}C. They can be classified as two types: Whole sumac (1-year old crop-new crop), and the skin (1-year old crop-new crop). Their sorption isotherms were plotted as shown in Figs.3.1-3.4. All sorption isotherms showed type II behavior. As expected, the equilibrium moisture contents increased with an increase in the water activity at any particular temperature and decreased with in increase in temperature at constant water activity. The increased temperature activated the water molecules to a higher energy levels and this allowed them break away from their sorption sites, thus decreasing the equilibrium moisture content

(Arslan, N., and Toğrul, H., 2005; Mayor et al., 2005; Menkov, N.D., 2000; Sogi et al., 2003).

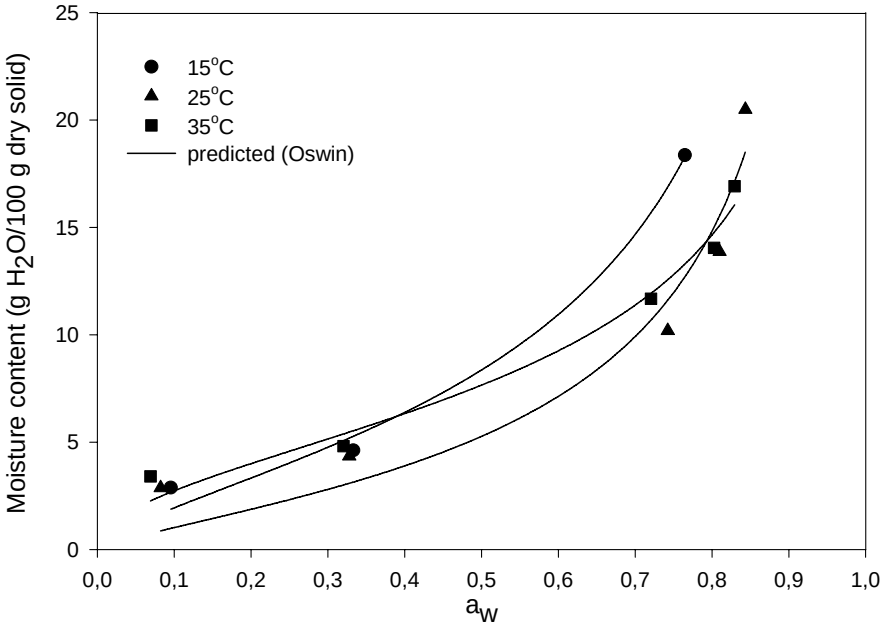

Figure 3.1. Sorption isotherms of 1-year old crop whole sumac berries

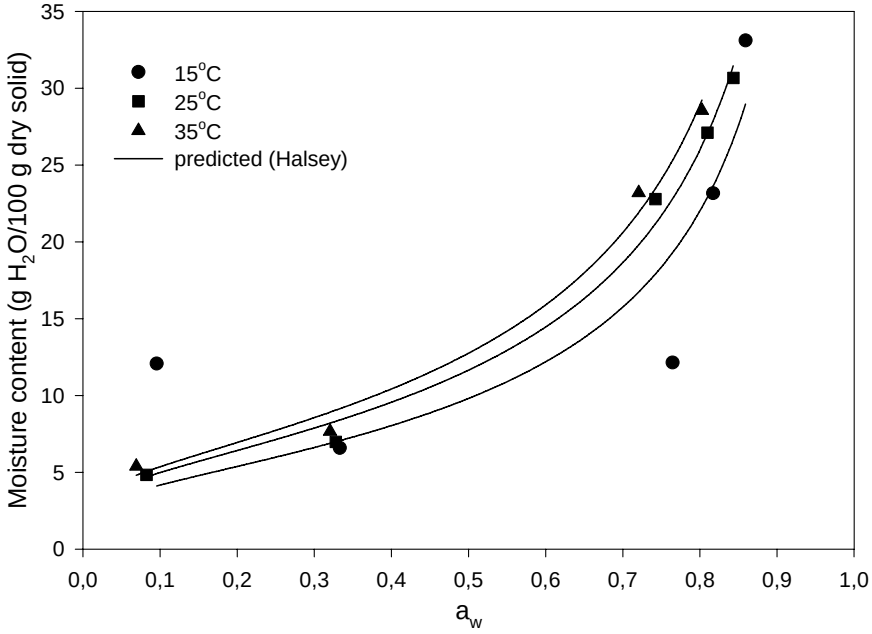

Figure 3.2. Sorption isotherms of new crop whole sumac berries

At low water activities, equilibrium moisture content for old crop whole sumac berries was lower than equilibrium moisture content for new crop whole sumac berry. This result indicated that old crop has lost a certain amount of water. This moisture loss reflected loss of moisture at equilibrium.

As Fig.3.1 and Fig.3.2 were evaluated it was seen that, up to a_w value of 0.4, increase in the equilibrium moisture content was very slow, after that point, both for old crop and new crop whole sumac berries, a certain increase in equilibrium moisture content was detected. Similar results were reported for karingda seed, kernel and hull (Suthar et al., 1997).

Different mathematical models such as Oswin, Halsey, BET linear, GAB, BET and Peleg were applied and the best for each sample was determined (Mayor et al., 2005). The corresponding mathematical expressions of these models are shown in Table 3.5.

Table 3.5. Models used to represent the sorption behaviors of sumac berries and concentrate

Name of the model	Model
Oswin	$X_{eq} = [A(a_w/(1-a_w))^B]$
GAB	$X_{eq} = [(X_M C K a_w)/(1-K a_w)(1- K a_w+C K a_w)]$
BET	$X_{eq} =(X_M C a_w)[1-(n+1)a_w^n+ n a_w^{n+1}]/(1-a_w)[1-(C-1)a_w-C\ a_w^{n+1}]$
BET linear	$a_w/(1-a_w)X_{eq}=(1/X_M C)+((C-1)\ a_w)/X_M C$
Peleg	$X_{eq} = K_1 a_w^{n}{}_1 + K_2 a_w^{n}{}_2$
Halsey	$a_w= \exp(-A/ X_{eq}^B)$

Oswin model was observed to be the best fitted model for 1-year old crop whole sumac berries, whereas for new crop whole sumac berries, Halsey was the best one. For 1-year old crop sumac skin, BET linear and for new crop sumac skin, Halsey were determined as the best fitted models as seen in Fig.3.3 and Fig3.4.

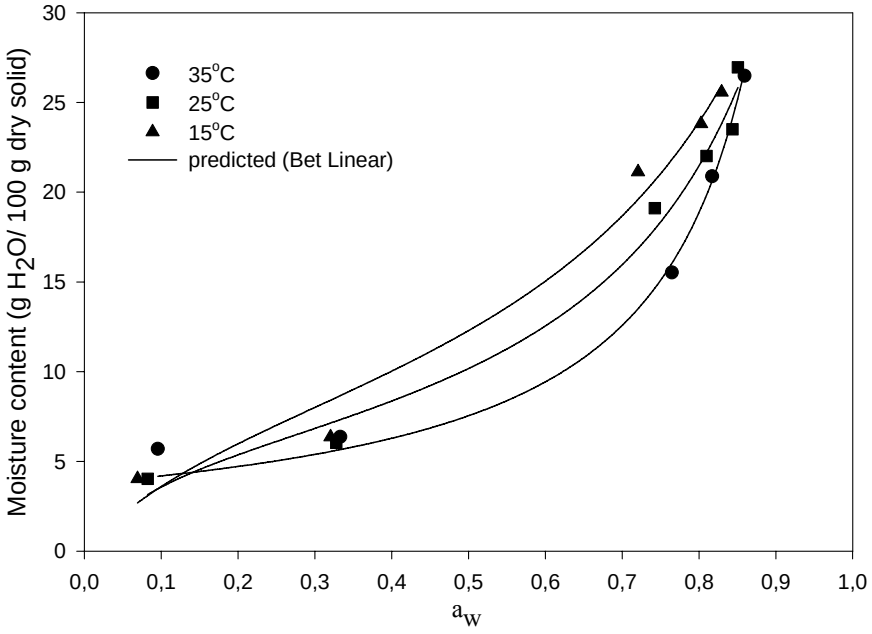

Figure 3.3. Sorption isotherms of 1-year old crop sumac skin

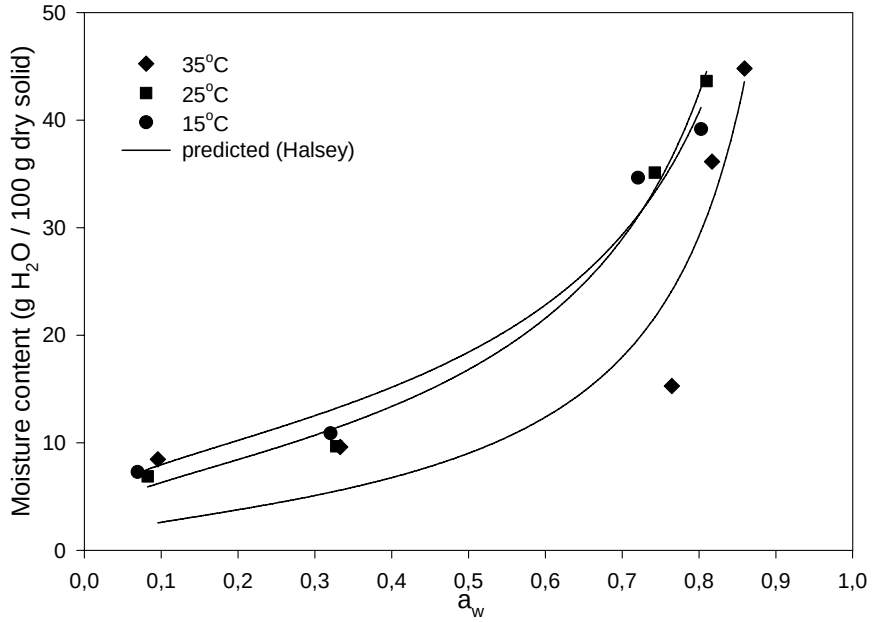

Figure 3.4. Sorption isotherms of new crop sumac skin

The parameters of the models fitted to the sorption data of sumac berries are shown in Table 3.5.

Table 3.5. Parameters for sorption isotherm models for sumac samples.

Sumac samples	Model	Parameters	Temperature		
			15°C	25°C	35°C
1-year old crop whole sumac berries	Oswin	A	8.3582	5.2761	7.6535
		B	0.6640	0.7450	0.4681
		R^2	0.9900	0.9306	0.9784
New crop whole sumac berries	Halsey	A	17.0669	22.2796	23.5474
		B	1.4031	1.4133	1.3849
		R^2	0.7085	0.9911	0.9896
1-year old crop sumac skin	BET linear	X_m	3.7719	6.7497	9.8948
		C	$1.6637x10^7$	9.1676	4.9107
		R^2	0.9901	0.9837	0.9793
New crop sumac skin	Halsey	A	5.5944	21.7603	44.5033
		B	0.9553	1.2215	1.4285
		R^2	0.8679	0.9929	0.9735

3.2.1. Comparison of the methods of measurement of sorption isotherms of sumac berries

Water activity measurements of different-aged sumac berries were measured by Rotronic Hygropalm AW 1 water activity display unit. The measurements were carried out at room temperature (23^{o}C) for 1-year old Siirt sumac and for 1, 2 and 3-years old Gaziantep sumac berries. The results were fitted to sorption isotherm models as shown in Figs.3.5-3.8.

From Figs.3.5-3.8, it was concluded that, the moisture content of 1-year old Siirt sumac berries and 1-year old Gaziantep sumac berries have higher moisture content than 3 and 2-years old sumac berries. This was attributed to the long storage time.

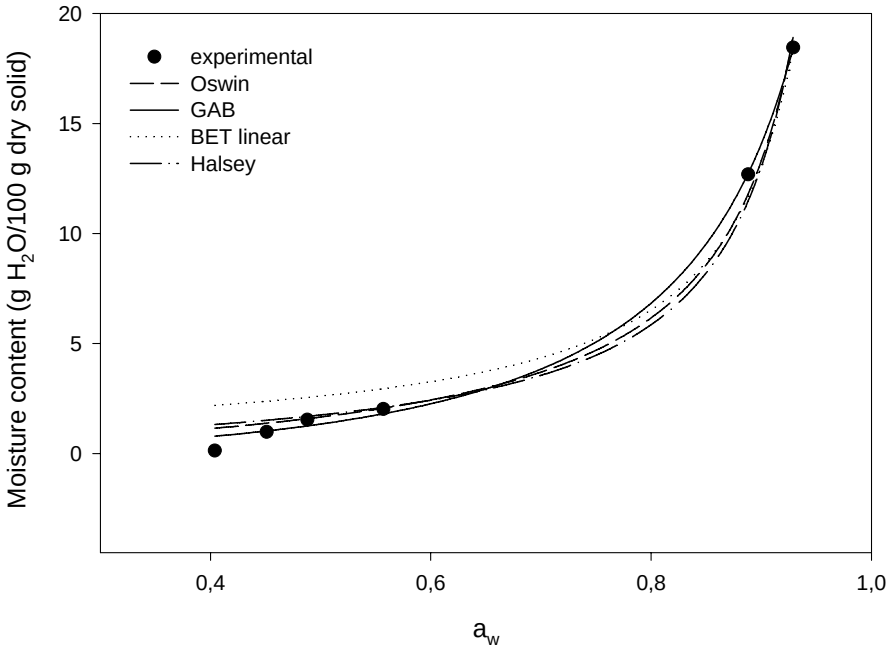

Figure 3.5. Sorption isotherms of 1-year old Siirt sumac berries at 23°C

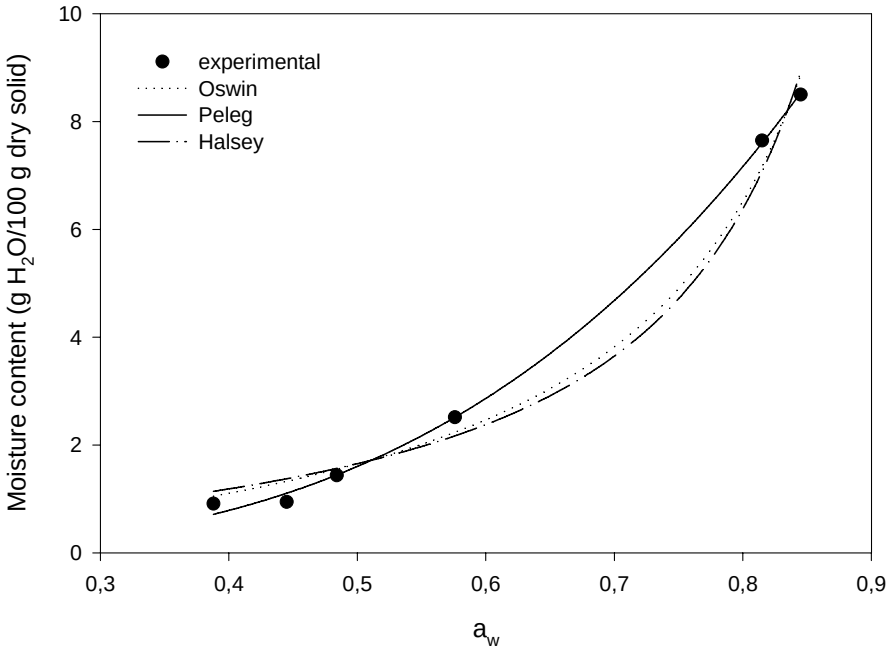

Figure 3.6. Sorption isotherms of 3-years old sumac berries at 23°C

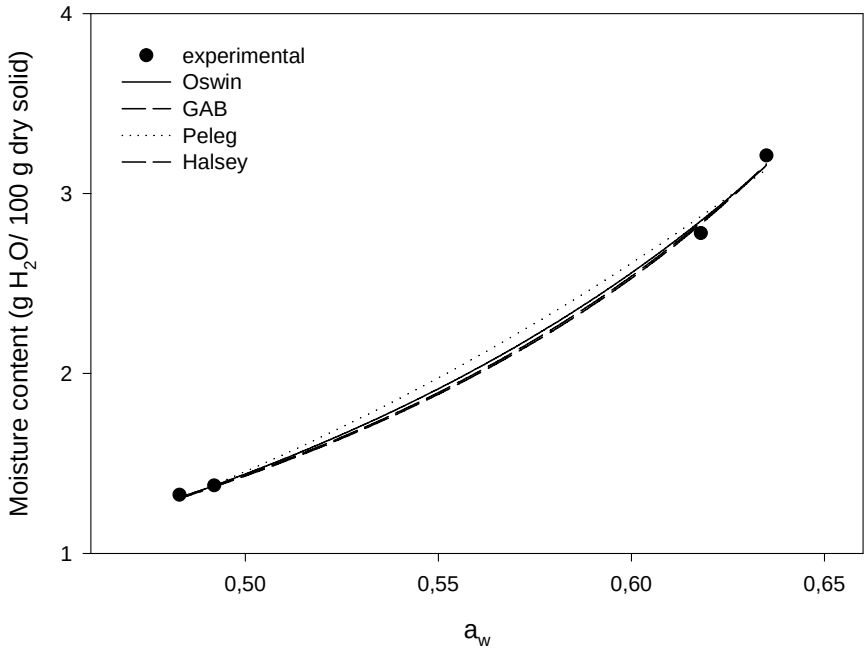

Figure 3.7. Sorption isotherms of 2-years old sumac berries at 23°C

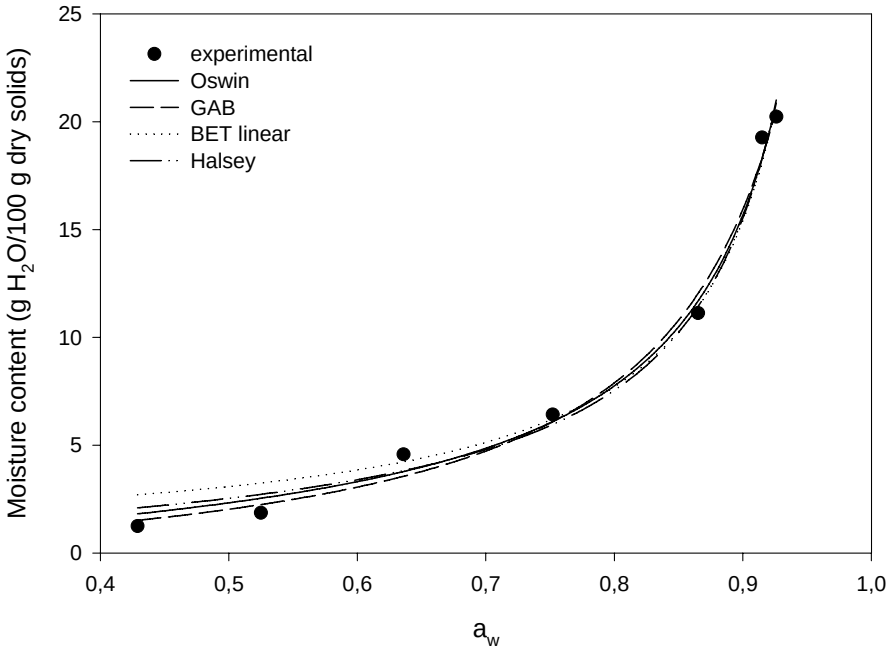

Figure 3.8. Sorption isotherms of 1-year old sumac berries at 23°C

For all samples, Oswin model was the best fitted model. Also, other sorption models; GAB, BET linear, Peleg, and Halsey were fitted. For 3-years old sumac berries Peleg were the best fitted models. Calculated correlation coefficients of all models were close to each other, ranging from 0.9134-0.9988. Although, sorption measurements were determined by different methods, when compared with section 3.2, similar results were obtained. But in the second part (by Rotronic measurement), samples were different from the method applied by salts.

3.3. Effect of TSS on the pH value of sumac concentrates

pH measurements were carried out at room temperature (23^{o}C) for two different sumac concentrate samples; second crop sumac concentrate(sumac with shoots) and sumac concentrate. Table 3.6 shows the variation of pH with TSS.

Table 3.6 shows that, change in total soluble solids did not change the pH value of the sumac concentrates significantly. It is known that the pH value of the buffers do not change by changing the concentration. Therefore, sumac concentrate was observed to have buffer property. That property may be attributed to the existence of phenolic compounds.

Table 3.6. Variation of pH with TSS for sumac and second crop sumac concentrate

Type of sumac concentrate	TSS (Brix)	pH
Second crop sumac concentrate(with shoots)	72.7	1.85
	33.0	2.38
	13.3	2.55
	6.4	2.60
	3.1	2.65
	1.6	2.70
	0.6	2.75
	0.3	2.82
	0.2	2.87
	0.1	2.96
Sumac concentrate	46.7	2.91
	19.4	3.03
	12.0	3.06
	7.0	3.07
	4.0	3.08
	0.2	3.15

3.4. Effect of soaking temperature on the extraction of sumac berries

Four temperatures were studied; 25, 40, 50, and 70°C. At these temperatures concentration (brix) were measured at definite time intervals. Concentration was plotted against time at each temperature separately. Figs.3.9-3.12 indicate the variation of concentration with time at different temperatures.

It is observed that as the temperature increases extraction rate of soluble solids of sumac increases. Therefore higher soluble solid content is determined at fixed time intervals.

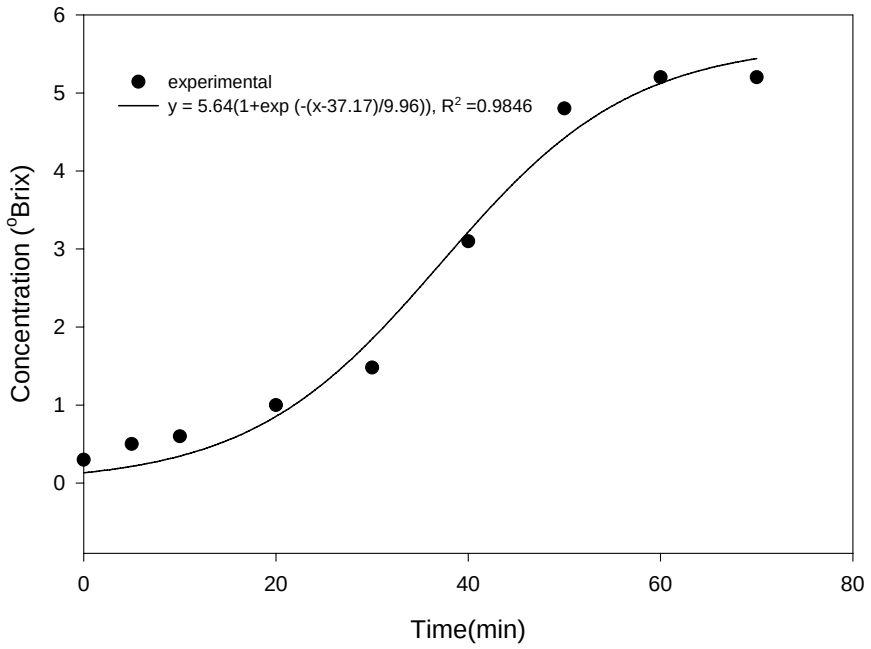

Figure 3.9. Variation of concentration with time during soaking at 25°C

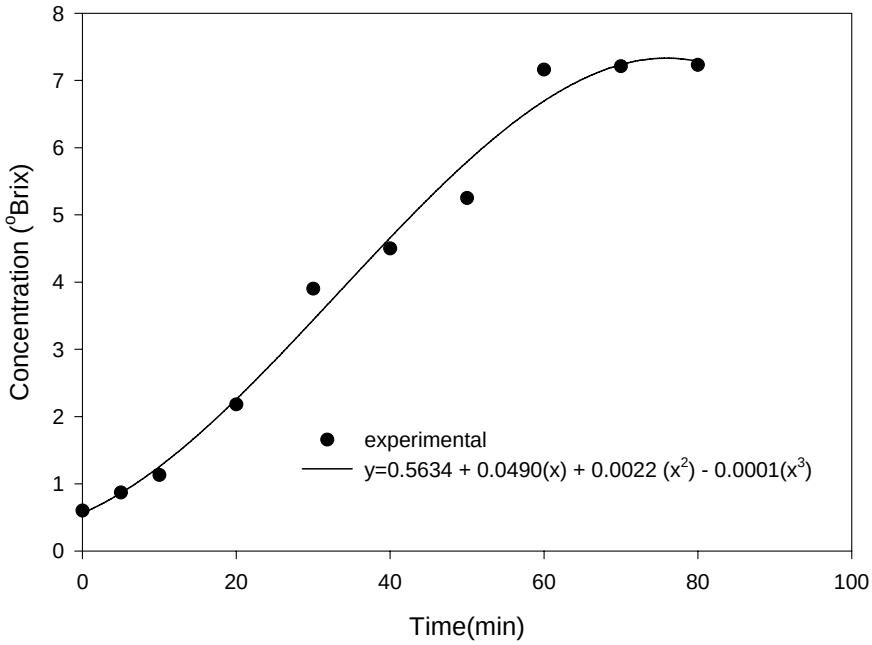

Figure 3.10. Variation of concentration with time during soaking at 40°C

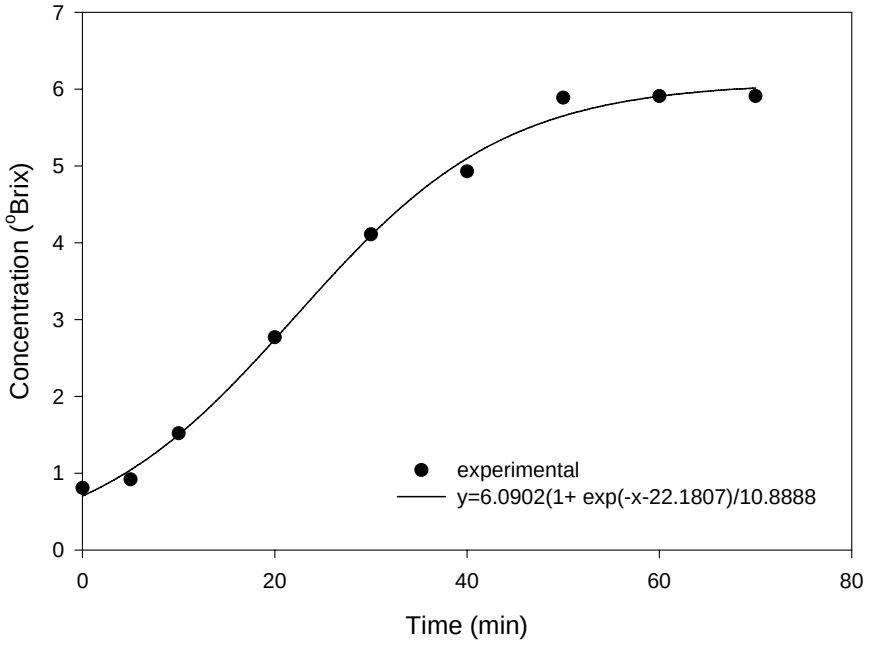

Figure 3.11. Variation of concentration with time during soaking at 50°C

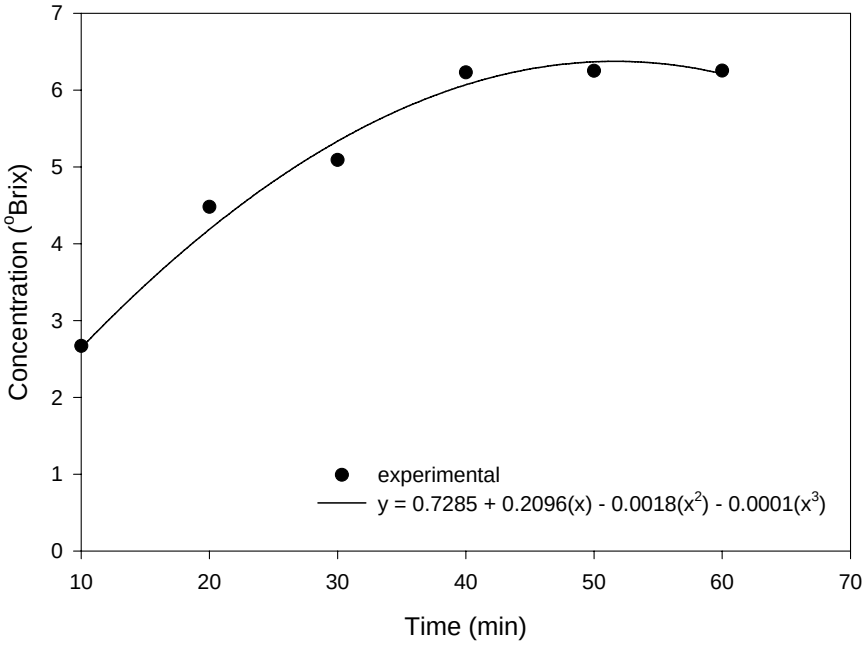

Figure 3.12. Variation of concentration with time during soaking at 70°C

From Fig.3.13, temperature effect on the soaking is seen clearly. Firstly initial brix values increased as the temperature increases. As the temperature increases, reaching to the equilibrium is faster.

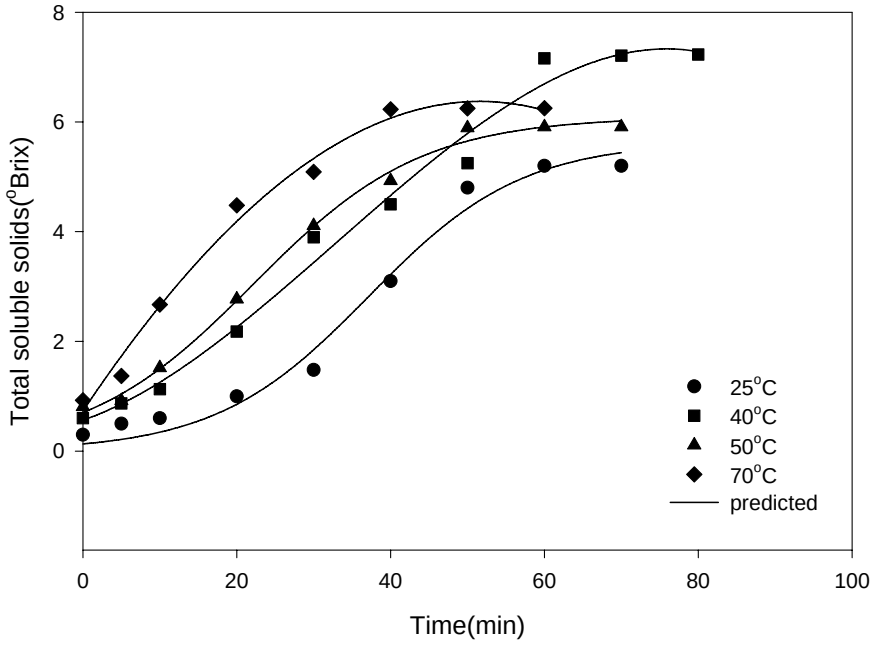

Figure 3.13. Variation of concentration with time at 25, 40, 50 and 70°C soaking

At all temperatures it was seen after 50 minutes, equilibrium was approached. After that, concentration changes were not significant ($p<0.05$).

Table 3.7 represents the regression analysis for leaching of sumac concentrates at different temperatures. For each temperature, best fitting was selected and their constants were determined.

Table 3.7. Regression analysis for leaching of sumac concentrates at different temperatures

Temperature (^oC)	Equation	R^2
25	$y = 5.64\ (1+ \exp(-(x-37.17)/9.96$	0.9783
40	$y = 0.5634 + 0.0490(x) + 0.0022\ (x^2) - 0.0001(x^3)$	0.9881
50	$y = 6.0902(1+ \exp(-x-22.1807)/10.8888)$	0.9967
70	$y = 0.7285 + 0.2096(x) - 0.0018(x^2) - 0.0001(x^3)$	0.9895

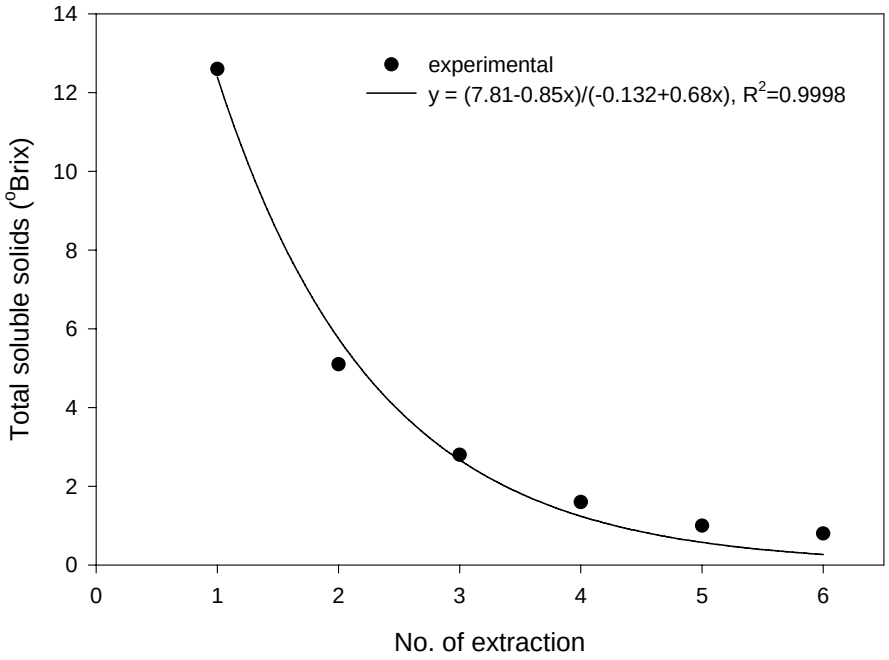

Figure 3.14. Yield of soluble solids in sumac berries as a function of no. of extractions at 17^oC.

In Figure 3.14, at 17^oC, brix values were measured at each extraction separately. It was seen that most effective is the first extraction and brix was measured as 12.6, but second extraction decreased suddenly to 4.2. There was a large difference between

first and second extraction. This property continued up to 8th extraction which resulted in 0.8 brix. This shows that in the first extraction majority of the soluble solids were solubilized in water, however still there was a portion of soluble solids.

3.5. Material balance for the determination of soluble solids after soaking

Fig.3.15 indicates the schematic diagram of material balance for the determination of soluble solids after soaking.

Nomenclature of the below diagram is as follows:

M_1 : mass of sumac berries

x_1: mass fraction of soluble solids

x_2: mass fraction of moisture

x_3: mass fraction of inerts

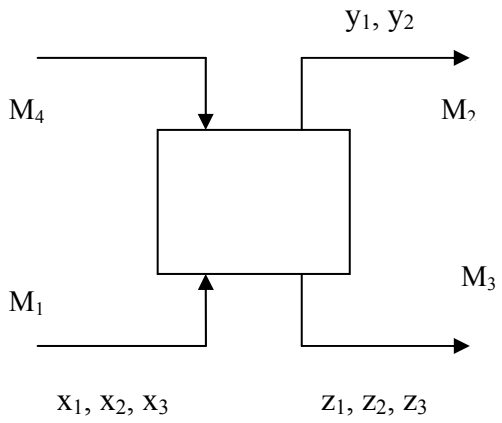

Figure 3.15. Schematic diagram for calculation of soaking

M_2 : mass of sumac juice after equilibration

y_1: mass fraction of soluble solids in the juice

y_2: mass fraction of water in the juice

M_3 :mass of pulp after equilibration

z_1: mass fraction of soluble solids in the pulp

z_2: mass fraction of moisture in the pulp

z_3: mass fraction of inerts in the pulp

M_4 : Mass of pure water

Considering the Fig.3.15 the following balances are performed:

a) Soluble solids balance

$$M_1x_1=M_2y_1+M_3z_1 \qquad (3.1)$$

b) Water balance

$$M_1x_2+M_4=M_2y_2+M_3z_2 \qquad (3.2)$$

c) Inerts balance

$$M_1x_3 =M_3z_3 \qquad (3.3)$$

d) Since the solution retained by the pulp(M_3) has the same concentration as that of the juice, then

$$y_1/y_2 = z_1/z_2 \qquad (3.4)$$

Here M_1, M_2, M_3, M_4, y_1, y_2 and x_2 are assumed to be specified. After some manipulation, x_1, x_3, z_1, z_2, z_3 are determined as follows:

$$x_1=(y_1/y_2)(M_4/M_1+x_2) \qquad (3.5)$$

$$x_3=1-[(z_1/z_2)(M_4/M_1)+x_2/z_2] \qquad (3.6)$$

$$z_2=(M_4/M_3)+(M_1/M_3)x_2-(M_1/M_3)y_2 \qquad (3.7)$$

$$z_1=(y_1/y_2)z_2 \qquad (3.4)$$

$$z_3=(M_1/M_3)(1-x_2/y_2)-(M_4/M_3)(y_1/z_y) \qquad (3.8)$$

In a representative sample of freshly extracted 5-years-old sumac juice:

For first extraction of sumac berries;

M1=273 g, M4=727 g, M3=385, M2=615 g y_1=0.053, thus x_1 was calculated from these values by using Equation (3.5), as:

$$x_1=0.148$$

Therefore, 14.8 % total soluble solids exist in 5-years-old sumac juice.

3.6. Density Measurements

Knowledge of physical properties of foods is fundamental in the design and control of food processes, and in quality control assessment. The accurate measurement or prediction of density is vital to the engineering practice in the food industry. Density of liquid foods is affected by composition and temperature

Figure 3.16 gives the variation of density with temperature at 30 brix. From this plot, it was seen that as the temperature increases, density decreases. At 53 °C, density was recorded as 1.15, but at 58°C density was recorded as 1.14. A 5°C increase in temperature decreased the density significantly.

As expected, the density decreases with temperature. This dependence is linear at low concentrations and becomes quadratic for more concentrated samples.

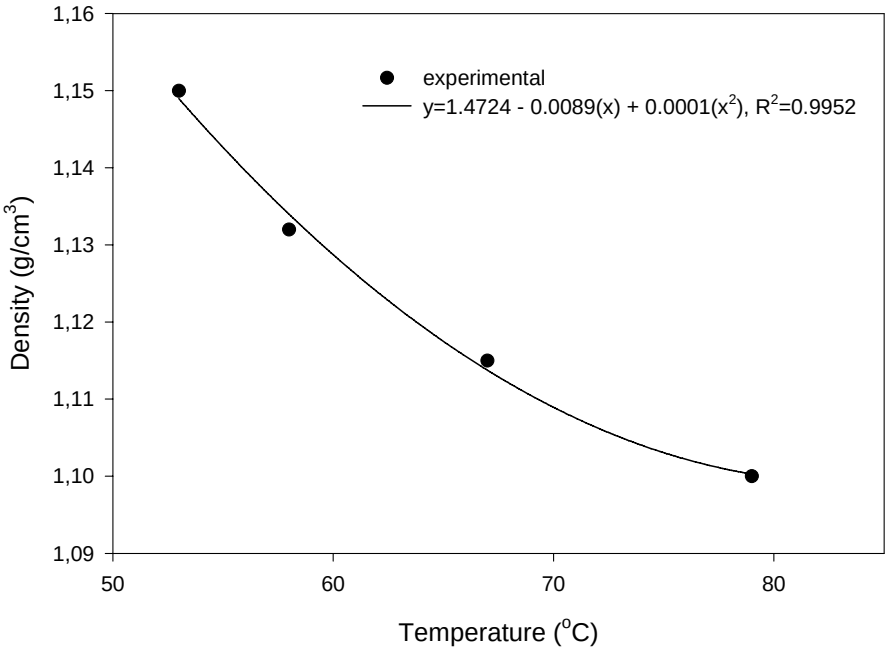

Figure 3.16. Variations of density of sumac concentrate with temperature for 30 brix

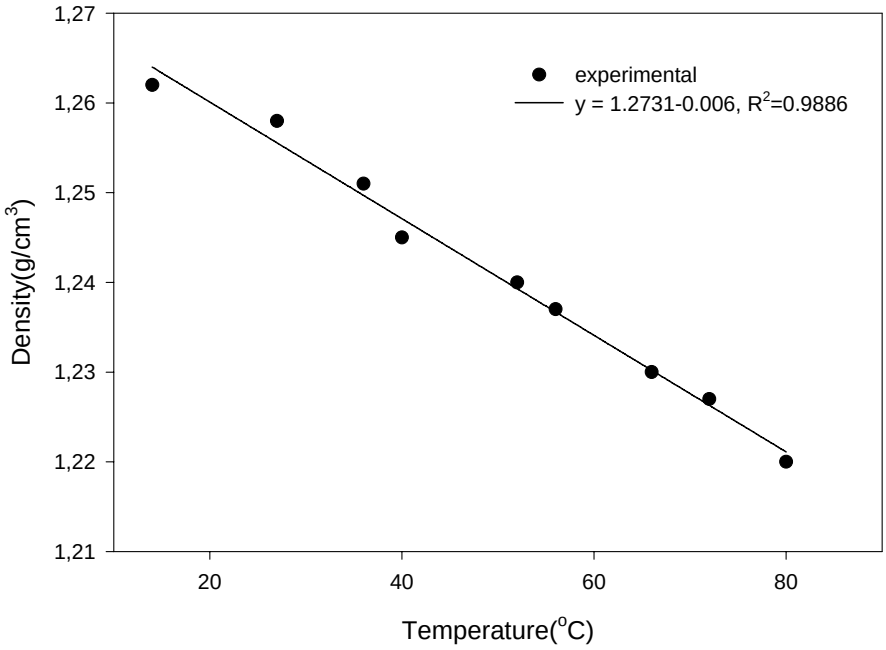

Figure 3.17. Variation of density of sumac concentrate with temperature for 55 brix

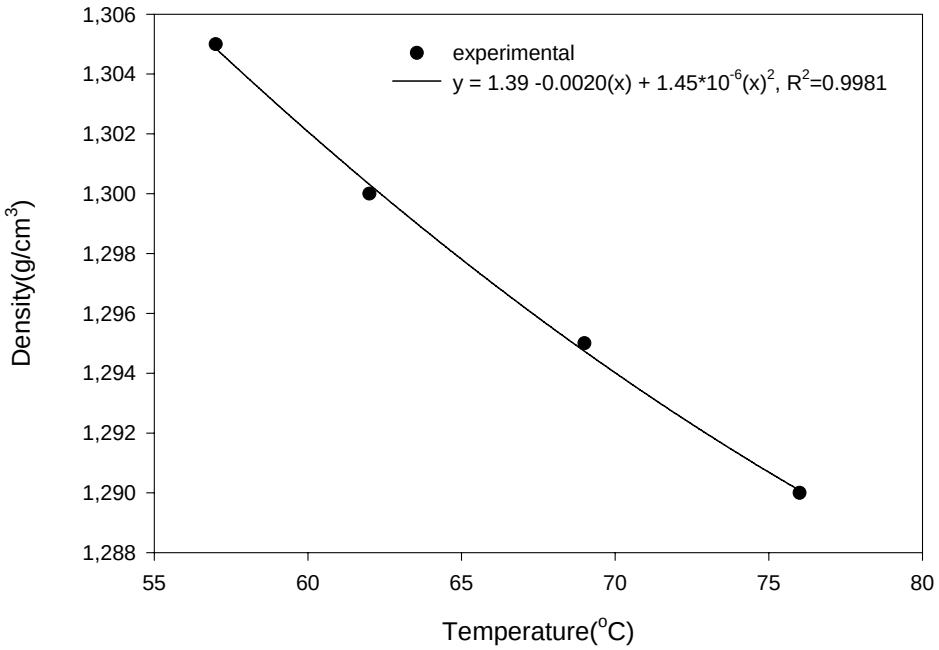

Figure 3.18. Variation of density of sumac concentrates with temperature for 69 brix

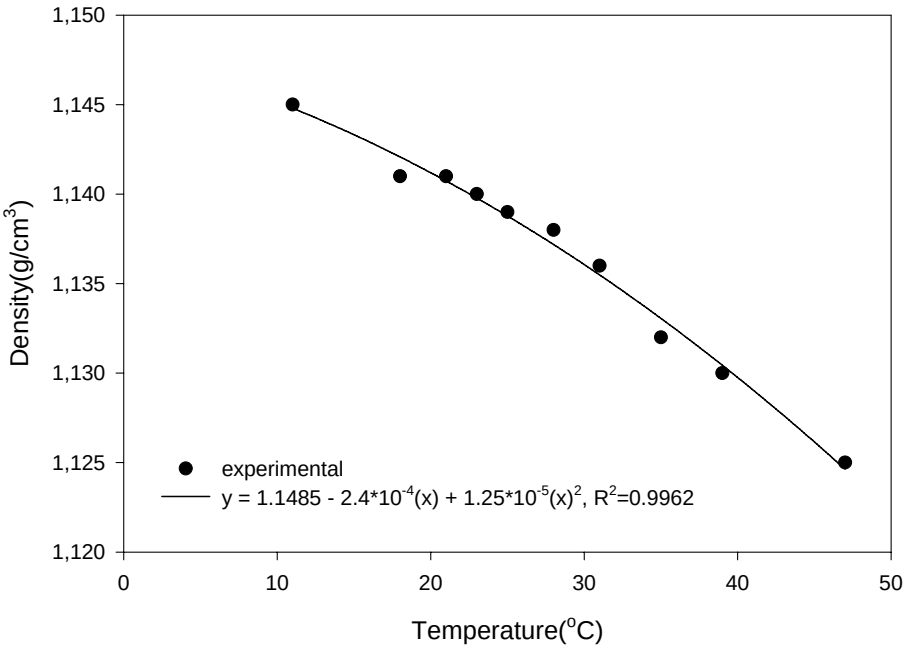

Figure 3.19. Variations of density of second extract sumac concentrate with temperature for 30 brix

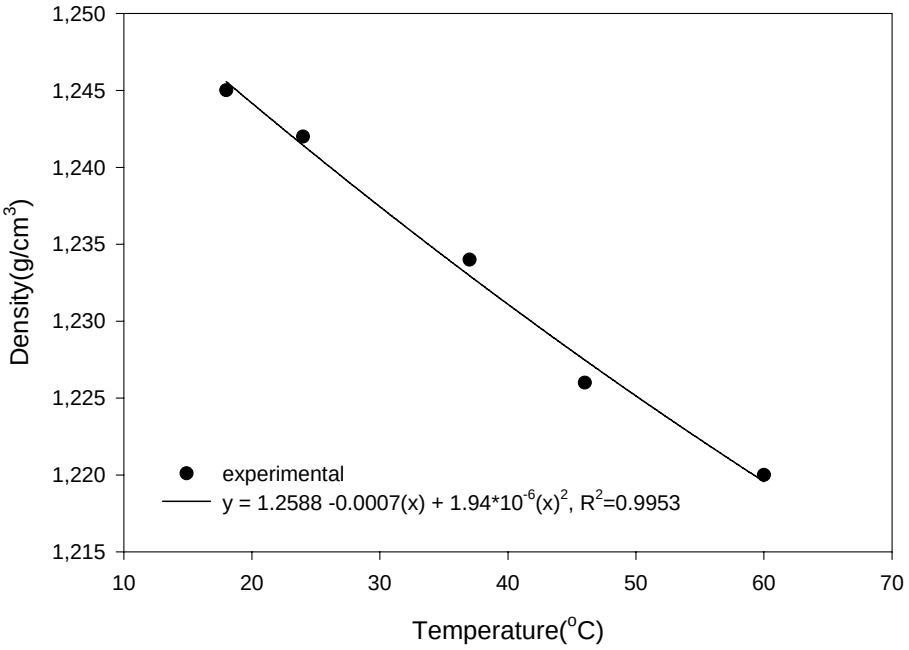

Figure 3.20. Variations of density of second extract sumac concentrate with temperature for 50 brix

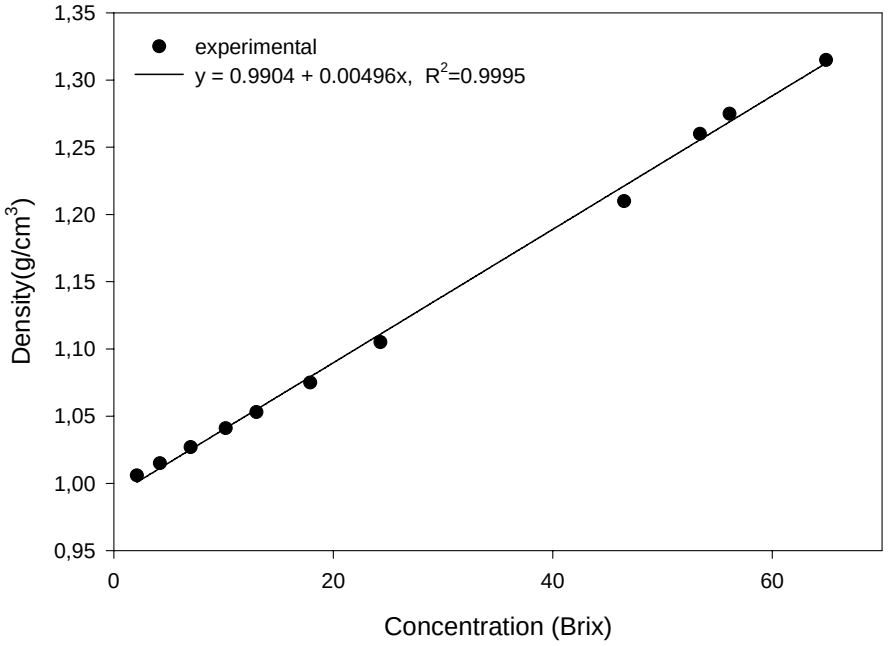

Figure 3.21. Density of sumac concentrate as a function of brix at 25°C.

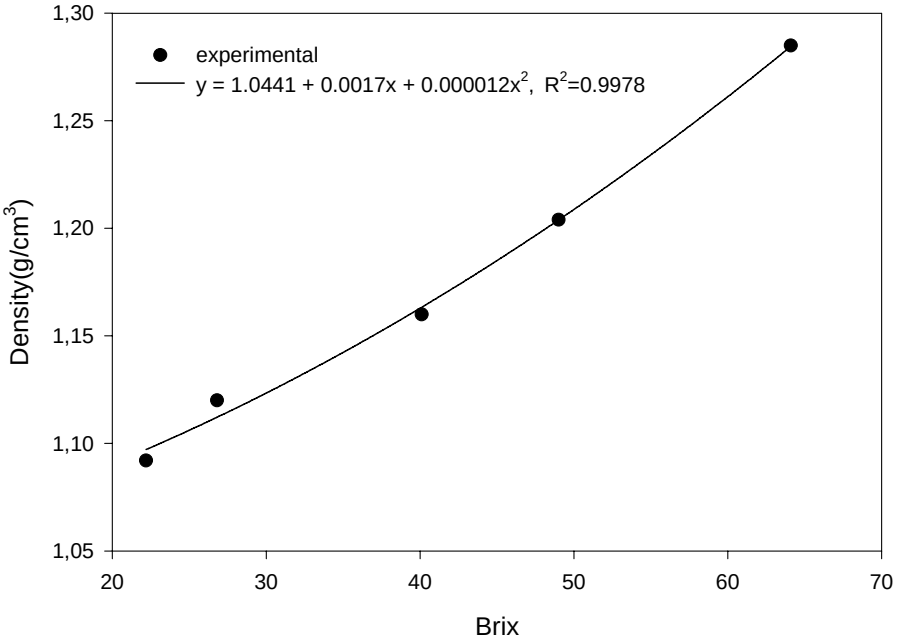

Figure 3.22. Density of second crop sumac concentrates as a function of brix at 25^0C

Table 3.8. Results of regression analysis of density of sumac concentrates and predicted constants

Type of concentrate	Model	Predicted constants				R^2
		a	b	x_0	y_0	
30 brix (1^{st}extract)	$y=y_0+a/(1+\exp(-x-x_0)/b)$	1.9914	-4.1675	38.3174	1.0928	0.9988
55 brix	$y=y_0+ax$	-0.006	-	-	1.2731	0.9886
69 brix	$y=y_0+ax+bx^2$	-0.0020	1.45×10^{-6}	-	1.3900	0.9981
30 brix (2^{nd} extract)	$y=y_0+ax+bx^2$	-2.4×10^{-4}	1.25×10^{-5}	-	1.1485	0.9962
50 brix (2^{nd} extract)	$y=y_0+ax+bx^2$	-0.0007	1.94×10^{-6}	-	1.2588	0.9953

When the Figs.3.16-3.20 were evaluated; it can be generalized that, as the temperature increases, density of sumac concentrate decreases even at each concentration (Tadini et al., 2005, Barbosa et al., 2003). Table 3.8 shows the regression analysis results of sumac concentrates. The best fit was obtained for 30 brix first extract sumac concentrate of R^2 of 0.9988. It can be concluded that 55 brix sumac concentrate was fitted linearly and 69 brix were fitted quadraticly and R^2

values of 0.9886 and 0.9981 respectively. It was seen that; 69 brix sumac concentrate was better fitted and has a higher R^2 value than 55 brix concentrate. Also the constant of 69 brix was higher than the value of 55 brix.

As the second extracts were compared, 30 brix sumac concentrate has higher correlation coefficient than 50 brix concentrate, since R^2 of 30 brix is 0.9962 whereas R^2 of 50 brix is 0.9953.

In this study, variation of density with brix was evaluated for both first crop and second crop. From the results it can be said that first crop density was significantly different from second crop sumac concentrate ($p<0.05$) and it was concluded that, concentration changes the density significantly.

3.7. Sorption Isotherms and Modeling of Sumac Concentrate

The importance of sorption data in considering drying problems is evident. The sorption data may be used for the proper choice of the end-point of the concentration or drying process that is the optimum residual moisture content of the final product.
To model the sorption curves, several empirical and semi-empirical equations have been proposed for the correlation of the equilibrium moisture content with the equilibrium relative humidity of the air surrounding food product (Kouhila, et al, 2001). The experimental curves were fitted by six equations: Oswin, GAB, BET, BET linear, Peleg and Halsey. Oswin, Halsey and BET linear are two-parameter equations; GAB and BET equations are three-parameter equations and Peleg is four-parameter equation. The models used for fitting are presented in Table 3.5.

The estimated constants and correlation coefficients are shown in Table 3.9. It can be seen that the Oswin equation presented the highest correlation coefficient values in the water activity range of $0.3 \leq a_w \leq 0.90$. BET model was applied to all experimental values, but it was not as suitable as to analyze and for the representation of the results. (Al-Muhtaseb et al., 2004). Therefore, obtained constants and correlation coefficients of BET model are not included in Table 3.9.

The parameters for the sorption models of sumac concentrate are shown in Table 3.9, together with the correlation coefficients. Correlation coefficient values (R^2) above 0.9304 were included and below this value, were not included. Therefore, constants of GAB model at 33.5°C and constants of Peleg model at 27.5 °C and 33.5°C were not included in Table 3.9.

The best fit was obtained by the models of Oswin, GAB, and Halsey for T=21°C; Oswin, GAB, BET linear and Halsey for T=22.5°C and T=27.5°C; Oswin, BET linear, and Halsey for T=33.5°C. Peleg model was suitable only for T=21°C.

Experimental and predicted values of sorption models are plotted on Figs.3.23-3.25. Examination of the results in Table 3.9 indicates that the Oswin, GAB, Halsey, Peleg and BET linear models are suitable to describe the sorption characteristics of the sumac concentrate.

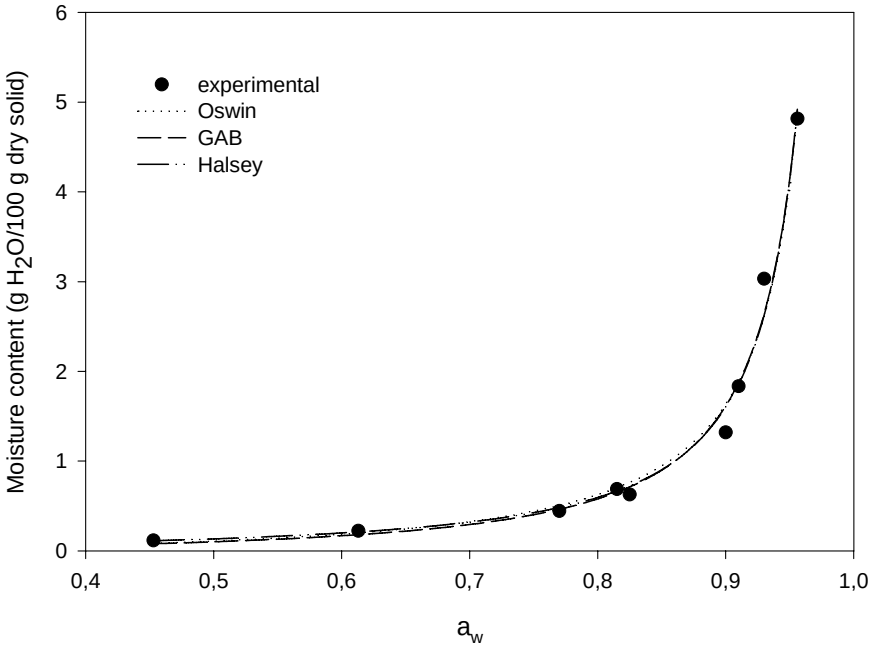

Figure 3.23. The best fitting sorption models of sumac concentrate at 21°C

Table 3.9. Parameter values of all models for the sorption of sumac concentrate

Model	Constant	Temperature(^{o}C)		
		21.0	27.5	33.5
Oswin	A	0.1006	0.1437	0.1588
	B	1.2629	0.5529	0.5628
	R^2	0.9865	0.9980	0.9975
GAB	K	1.0109	1.0084	-
	X_M	0.0074	2.0684	-
	C	4.8729	0.1220	-
	R^2	0.9842	0.9991	-
BET linear	X_M	0.1897	0.0952	0.0983
	C	16.38×10^5	9.7259	12.6714
	R^2	0.9304	0.9959	0.9984
Peleg	K_1	12.5847	-	-
	K_2	0.7911	-	-
	n_1	24.5746	-	-
	n_2	2.3526	-	-
	R^2	0.9927	-	-
Halsey	A	0.1505	0.0408	0.0422
	B	0.7578	1.4663	1.5427
	R^2	0.9860	0.9948	0.9962

For T=21 ^{o}C, best fit was obtained by Peleg model with correlation coefficient of 0.9927. GAB and Oswin model were the best fitted models for the description of experimental data at 27.5 ^{o}C. At 33.5 ^{o}C, best fitted model was BET linear.

The common model for all temperatures was selected as Oswin model. Comparison between the best fit (Oswin) and the experimental values was shown in Fig.3.26. The data indicate that the equilibrium moisture content decreases with increasing temperature at a constant water activity. At increased temperatures water molecules get activated to higher energy levels, causing them to become less stable and break away from the water binding sites of the food material, thus decreasing the equilibrium moisture content. As temperature varies, the excitation of molecules, as

well as the distance, thus attraction between molecules, varies. This causes the amount of desorbed water to change with temperature at given relative humidity. (Al-Muhtaseb, et al., 2004; Vazquez, et al, 2003).

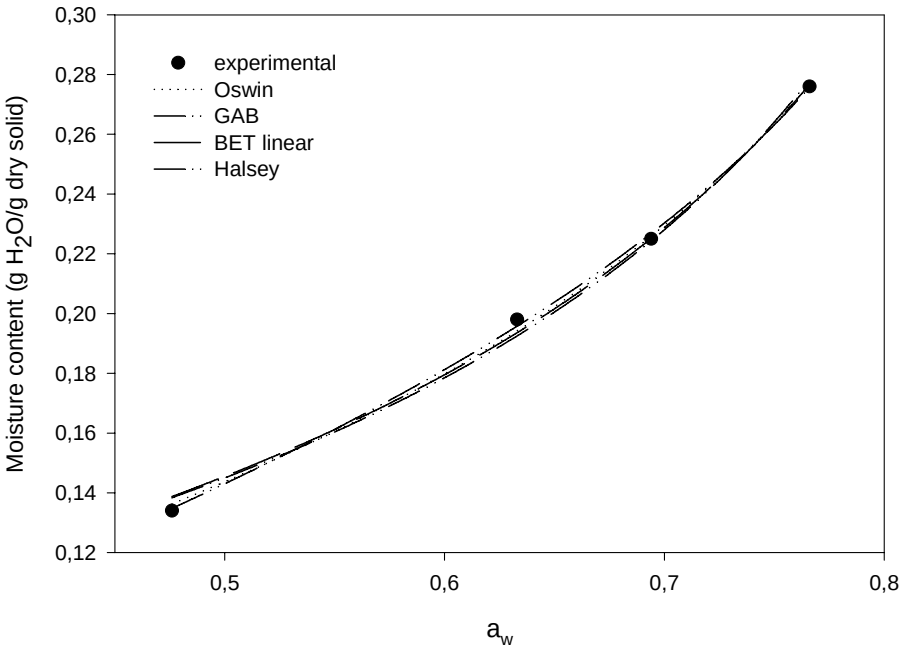

Figure 3.24. The best fitting sorption models of sumac concentrate at 27.5 ^{o}C

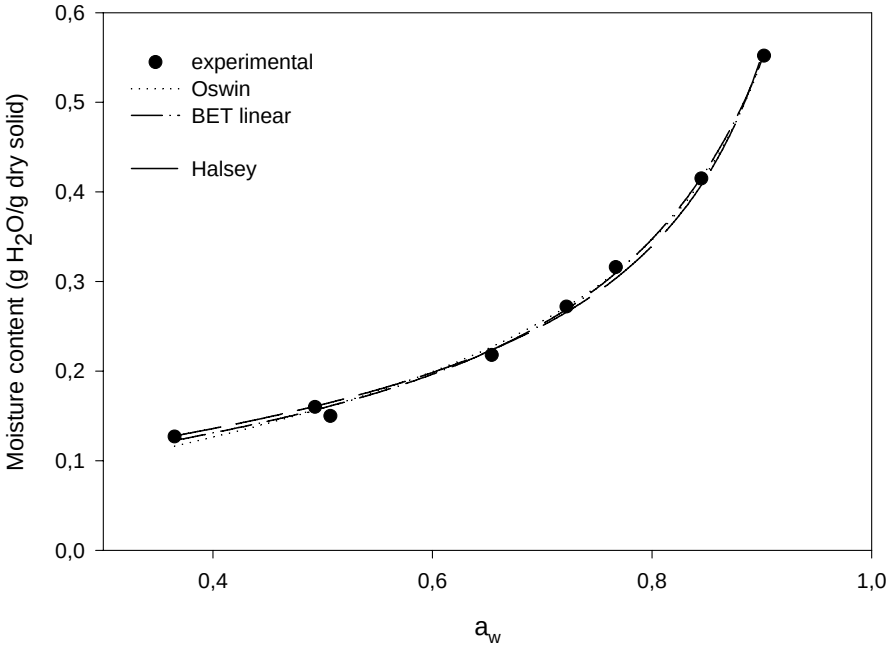

Figure 3.25. The best fitting sorption models of sumac concentrate at 33.5 ^{o}C

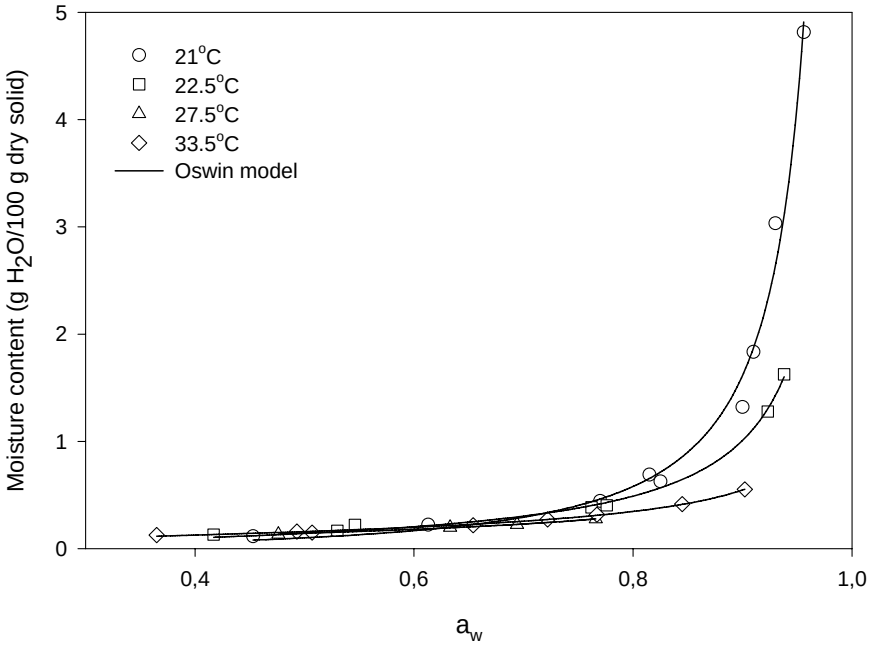

Figure 3.26. Experimental and predicted data with Oswin model of sumac concentrate at several temperatures

3.8. Rheological Properties of Sumac Concentrate

In order to determine the rheological behavior of sumac concentrate Newtonian equation was applied (Equation 3.9).

$$\sigma = \eta\gamma \qquad (3.9)$$

From this law, flow types were determined. A slight deviation from linearity for 70°Brix indicated the existence of a very small yield stress.

In addition to the power law, the generalized Herschel-Bulkley model (Equation 3.10) have been proven useful in developing mathematical models to solve food process engineering problems involving wide shear rate ranges (Steffe, 1992). The flow behavior of sumac concentrate with color values of L=2.43, a=4.47, b=0.36, YI= 181.96 were evaluated firstly by fitting the shear stress-shear rate data to this model.

$$\sigma-\sigma_0 = K\gamma^n \qquad (3.10)$$

where, σ, σ_0, K, γ, and n are shear stress, shear yield, apparent viscosity, shear rate, and flow behavior index respectively. The numerical values of the parameters obtained from fitted data are given in the Table 3.11. Figure 3.27 on the other hand, shows typical rheological flow curves of sumac concentrate at different temperatures.

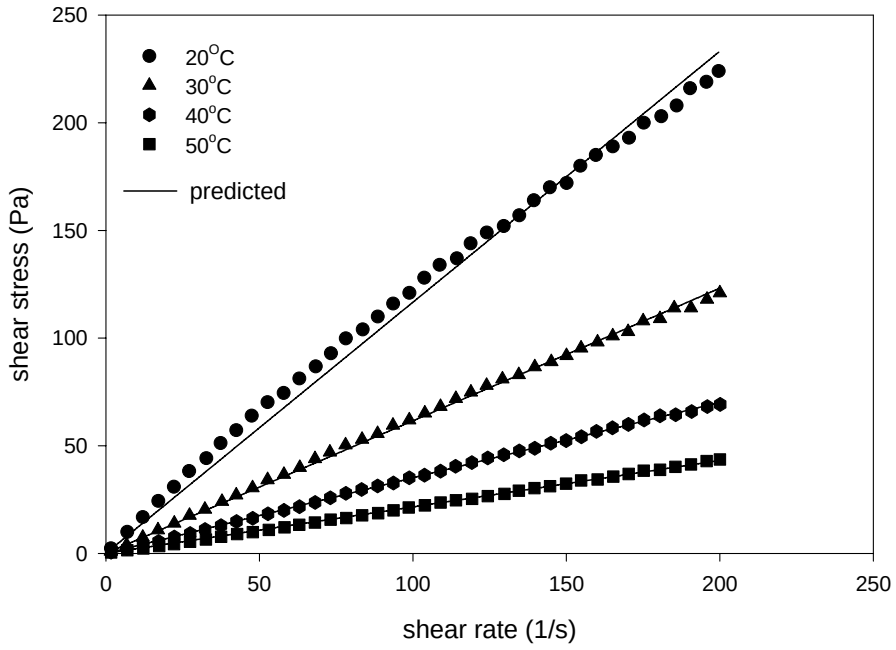

Figure 3.27. Flow behaviours of sumac concentrate with TSS of 70 °Brix at different temperatures.

When the results presented in Table 3.10 are examined together with Fig.3.27, sumac concentrate seems to exhibit a slight yield stress (σ_0=3.05 pa) with shear-thinning behavior (n=0.85) corresponding to the most concentrated (70°Brix) sample at the lowest temperature (20°C) studied. As expected, dilution gave rise to conform to the Newtonian behavior.

It should be pointed out that the existence of yield stresses is controversial; they may be artifacts resulting from high Newtonian viscosity at low shear rates as it was the case here. The rest of the more dilute samples showed essentially Newtonian behaviors as it is apparent from the linearity of the curves in Fig.3.27. (Barnes and Walter, 1985). For this reason the same data were also fitted to power law model

which is a special case of Herschel-Bulkley model with shear yield. R^2 values were higher than 0.99 for both models.

Table3.10. Parameters of the Hershley-Bulkey model describing dependency of viscosity on TSS at different temperatures for sumac concentrate.

TSS (^{o}Brix)	Temperature (^{o}C)	K (Pa.s^n)	n	σ_0 (Pa)	R^2
70.0	20	2.4689±0.110	0.8530±0.008	3.0518±0.860	0.9997
	30	0.9001±0.004	0.9273±0.008	1.5230±0.440	0.9997
	40	0.4026±0.020	0.9754±0.009	0.7181±0.260	0.9996
	50	0.1882±0.010	1.0281±0.0078	0.0996±0.130	0.9998
60.0	20	0.1860±0.010	1.0150±0.009	0.0932±0.130	0.9997
	30	0.1025±0.010	1.0311±0.010	0.0553±0.100	0.9994
	40	0.0521±0.020	1.0798±0.010	0.1103±0.060	0.9995
	50	0.0340±0.030	1.0950±0.014	0.1328±0.010	0.9992
56.0	20	0.0806±0.005	1.0579±0.012	0.0767±0.009	0.9994
	30	0.0440±0.003	1.0845±0.011	0.1366±0.050	0.9994
	40	0.0521±0.003	1.0798±0.010	0.1103±0.060	0.9995
	50	0.0340±0.003	1.0950±0.014	0.1328±0.050	0.9992
50.0	20	0.0806±0.005	1.0579±0.012	0.0767±0.009	0.9994
	30	0.0440±0.003	1.0845±0.011	0.1366±0.050	0.9994
	40	0.0318±0.004	1.0742±0.021	0.1307±0.070	0.9983
	50	0.0196±0.020	1.1077±0.020	0.1736±0.050	0.9984

Figs. 3.28 - 3.29 show the changes in viscosity coefficient, K; and flow behaviour index, n; according to total soluble solids, respectively with their standard deviations. Viscosity coefficient K stayed constant between 50 and 60 brix, but for 70 brix, there was a certain increase.

For only 70^o Brix sumac concentrate, there was a significant effect of total soluble solid content on the flow behaviour ($p<0.05$). There was a significant increase of viscosity coefficient at this concentrate. Also a slight decrease was observed in the flow behaviour index n only at 70^o Brix concentration. The flow behaviour index is very close to 1.0 for most fruit concentrates.

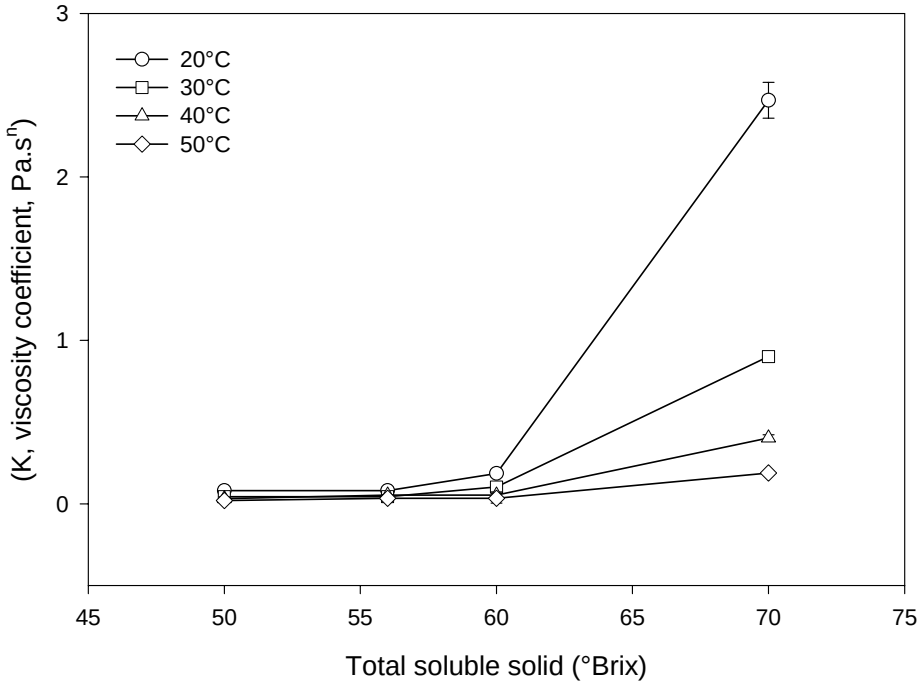

Figure 3.28. Variation of viscosity coefficient with total soluble solids at 20, 30, 40 and 50°C.

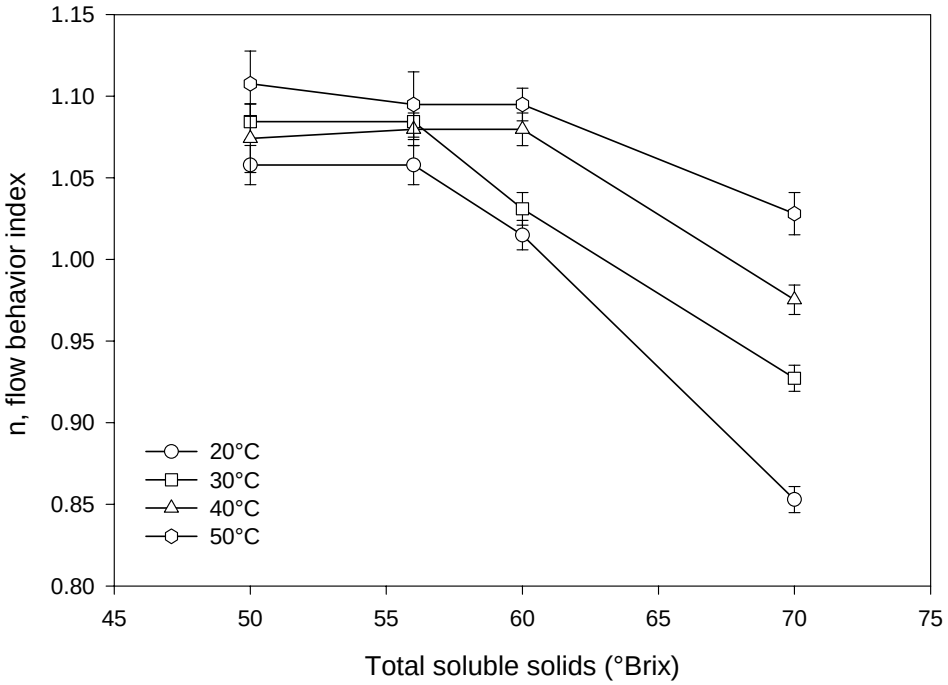

Figure 3.29. Variation of flow behaviour index with total soluble solid at 20, 30, 40 and 50°C

3.8.1. Effect of Total Soluble Solids Content on Rheological Behavior of Sumac Concentrate

Variation of viscosity of sumac concentrate with TSS is presented in Table 3.11 and shown in Fig. 3.30 for four different temperatures. Concentration of both soluble and insoluble solids is reported to have a strong effect on the viscosity of Newtonian fluids or the consistency coefficient and the apparent viscosity of non-Newtonian fluid foods (Juszczak and Fortuna, 2003). As expected, this effect is more noticeable at lower temperatures.

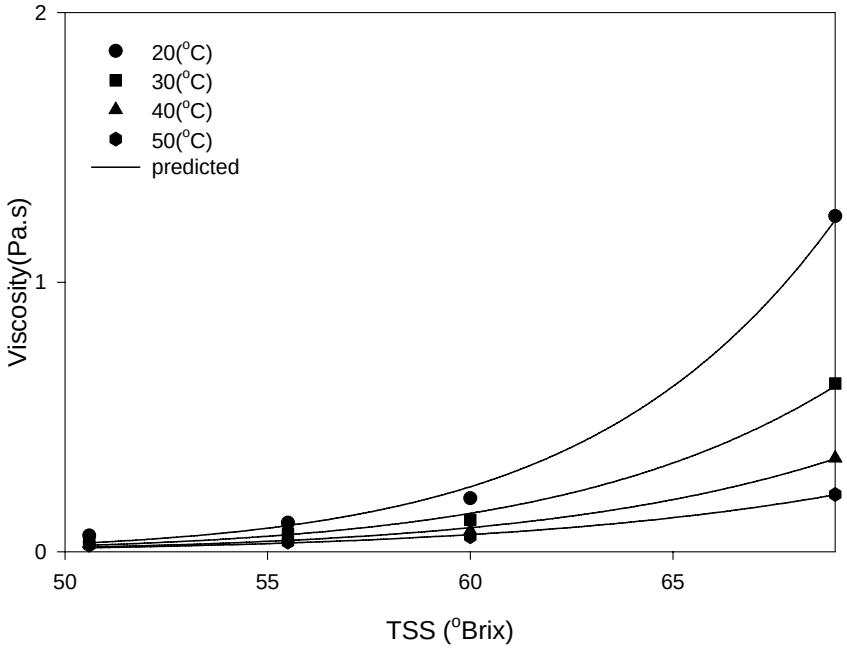

Figure 3.30.Variation of viscosity of sumac concentrates with TSS at different temperatures.

Two different models were used to evaluate the variation of viscosity of sumac concentrate with TSS: The power law model,

$$\eta = \eta_1 C^{b}_{1} \quad (3.11)$$

and the exponential model.

$$\eta = \eta_2 e^{b}_{2}{}^{C} \quad (3.12)$$

Here, η, and C are the viscosity and concentration in Pa.s and °Brix respectively, while η_1, η_2, b_1 and b_2 are the parametric constants to be determined from the fitted data.

Table 3.11.Viscosity values of the sumac concentrate obtained from Newtonian model at different TSS and temperature (Equation 3.9).

TSS (°Brix)	T (°C)	η (Pa.s)	R^2
70.0	20	118.0720	0.9914
	30	63.3392	0.9984
	40	35.5431	0.9995
	50	21.8728	0.9992
60.0	20	20.2211	0.9995
	30	11.7761	0.9988
	40	7.9385	0.9979
	50	5.6323	0.9974
56.0	20	10.6651	0.9984
	30	6.8922	0.9979
	40	7.9385	0.9979
	50	5.6347	0.9974
50.0	20	10.6651	0.9984
	30	6.9922	0.9979
	40	4.7634	0.9974
	50	3.5296	0.9970

The numerical values of the parameters appearing in Equations 3.11 and 3.12 are given in Table 3.12 and 3.13 respectively for temperatures of 20, 30, 40, and 50 ^oC. The exponential model was observed to give a slightly better fit than the power law as it was deduced from the higher R^2 values (0.997 vs. 0.994) at each temperature in question. This is in agreement with the fact that, the power law equation tends to give better results for puree-type foods, whereas the exponential model is used in concentrated fruit juices having small amounts of insoluble solids (Ibarz, et. al., 1993).

Table 3.12. Parameters of the power law model describing dependency of viscosity on TSS at different temperatures for sumac concentrate.

Temperature (°C)	η_1 (mPa.s)	b_1 (°Brix)	R^2
20	$4.308x10^{-19}$	$1.167x10^{1}$	0.9969
30	$3.488x10^{-17}$	$1.047x10^{1}$	0.9956
40	$5.359x10^{-16}$	$9.684x10^{0}$	0.9947
50	$3.069x10^{-14}$	$8.613x10^{0}$	0.9931

Table 3.13. Parameters of the exponential model describing dependency of viscosity on TSS at different temperatures for sumac concentrate.

Temperature (°C)	η_2 (mPa.s)	b_2 (°Brix)	R^2
20	$1.882x10^{-3}$	$1.942x10^{-1}$	0.9986
30	$3.753x10^{-3}$	$1.742x10^{-1}$	0.9979
40	$7.945x10^{-3}$	$1.548x10^{-1}$	0.9969
50	$1.643x10^{-2}$	$1.372x10^{-1}$	0.9961

3.8.2. Effect of Temperature on Rheological Behaviors of Sumac Concentrate

The variation of viscosity with temperature could be described by Arrhenius type relationship:

$$\eta = \eta_{\infty} \exp(E_a/RT) \quad (3.13)$$

where, η is viscosity (Pa.s), η_{∞} is material's constant (Pa.s), E_a is the flow activation energy (kj/mol), R is the gas constant (kj/mol.K), and T is the absolute temperature (K). Table 3.14 gives above constants as determined by fitting the related data to Equation 3.13 together with R^2 values being grater than 0.994 for each case.

Table 3.14. Parameters of Arrhenius equation for sumac concentrate with different TSS

TSS (°Brix)	η_∞ (mPa.s)	$E_a x10^3$ (kj/mol)	R^2
50.0	$2.27x10^{-3}$	24.78	0.9965
56.0	$3.83x10^{-4}$	30.55	0.9946
60.0	$1.12x10^{-4}$	35.05	0.9968
70.0	$2.58x10^{-6}$	48.72	0.9989

Figure 3.31 shows this trend at different TSS. As seen, the viscosity depends strongly on temperature especially for the more concentrated samples. This can also be deduced from the increasing activation energy values with TSS indicating that viscosity is more sensitive to temperature for samples having higher TSS. Thus, the viscosity at 20 ^oC is 4.36 times grater than the value at 50 ^oC with TSS of 70 ^{o}Brix as compared to the value of 3.02 times, in the same temperature range, for the sample with TSS of 50.0 ^{o}Brix. (Table 3.11). Similar behaviors have been observed by various researchers for other clarified juices (Kaya and Sözer, 2005).

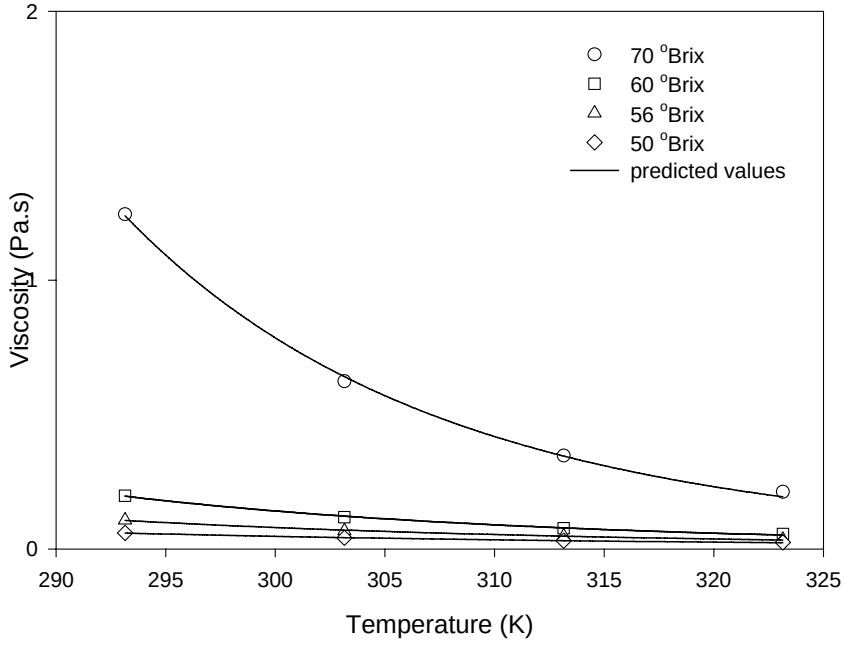

Figure 3.31. Variation in the viscosity of sumac concentrates with temperature at different TSS.

3.8.3. Combined Effect of Temperature and Concentration on Rheological Behaviours of Sumac Concentrate

It is very useful to obtain a simple equation describing the combined effect of temperature and concentration on the material's viscosity.

To evaluate the effect of both the temperature and the soluble solid content on the viscosity of sumac concentrate, two models were used:

$$\mu = \mu_3 \exp(b_3 C + E_a/RT) \quad (3.14)$$

$$\mu = \mu_4 C^{b_4} \exp(E_a/RT) \quad (3.15)$$

where: μ is the viscosity (mPa.s), E_a is the flow activation energy (J/mol), R is the gas constant (J / mol.K), T is the absolute temperature (K), C is the soluble solid content (^{o}Brix), μ_3, μ_4, b_3 and b_4 are constants.

Finally the equations which allow the viscosity values to be obtained at different temperatures and soluble solid content for the sumac concentrate were proposed as:

$$\mu = 9.63\times10^{-1}\exp(33.16\times10^3/RT)+0.132C \quad R^2=0.9693 \quad (3.16)$$

$$\mu = 3.31\times10^{-21}C^{7.84}\exp(33.16\times10^3/RT) \quad R^2=0.9543 \quad (3.17)$$

It seems that the Equation (3.16) gives slightly better fit than the Equation (3.17). Since it has higher values of R^2 coefficients. Therefore, Equation (3.16) was selected to show the combined effect of soluble solids and temperature.

When multiple regression analysis were performed for the viscosity coefficient (K value) and flow behaviour index (n); both total soluble solid and temperature have significant effect at $p<0.05$ significance level.

Each temperature at each concentration has significant effect ($p<0.05$) on the K values. For 56 and 50 Brix sumac concentrates; flow behaviour index (n value) were not significantly different, but for 70 and 60 brix sumac concentrates, were significantly different from each other and also, significantly different from 56 and 50 Brix sumac concentrates ($p<0.05$).

3.9. Color Measurements of Sumac Concentrate

3.9.1. Kinetic evaluation

The color degradation kinetics of food products is a complex phenomenon and dependable models to predict experimental color change, which can be used in engineering calculations, are limited. However, empirical mathematical modeling techniques may be used to determine the end point and kinetic effect. The kinetic parameters namely, reaction order, rate constant and activation energy provide useful information on the quality changes which occur during thermal processing (Ahmed et al, 2004). Color can be used to design adequate thermal processing conditions for maximizing final product quality if its kinetics is determined (Silva, and Silva, 1999). Anthocyanins are well-known natural colorants, which provide bright red color in foods. Sumac contains certain amount of anthocyanins which give the red color. The primary problem with the application of anthocyanins as food colorants is their vulnerability to temperature. (Kırca et al., 2007). Skrede et al., (2000) recently reported that anthocyanins as well as other polyphenolics are readily oxidized because of their antioxidant properties and thus, susceptible to degradative reactions during various processing unit operations. (Paz and Pinto, 2002). Anthocyanins may be subjected to alterations during processing and storage. For example, marked changes and degradation of anthocyanins were observed during processing of blueberries and strawberries into juice and concentrate (Fügel et al., 2005).

The effect of thermal processing on the Hunter color values of sumac concentrate was studied. Color changes of the sumac extracts and their zero- and first-order fittings are shown in Figs.3.32-3.49 for different temperatures. Initial color values of 10 ^{o}Brix concentrate were, L=10.52, a=34.20, b=17.49 and of 37 ^{o}Brix were L=1.15, a=6.50, b=1.16.

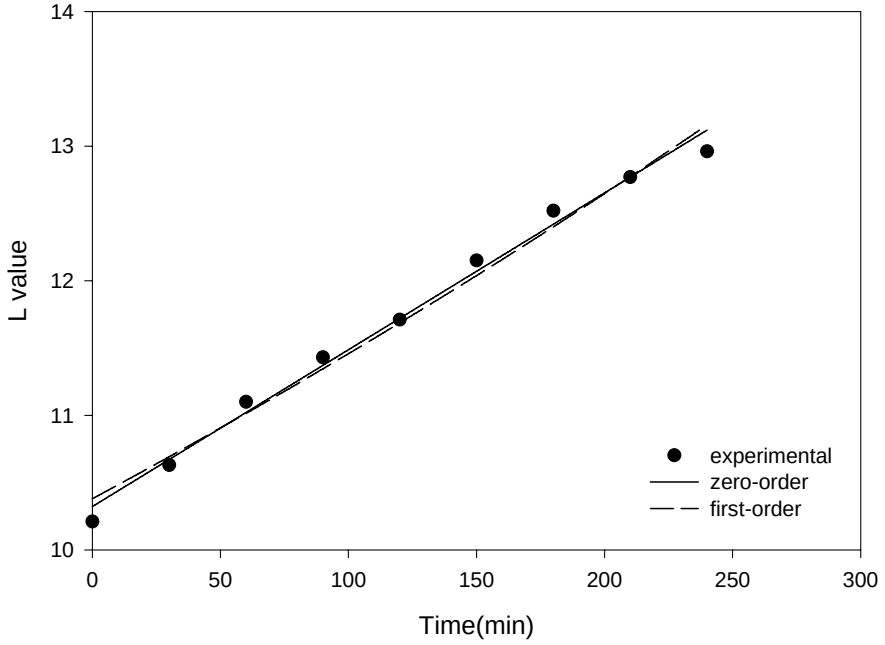

Figure 3.32. Variation of L-value of 10 brix sumac concentrate with time at 40^{o}C.

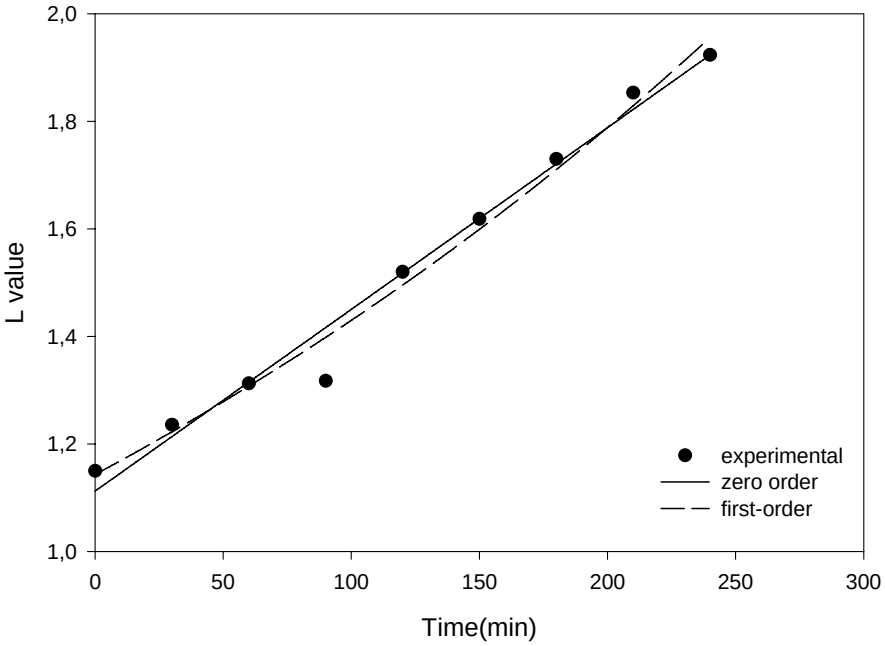

Figure 3.33. Variation of L-value of 37 brix sumac concentrate with time at 40^{o}C

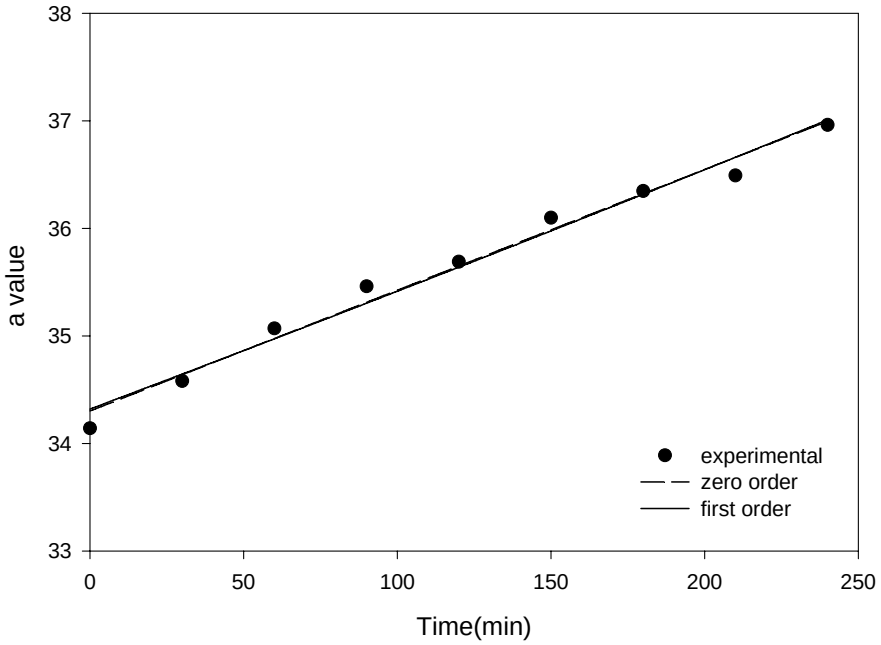

Figure 3.34. Variation of a-value of 10 brix sumac concentrate with time at 40°C.

The complexity of fruit juices and derivatives implies a wide range of enzymatic and non-enzymatic browning reactions caused by thermal treatments. Consequently it is difficult to establish a reaction mechanism and to obtain a kinetics model describing the global process adequately (Ibarz et al., 1999; Chutintrasri and Noomhorm, 2007). These kinetic models are expressed by the following equations:

$$\text{Zero order: } C = C_0 + k_0 t \qquad (3.18)$$

$$\text{First order: } C = C_0 \exp(k_1 t) \qquad (3.19)$$

where C is the concentration of color value of interest, studied at time t, C_0 is the value at time zero, k_0 is the zero-order kinetic constant, and k_1 is the first-order kinetic constant.

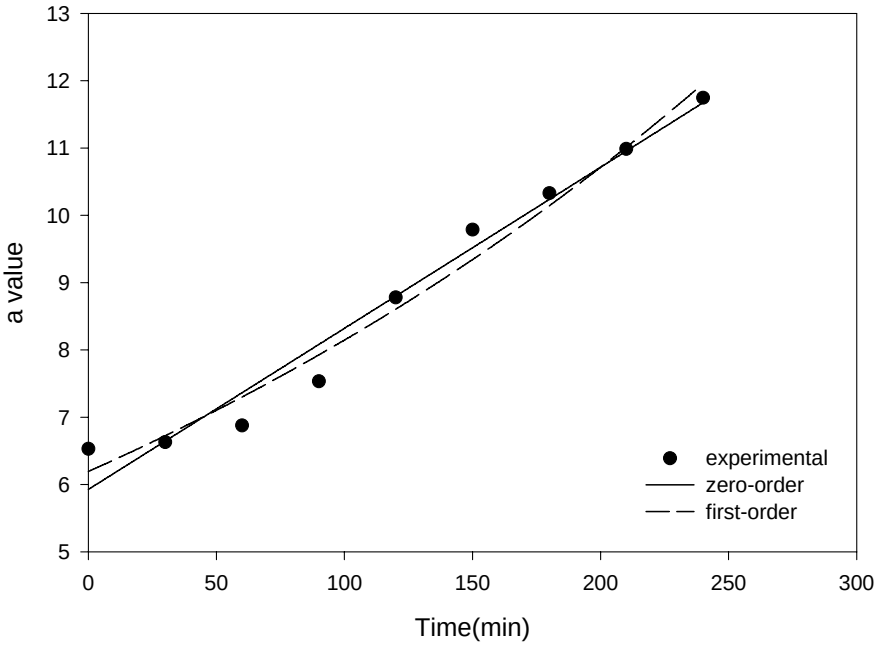

Figure 3.35. Variation of a-value of 37 brix sumac concentrate with time at 40°C.

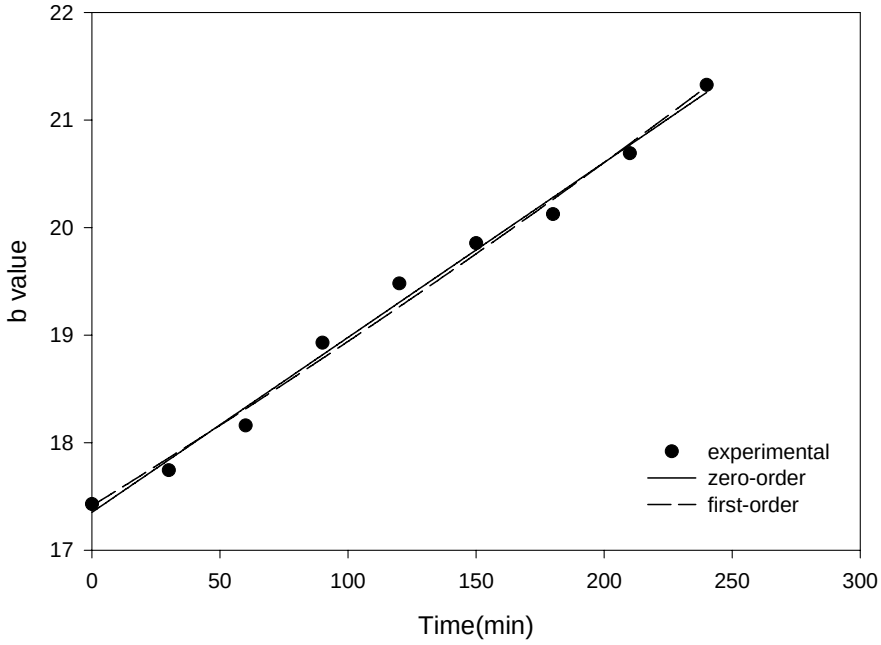

Figure 3.36. Variation of b-value of 10 brix sumac concentrate with time at 40°C.

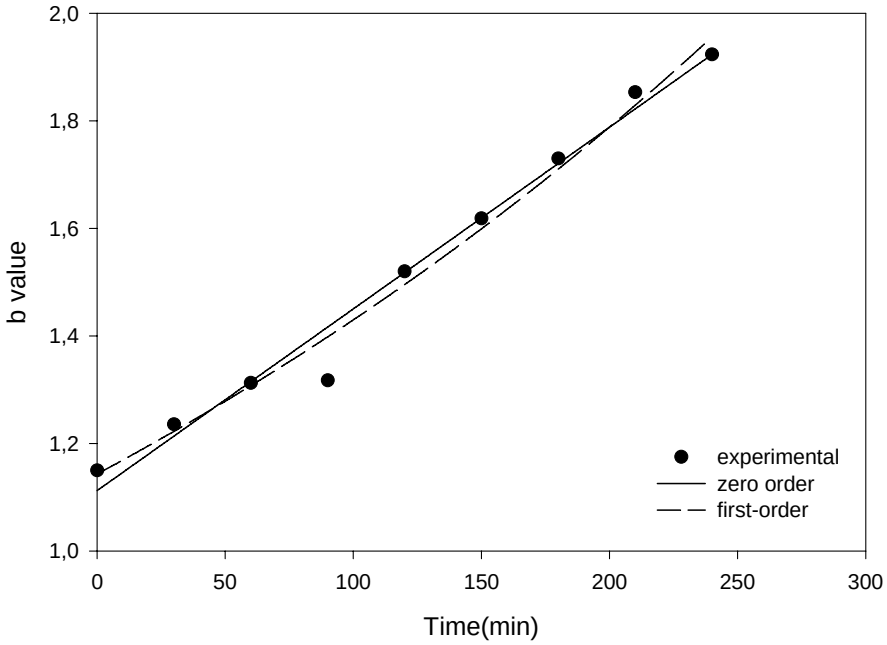

Figure 3.37. Variation of b-value of 37 brix sumac concentrate with time at 40^{o}C.

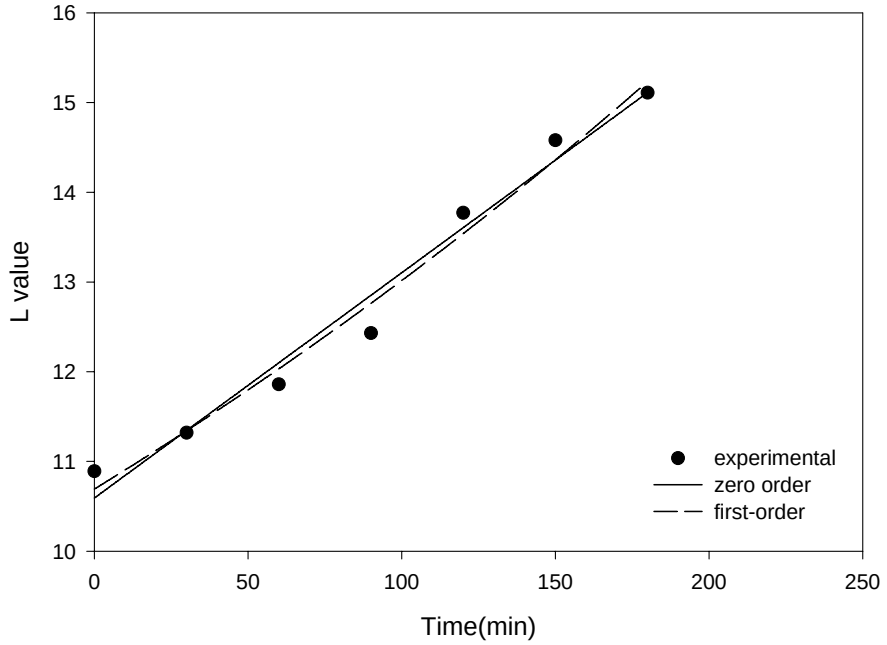

Figure 3.38. Variation of L-value of 10 brix sumac concentrate with time at 60^{o}C.

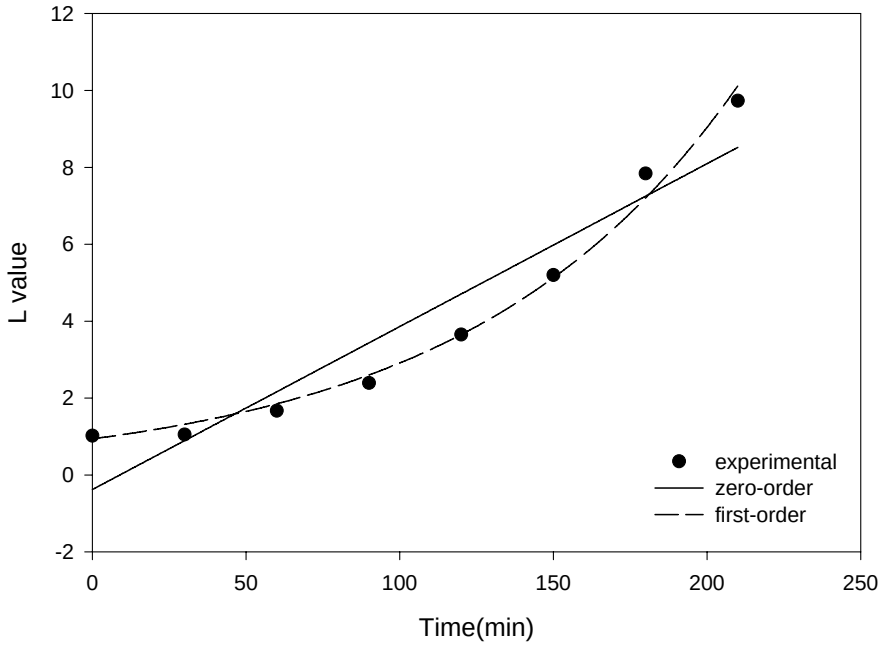

Figure 3.39. Variation of L-value of 37 brix sumac concentrate with time at 60°C

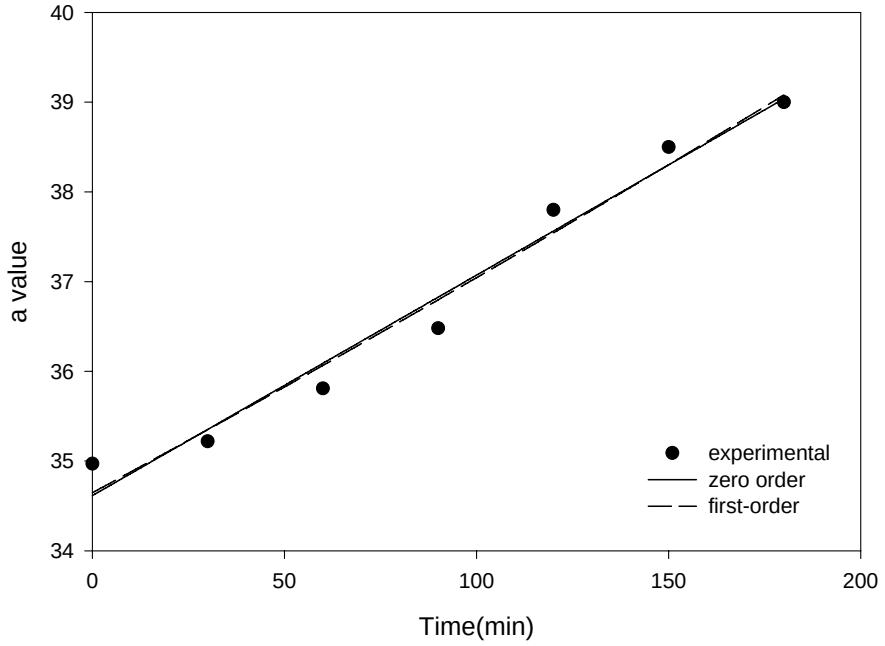

Figure 3.40. Variation of a-value of 10 brix sumac concentrate with time at 60°C

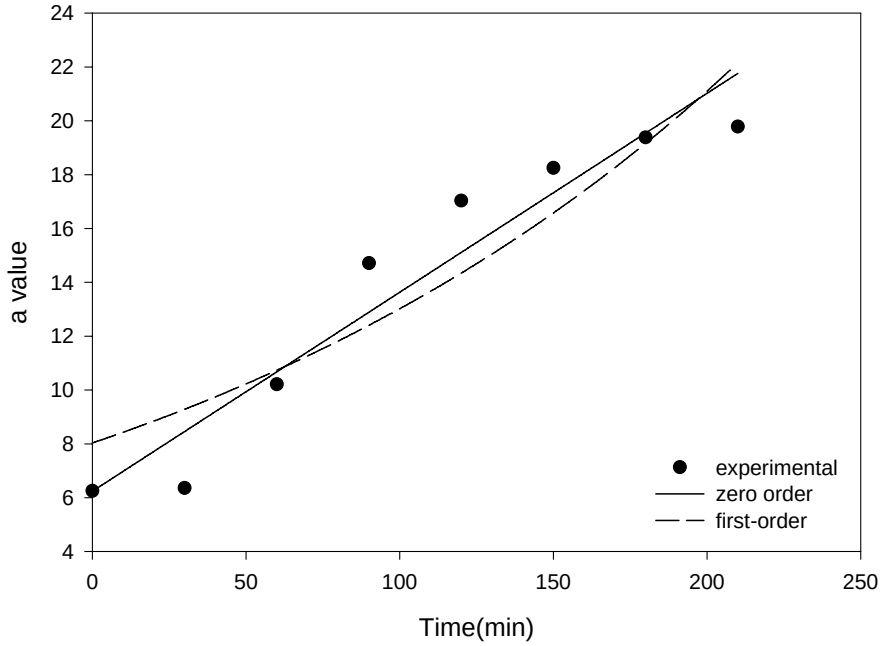

Figure 3.41. Variation of a-value of 37 brix sumac concentrate with time at 60^{o}C

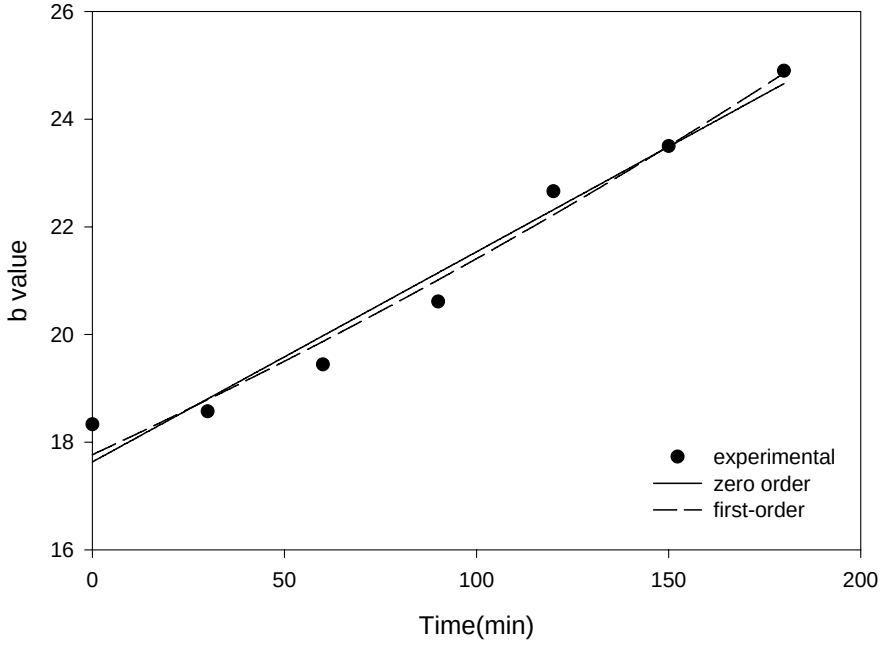

Figure 3.42. Variation of b-value of 10 brix sumac concentrate with time at 60^{o}C

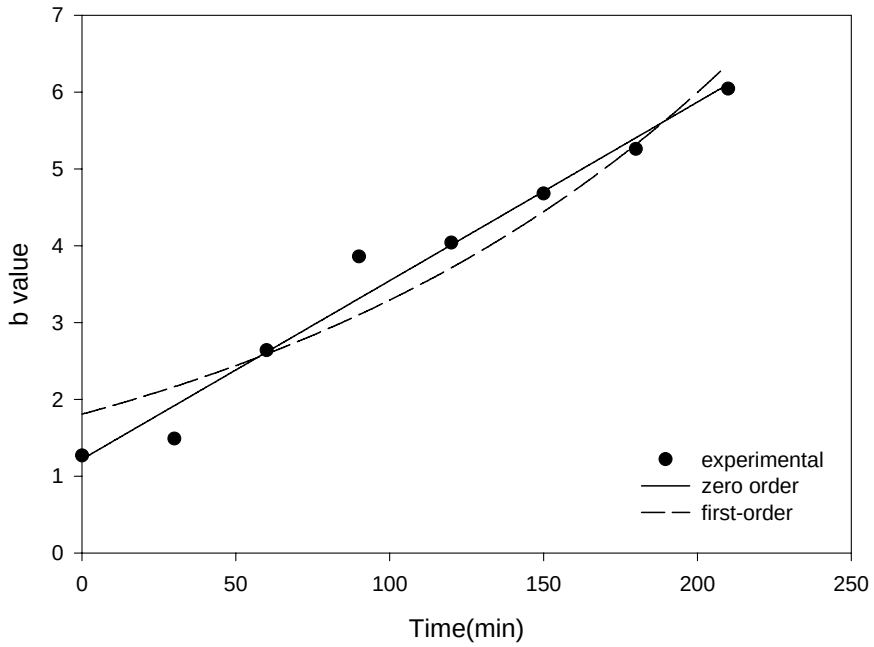

Figure 3.43. Variation of b-value of 37 brix sumac concentrate with time at 60^{o}C

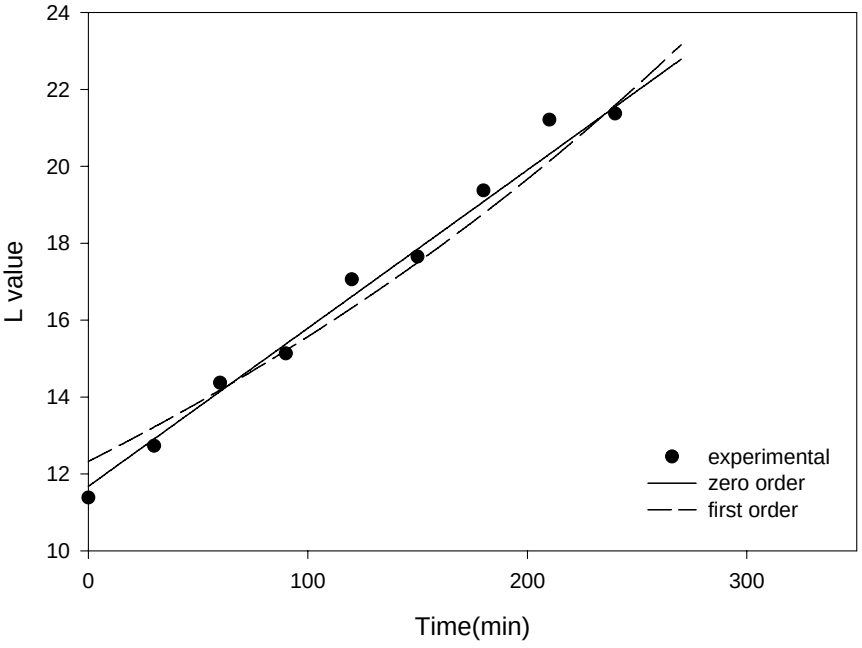

Figure 3.44. Variation of L-value of 10 brix sumac concentrate with time at 80^{o}C

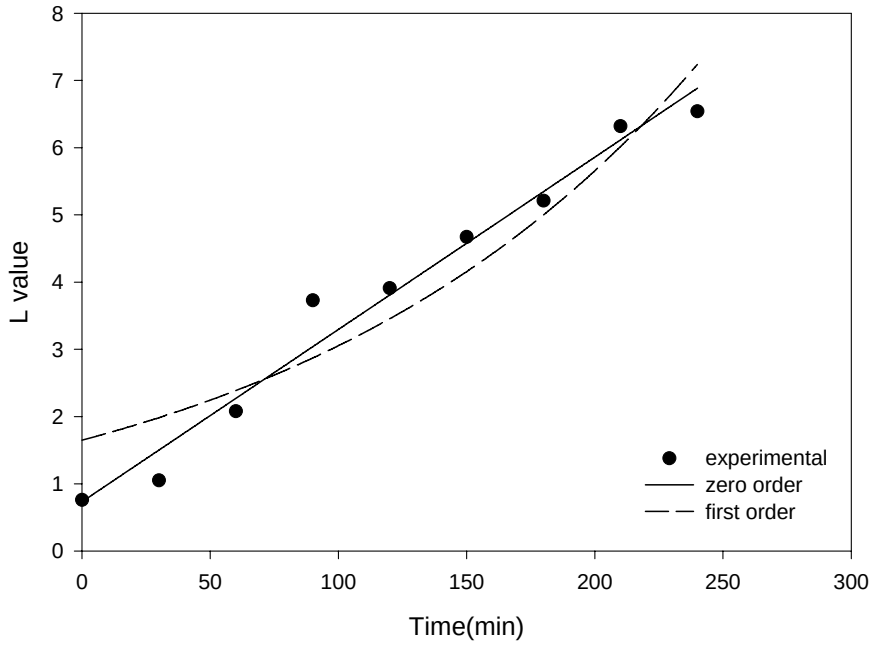

Figure 3.45. Variation of L-value of 37 brix sumac concentrate with time at 80^{o}C

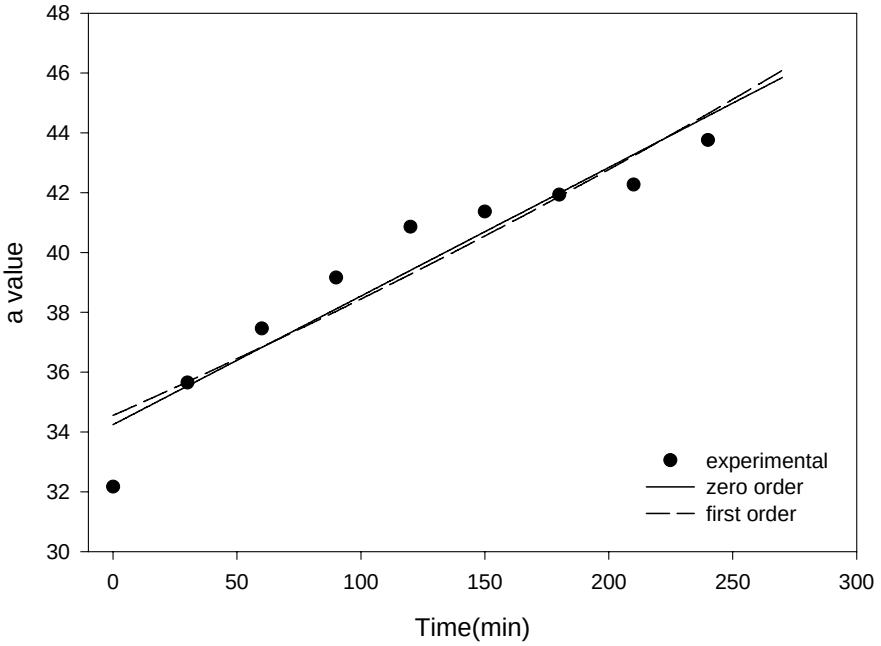

Figure 3.46. Variation of a-value of 10 brix sumac concentrate with time at 80^{o}C

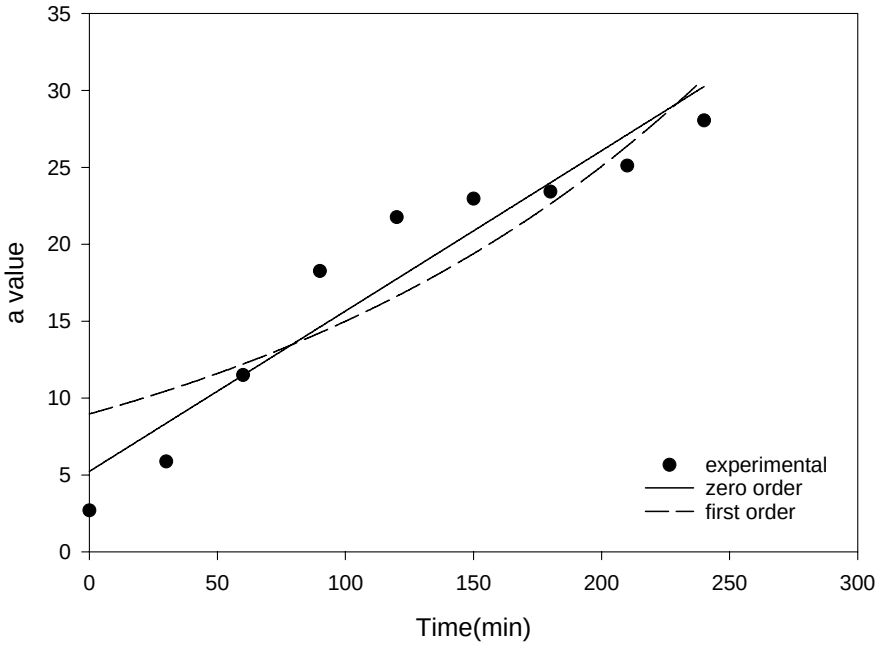

Figure 3.47. Variation of a-value of 37 brix sumac concentrate with time at 80°C

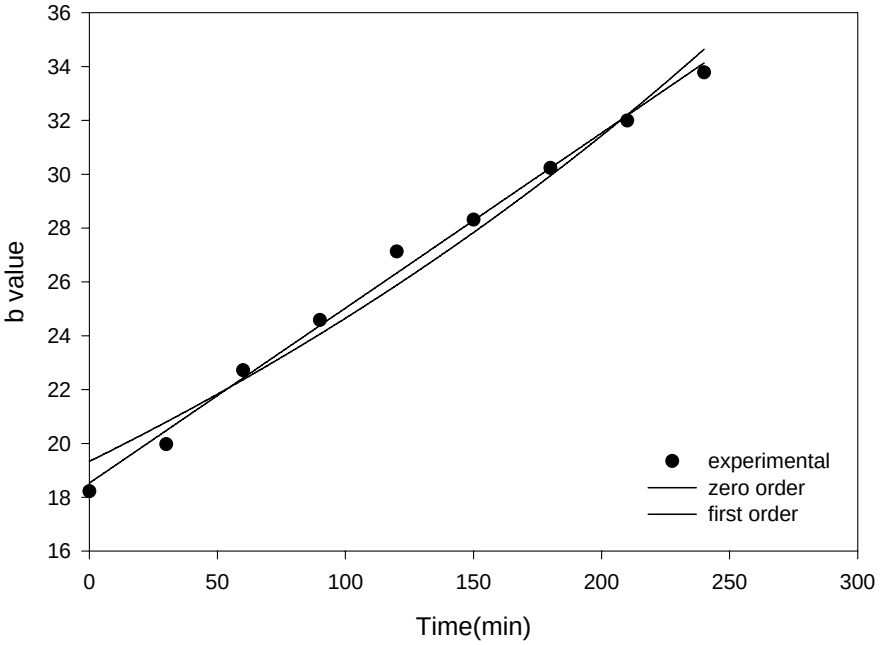

Figure 3.48. Variation of b-value of 10 brix sumac concentrate with time at 80°C

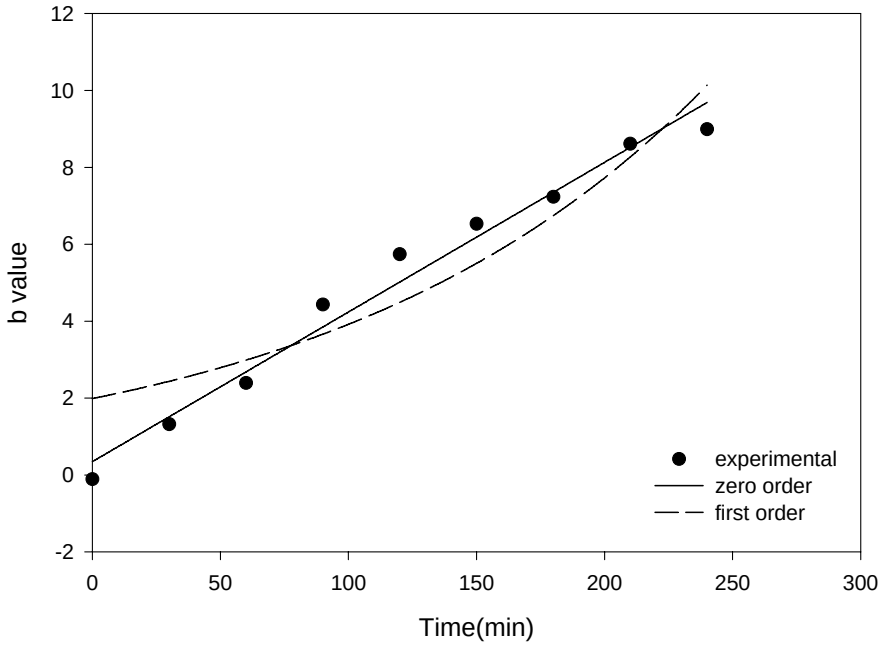

Figure 3.49. Variation of b-value of 37 brix sumac concentrate with time at 80°C

The evaluation of the Hunter color parameters (L, a, and b values) with the time were applied to zero- and first-order models. The values of the parameters obtained from these fittings are given in Table3.15 and Table 3.16 respectively.

Table 3.15. Zero-order kinetic parameters of sumac concentrates for Hunter color values at different concentration and temperatures.

TSS in concentrate	Temperature (°C)	Parameter	Zero-order model		
			$k_0(min^{-1}) \pm SE$	$C_0 \pm SE$	R^2
10 brix	40	L	0.0117±0.0004	10.3213±0.0596	0.9911
		a	0.0112±0.0005	34.3015±0.0753	0.9848
		b	0.0163±0.0006	17.3523±0.0827	0.9912
	60	L	0.0251±0.0018	10.5918±0.1929	0.9754
		a	0.0246±0.0019	34.6143±0.2018	0.9719
		b	0.0390±0.0032	17.6311±0.3461	0.9674
	80	L	0.0411±0.0018	11.6738±0.2928	0.9844
		a	0.0430±0.0052	34.2452±0.7364	0.9085
		b	0.0650±0.0018	18.5222±0.2628	0.9944
37 brix	40	L	0.0034±0.0002	1.1123±0.0263	0.9796
		a	0.0239±0.0016	5.9270±0.2309	0.9690
		b	0.0045±0.0002	1.0592±0.0343	0.9808
	60	L	0.0424±0.0055	0.3800±03210	0.9082
		a	0.0739±0.0085	6.2358±1.0676	0.9263
		b	0.0232±0.0015	1.2202±0.1885	0.9755
	80	L	0.0256±0.0016	0.7324±0.2223	0.9748
		a	0.1042±0.0121	5.2291±1.7323	0.9134
		b	0.0389±0.0022	0.3444±0.3134	0.9782

The variation of L, a, and b values were described both by the zero- and the first-order kinetics. However, the zero-order kinetic model was preferred because of the better fit. At low temperatures, the kinetic constants were also low.

All color parameters (L, a, and b values), showed similar behavior for kinetic fittings. Since, sumac concentrates have intense red color due to presence of anthocyanins, "a" value and therefore "L" value were more important for the kinetic evaluation.

Table 3.16. First-order kinetic parameters of sumac concentrates for Hunter color values at different concentration and temperatures.

TSS in concentrate	Temperature (^oC)	Parameter	First-order model		
			$k_1(min^{-1}) \pm SE$	$C_0 \pm SE$	R^2
10 brix	40	L	0.0010±0.0000	10.3795±0.0745	0.9846
		a	0.0003±0.0000	34.3193±0.0791	0.9826
		b	0.0008±0.0000	17.4126±0.0840	0.9901
	60	L	0.0020±0.0001	10.6917±0.1542	0.9817
		a	0.0007±0.0000	34.6458±0.1877	0.9745
		b	0.0019±0.0001	17.7651±0.2707	0.9771
	80	L	0.0023±0.0002	12.3236±0.3862	0.9844
		a	0.0011±0.0001	34.5515±0.7683	0.8887
		b	0.0024±0.0001	19.3296±0.4531	0.9783
37 brix	40	L	0.0022±0.0010	1.1432±0.0204	0.9844
		a	0.0027±0.0002	6.1941±0.1739	0.9761
		b	0.0029±0.0001	1.1094±0.0174	0.9931
	60	L	0.0113±0.0006	0.9376±0.1033	0.9904
		a	0.0048±0.0009	8.0298±1.1783	0.8519
		b	0.0060±0.0080	1.8078±0.2401	0.9238
	80	L	0.0062±0.0009	1.6489±0.2935	0.9013
		a	0.0051±0.0011	8.9690±1.8906	0.8039
		b	0.0068±0.0012	1.9865±0.4831	0.8698

SE: Standart error of estimation

3.9.2. Effect of temperature

The temperature sensitivity of rate constants was analyzed using the Arrhenius equation, $k=k_0 exp\ (-E_a/RT)$. k_0 is the frequency factor (min^{-1}), E_a is the activation energy(kj/mol), R is the universal gas constant (8.314 J/mol/K) and T is the absolute temperature (K). To determine the effect of temperature on the parameters studied, the constants obtained were fitted to an Arrhenius-type equation in each of the kinetic models studied.

Figs. 3.50-3.51 indicated the temperature dependency of 10 brix and 37 brix sumac concentrates for zero-order consideration. The average activation energies for L, a, and b values with their frequency factors (k_0) in the range of 40-80^oC are shown in Table 3.18.

It can be concluded that, the rates of change of color parameters increased as the heating temperature became higher by the concentration increase.

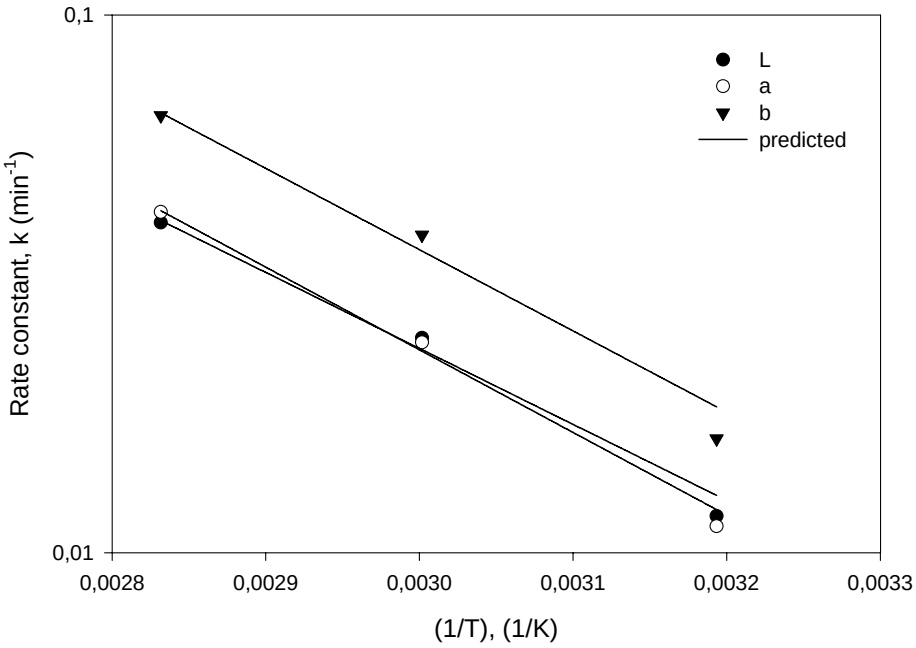

Figure 3.50. Temperature dependency of L, a, b values for 10 brix sumac extract

From Table 3.17, it is seen that; the activation energy for change in L value, for 10 brix sumac concentrate 26.97 kj/mol but for 37 brix sumac concentrate 36.67 kj/mol. Increase in concentration from 10 to 37 brix affected the activation energy significantly. Also, 'a' and 'b' values showed similar behaviors. It can be concluded that; mostly, lightness was changed by applying heat treatment. The same behaviors are observed when Fig.3.51 is examined.

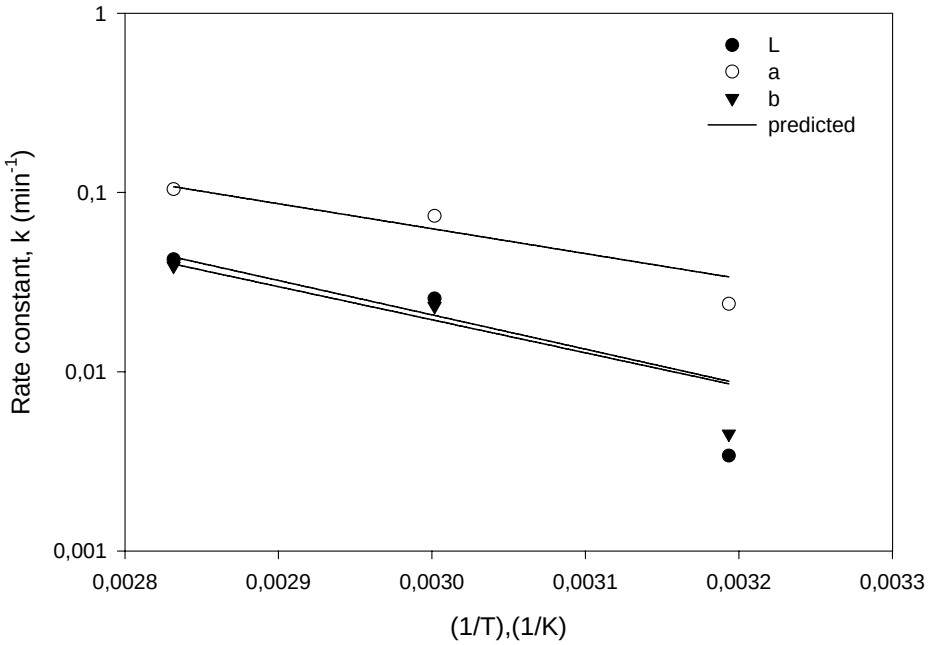

Figure 3.51. Temperature dependency of for L, a, b values for 37 brix sumac extract

Table 3.17. Parameters of Arrhenius equation for changes in L, a, and b values

Type of concentrate	Hunter color value	$k_{0\times}10^3$ (min^{-1})	E_a (kj/mol)	R^2
10 brix	L	0.40369	26.97	0.9931
	a	0.97186	29.42	0.9969
	b	1.24971	28.93	0.9890
37 brix	L	11.5994	36.67	0.9267
	a	0.93577	34.55	0.9268
	b	6.73264	35.34	0.9456

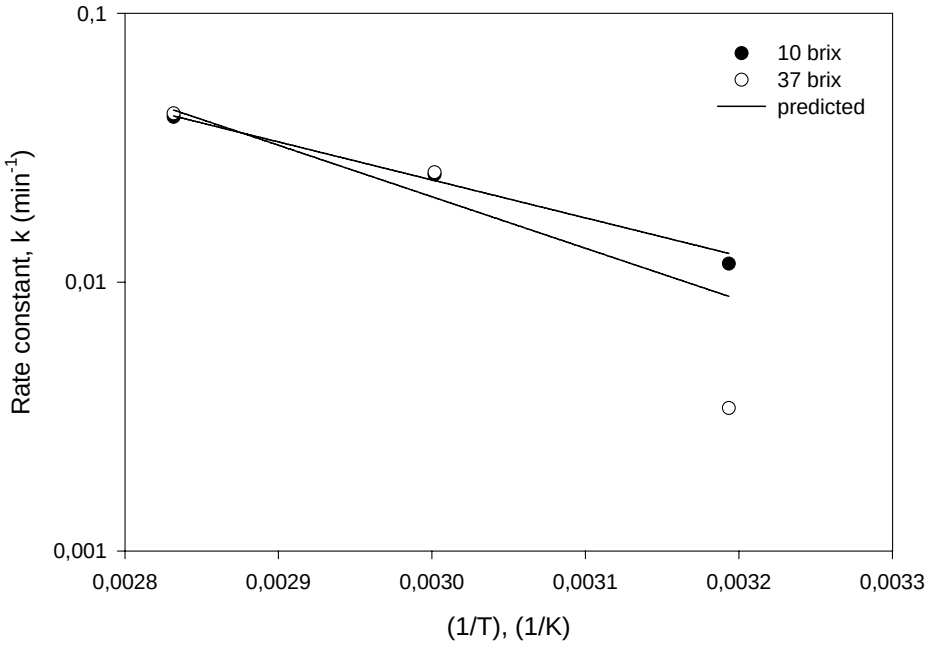

Figure 3.52. Dependency of rate constants of L values on temperature for 10 and 37 ^{o}Brix sumac concentrates

3.10. Total phenolic matter of sumac concentrate

In this part, sumac varieties were investigated in terms of total phenolic matter. A calibration curve was prepared firstly. Fig.3.53 shows the calibration curve together with the fitted equation.

Table 3.18 shows the different types of sumac concentrates and their phenolic matter content in terms of gallic acid. All determinations were performed according to the Folin-Ciocalteau method (Makkar, 2003).

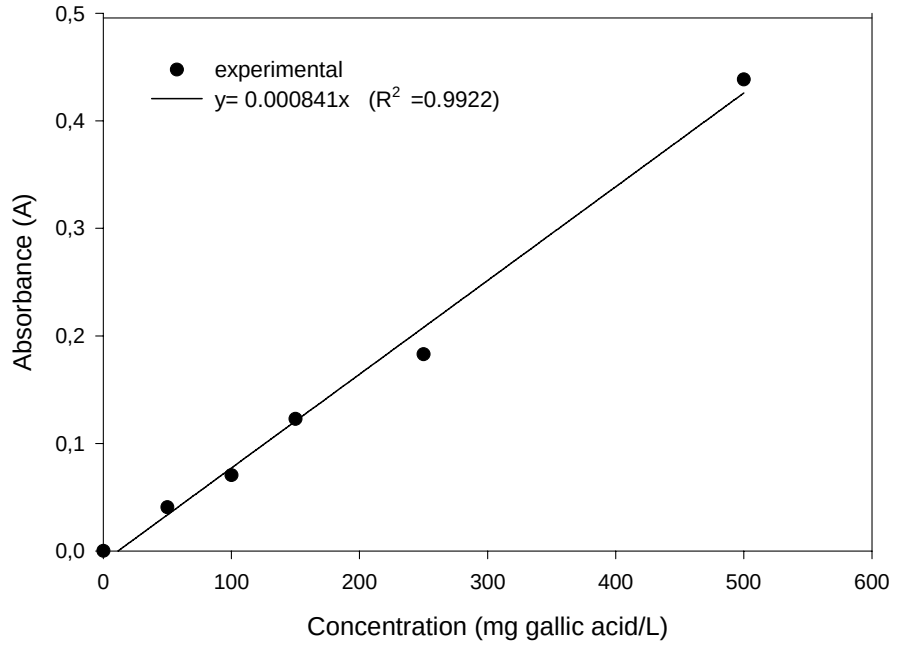

Figure 3.53. Calibration curve for gallic acid determination at 765 nm

Seven types of sumac concentrates were investigated for their phenolic matter content. Among these concentrates, extract of sumac with stems had the highest phenolic matter. This high value comes from stem characteristics, since stems of sumac has high phenolic matter. Sumac concentrate of Nizip and Siirt varieties had lower phenolic matter than other types of sumac concentrates.

Table 3.18. Total phenolic matter of 52.5 ^{o}Brix sumac concentrates

Type of sumac concentrate	Total Phenolic Matter (mg gallic acid/L)
2-years old crop (1st extract)	0.2452
Extract of sumac with stems	0.3547
Sumac of Nizip (hot extract)	0.1055
Sumac of Siirt (cold extract)	0.1402
New crop (1st extract)	0.2985
1-year old crop (1st extract)	0.2844
1-year old crop (2nd +3rd extract)	0.2845

Type of crop affected the phenolic matter content. Concentration of these samples was not the same, but in order to compare, concentrations were extrapolated to same value (52.5 ^{o}Brix). Two years old (1st extract) has 0.2452 mg gallic acid/L. However, one year old crop extract (1st extract) has 0.2844 mg gallic acid/L. This was not a big difference, but it comes from the crop time. As the time passed through, phenolic matter loss occurred due to oxidation. Sumacs of Nizip and Siirt region have the lowest content of phenolic matter. And also, sumac of Nizip was processed as hot extracted and it was lower than Siirt sumac (cold extract). This difference may be due to the type of extraction. Application of heat could decrease the phenolic matter content. This effect should be investigated in details.

3.11. Total monomeric anthocyanin content of sumac concentrate

Anthocyanin pigment content has a critical role in the color quality of many fresh and processed fruit and vegetables. Since, sumac concentrate has certain anthocyanin content, in this study, the variation in the anthocyanin content with year of harvesting was investigated. Also, effect of processing conditions on the quantity of anthocyanin was investigated.

Table 3.19 shows the anthocyanin content of different type of sumac concentrate. It was seen that, non processed new crop sumac extract has the highest quantity of anthocyanin (614 mg/l) when compared with new crop sumac concentrate which was concentrated in rising film evaporator (342 mg/l). Therefore, it can be said that evaporation process reduced the anthocyanin content approximately to half.

Table 3.19. Total monomeric anthocyanin content of sumac concentrate according to year of harvesting of berries

Type of concentrate	Total monomeric anthocyanin content in 73.7 Brix (mg/l)
New crop (non processed) extract	614.0
New crop (concentrated in rising film evaporator)	342.0
3 years cold extract	107.5
2 years cold extract	90.5
1 year cold extract	65.8

3.12. Indices for pigment degradation, polymeric color, and browning for sumac Concentrate

Indices for anthocyanin degradation of an aqueous extract, juice, or wine can be derived from a few absorbance readings of a sample that has been treated with sodium bisulfite. Anthocyanin pigments will combine with bisulfite to form a colorless sulfonic acid adduct. Polymerized colored anthocyanin-tannin complexes are resistant to bleaching by bisulfite, whereas the bleaching reaction of monomeric anthocyanins will rapidly go to completion. The absorbance at 420 nm of the bisulfite-treated sample serves as an index for browning. Color density is defined as the sum of absorbances at the $\lambda_{vis\text{-}max}$ and at 420 nm. The ratio between polymerized color and color density is used to determine the percentage of the color that is contributed by polymerized material (Giusti and Wrolstad, 2001).

The $\lambda_{vis\text{-}max}$ was found to be 523 nm at the spectrophotometer by scanning. Therefore, all measurements were done at, 420 nm, 523 nm and 700 nm. Color density, polymeric color and percent polymeric color are calculated according to following equations respectively, where DF is the dilution factor of original sample.

Color density = $[(A_{420\ nm}-A_{700\ nm}) + (A_{\lambda vis\text{-}max}- A_{700\ nm})] \times DF$ (for control sample (treated with water))

Polymeric color = $[(A_{420\ nm}-A_{700\ nm}) + (A_{\lambda vis\text{-}max}- A_{700\ nm})] \times DF$ (for bisulfite bleached sample).

Percent polymeric color = (polymeric color/color density) × 100

Table 3.20 indicates the % polymeric color values of various sumac concentrates. It is seen that old years crops of sumac concentrates have high polymeric color. This mean that, as the sumac berries were stored for long times, coloring reactions are more probable. Therefore, their % polymeric color has higher than new crop.

Table 3.20. % Polymeric color of sumac concentrates

Type of concentrate	% Polymeric color in 73.7 Brix
New crop not processed extract	43.72
New crop (concentrated in rising film evaporator)	46.95
3 years-old cold extract	67.82
2 years-old cold extract	68.66
1 year cold extract	39.97

3.13. Identification of Organic Acids in Sumac Concentrate

3.13.1. Identification of organic acids in sumac concentrates by HPLC

HPLC chromatograms of some standard organic acids are shown Figures 3.54-3.58. The retention times of standard organic acids are reported in Table 3.21.

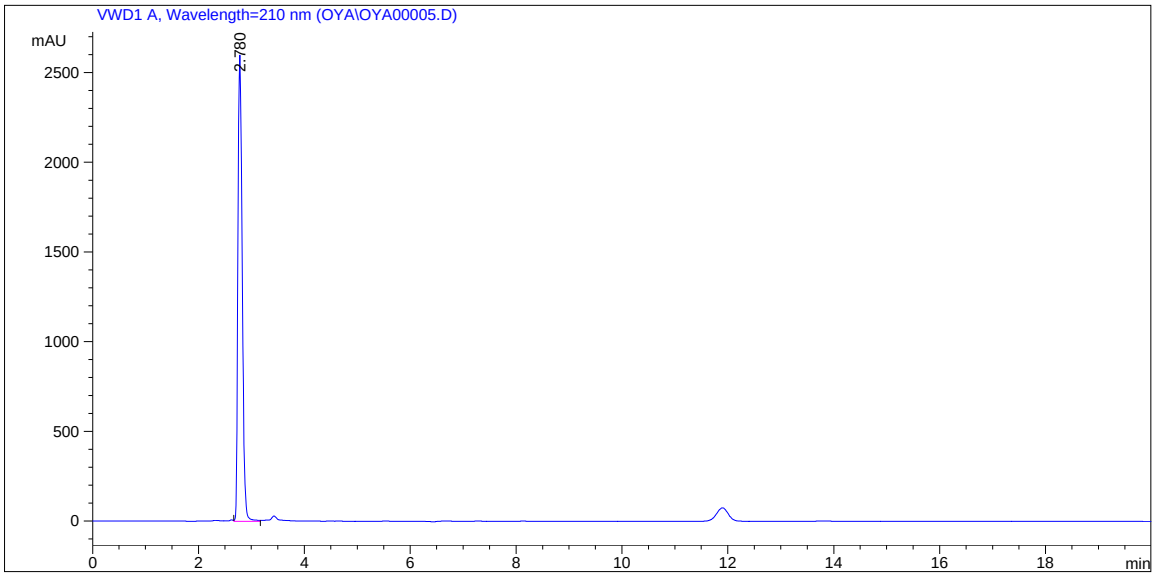

Figure 3.54. Chromatogram of standard tartaric acid

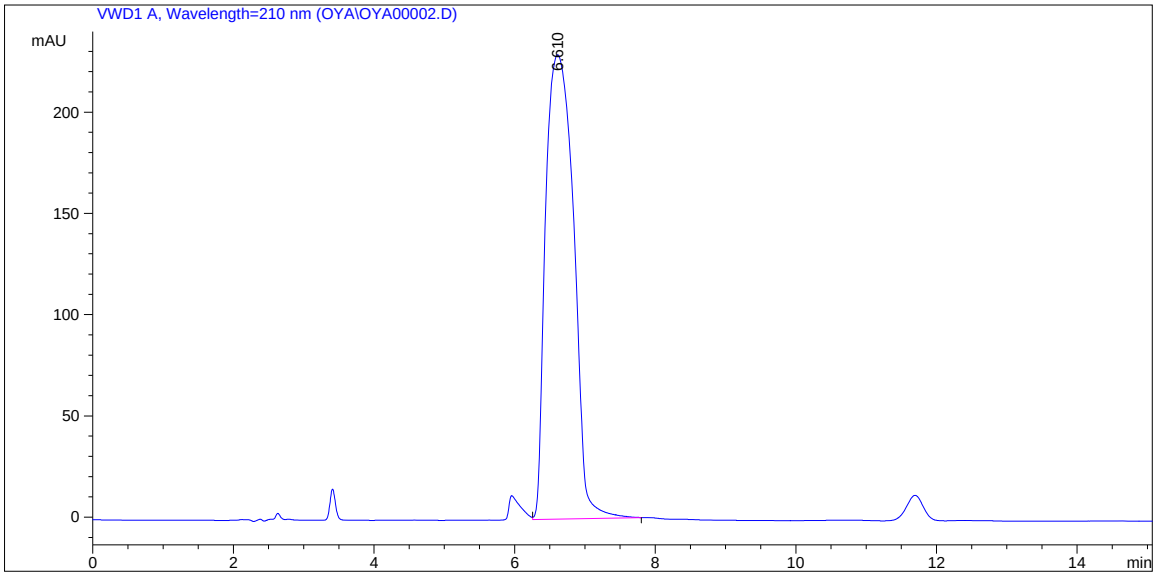

Figure 3.55. Chromatogram of standard succinic acid

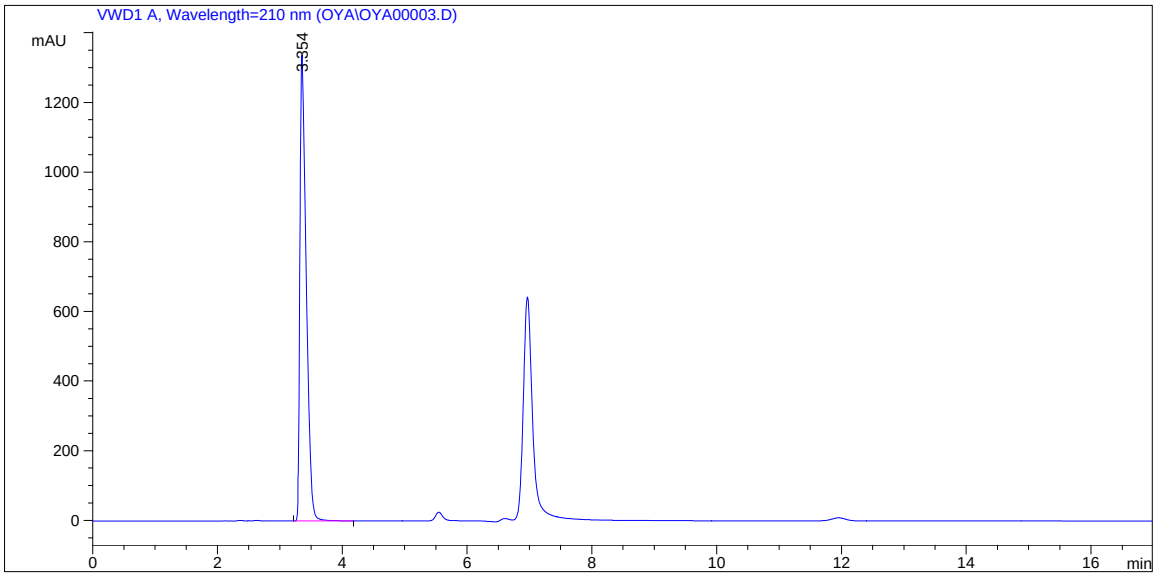

Figure 3.56. Chromatogram of standard malic acid

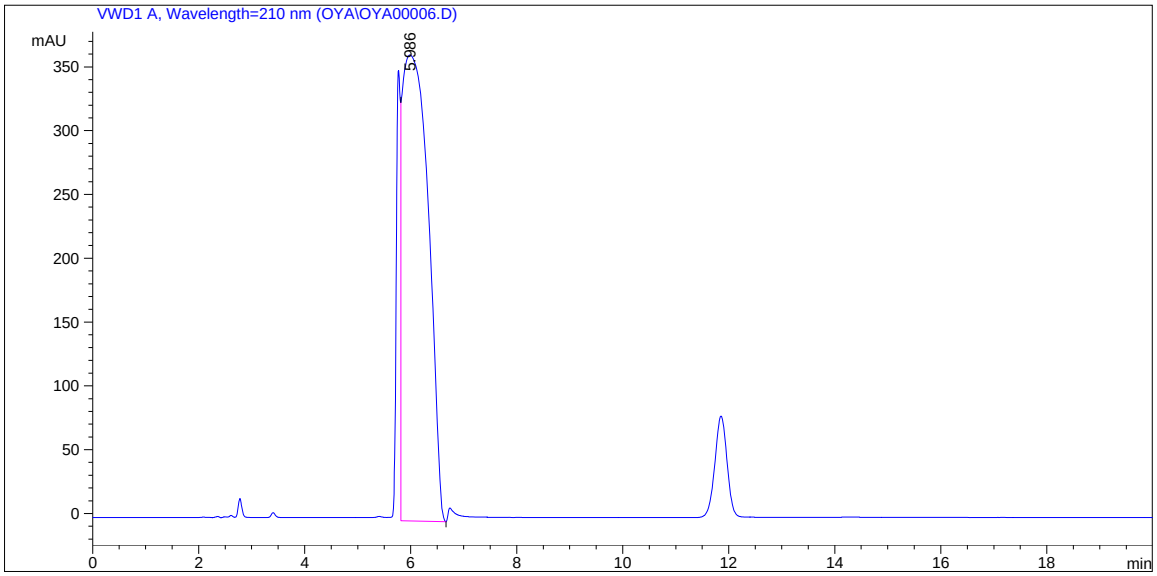

Figure 3.57. Chromatogram of standard citric acid

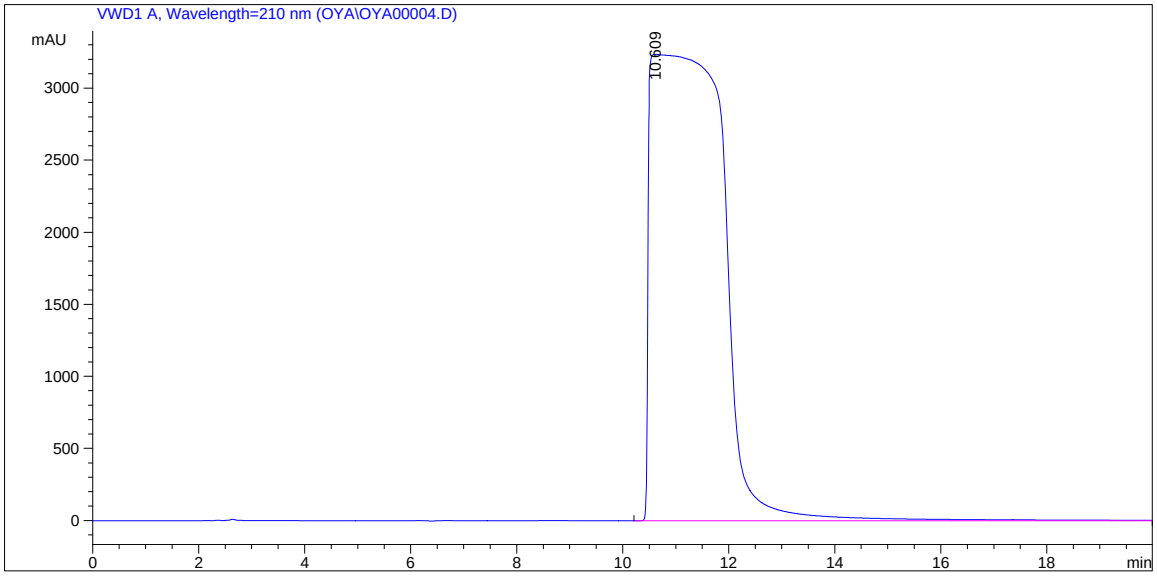

Figure 3.58. Chromatogram of standard gallic acid

Table 3.21. Standard organic acids and their detected retention times for 1% w/v concentration

Organic acid	Retention time (min)
Tartaric acid	2.780
Succinic acid	6.610
Malic acid	3.354
Citric acid	5.986
Gallic acid	10.609

Mixture of these standard organic acids was injected and their chromatograms are shown in Figure 3.59. In this mixture, quantities are equal in volume and concentration, but peak of gallic acid with 11.292 min. of retention time was reported as the largest amount of the organic acid. This is due to the higher response of gallic acid according to other organic acids. Therefore, response was done to determine the accurate area of gallic acid. A response factor was calculated by taking the area of malic acid as a standart and dividing it by the area of gallic acid, a correlation factor was calculated as 0.014. Multiplying the area of gallic acid by this factor gave the accurate area of standard gallic acid.

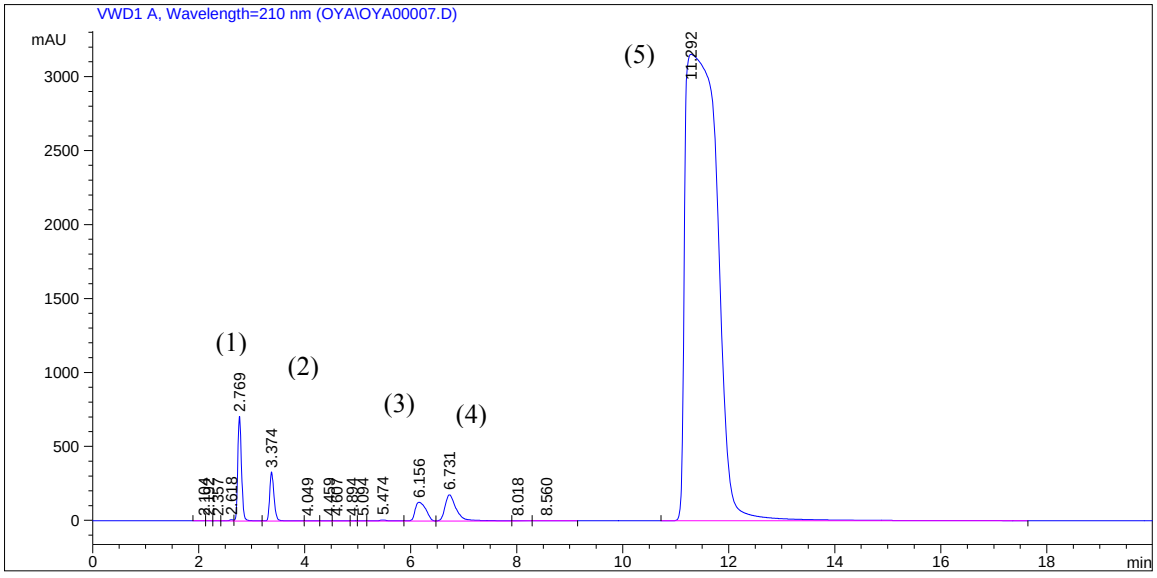

Figure 3.59. Chromatogram of mixture of five standart organic acids. (1) Tartaric acid, (2) Malic acid, (3) Succinic acid, (4) Citric acid, (5) Gallic acid.

Different sumac concentrates were determined for their organic acid compositions. Fig.3.60 represents the chromatogram of Gaziantep sumac concentrate for its organic acids.

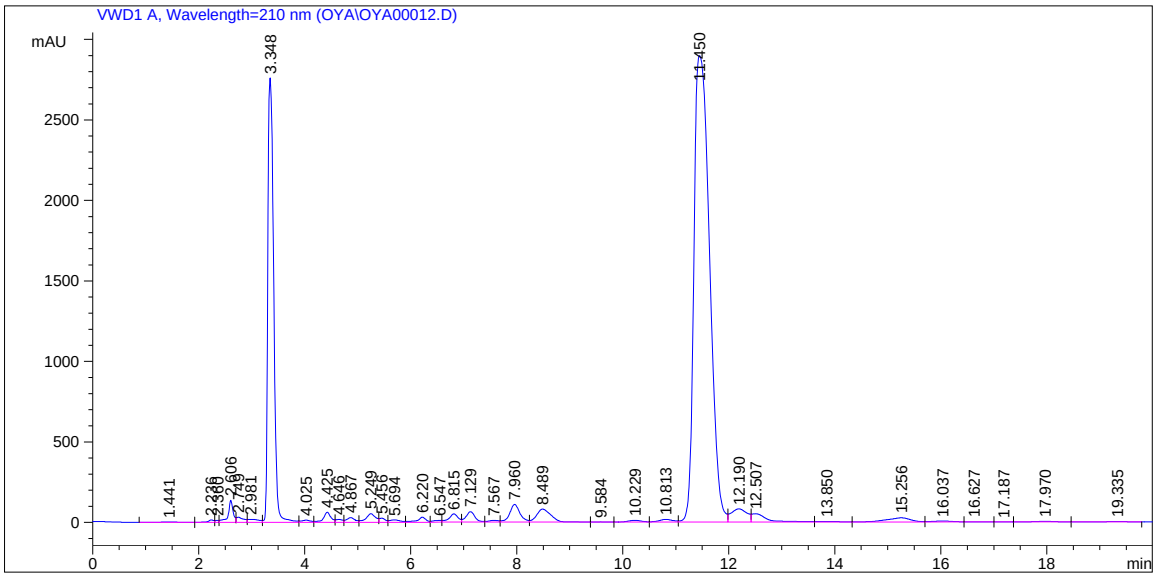

Figure 3.60. Chromatogram of organic acids contained in Gaziantep sumac concentrate

From Fig.3.60, it is shown that main organic acids found in sumac concentrate are malic acid and gallic acid when compared with the chromatogram of standard organic acids. After correlation of peak areas, it was concluded that 22.36% of total organic acid found in this sumac concentrate sample was malic acid and 22.38% was gallic acid.

Fig.3.61. represents the chromatogram for sumac concentrate of Siirt region. It is seen that, major organic acids found in sumac concentrate are again malic acid and gallic acid. % concentrations are different from Gaziantep sumac. In the Siirt sumac concentrate, 35.55% of total organic acid existing was malic acid and 28.58% gallic acid. This difference from Gaziantep sumac could be due to the regional differences.

Chromatogram of organic acids for concentrate of Nizip sumac is shown in Fig.3.62. Same result was obtained for Nizip sumac. Malic acid and gallic acid are the main organic acids included in this concentrates. It was concluded that 32.45% of total organic acids found in sumac concentrate was malic acid and 44.59% was gallic acid.

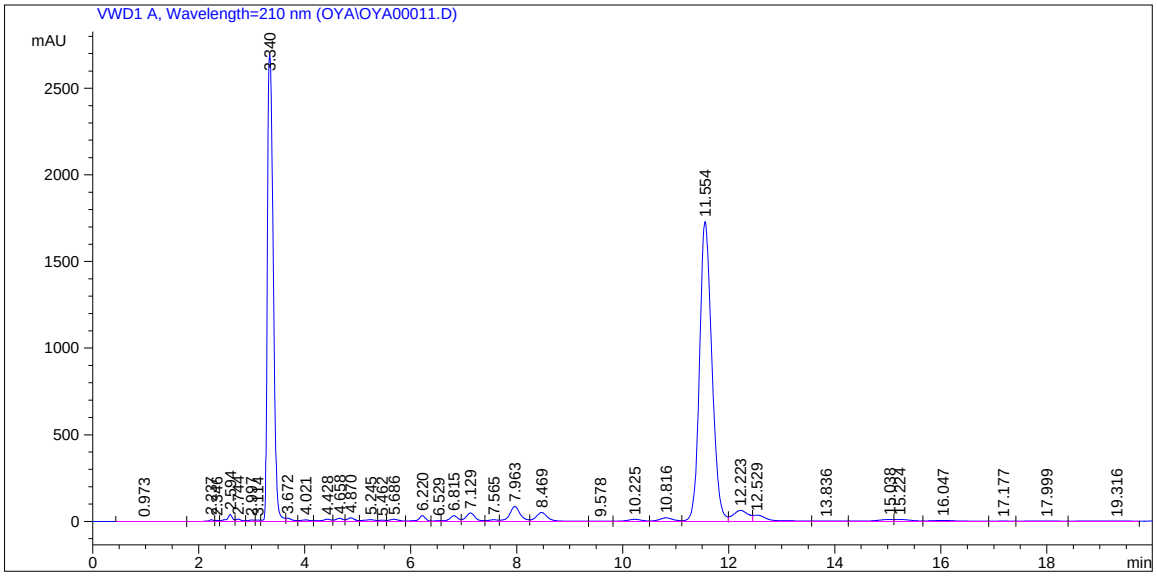

Figure 3.61. Chromatogram of organic acids contained in Siirt sumac concentrate

All chromatograms without certain difference represent the same organic acid profiles. It can be resulted that sumac concentrates were found to contain malic acid and gallic acid mainly. In all chromatograms, there are a lot of small peaks. These peaks are belong to the phenolic matter of sumac. Malic acid which is the main acids of many fruits and vegetables exists in sumac concentrates. Gallic acid is the second most abundant acid in sumac concentrate.

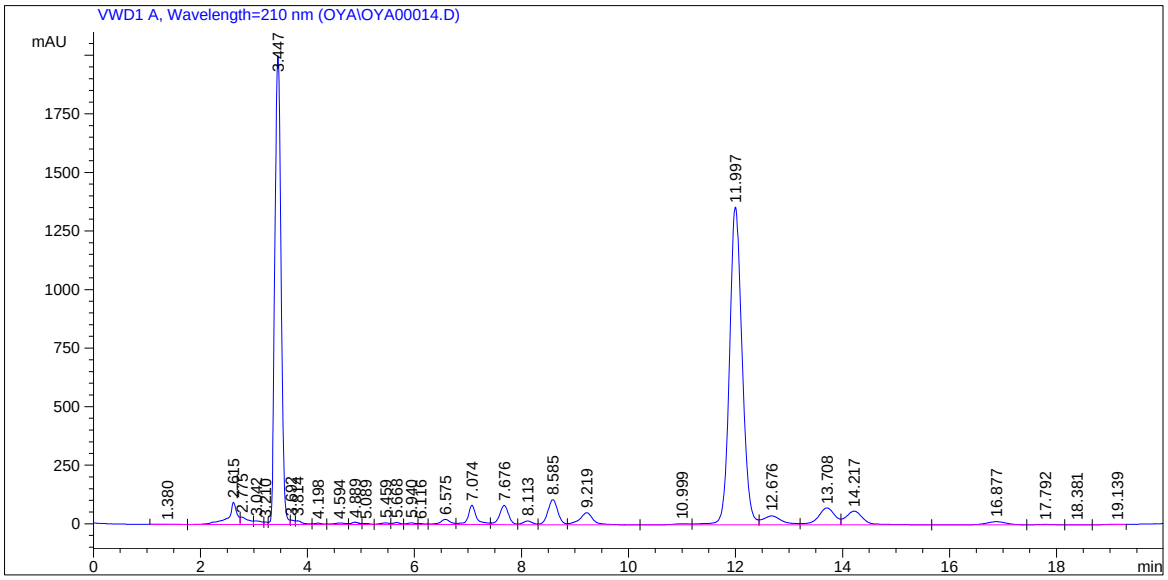

Figure 3.62. Chromatogram of organic acids contained in Nizip sumac concentrate

Fig.3.63 and Fig.3.64 represent the calibration curves of malic acid and gallic acid respectively. Concentration range of 0.05-1% was used for the calibration.

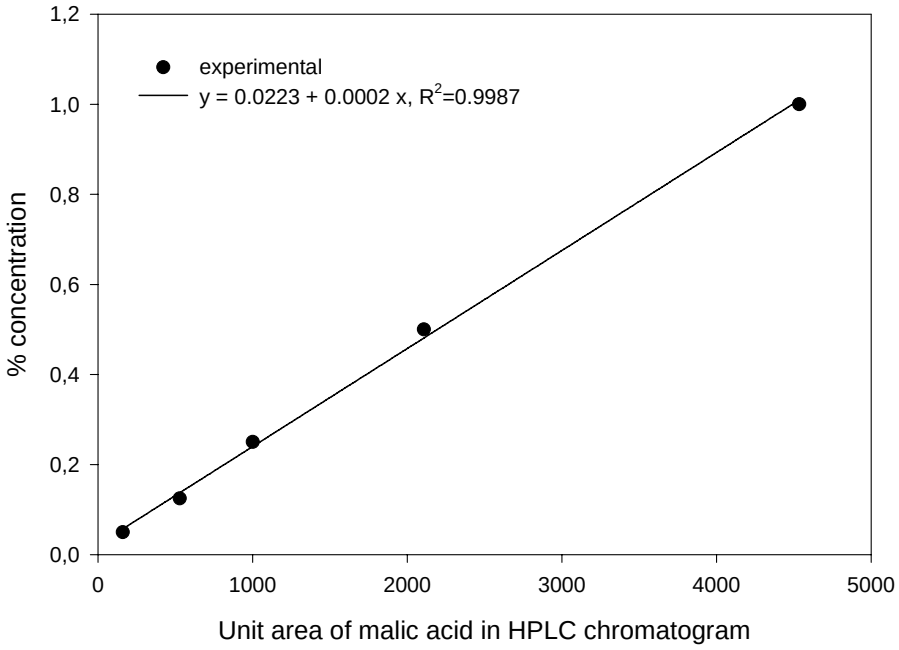

Figure 3.63. Calibration curve of malic acid

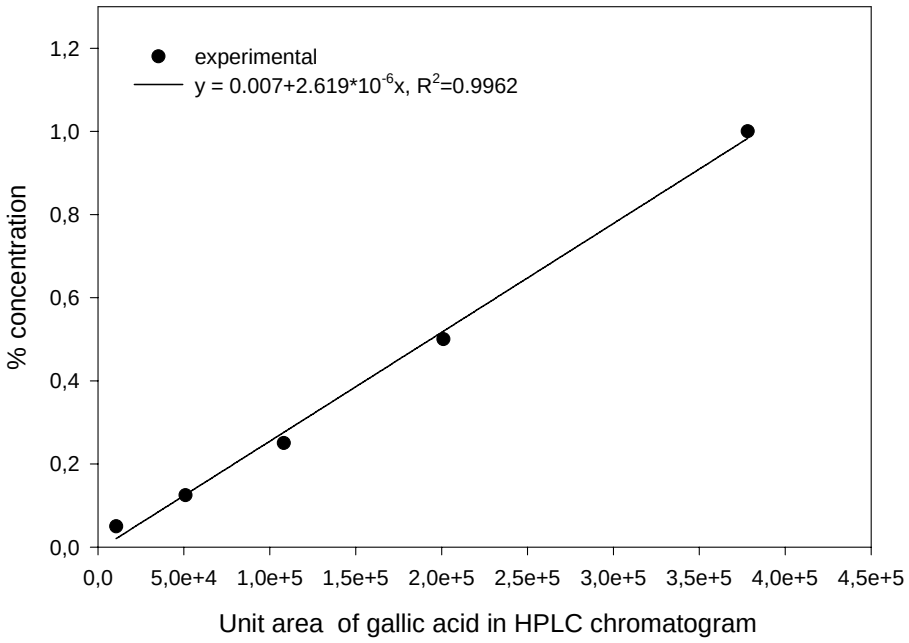

Figure 3.64. Calibration curve of gallic acid

Malic acid and gallic acid content of Gaziantep, Siirt and Nizip sumacs were determined by using the calibration curves contained in Figs.60, 61 and 62 respectively. Gaziantep sumac contains 42.67% malic acid and 10.162% gallic acid, Siirt sumac contains 41.89% malic and 9.54% gallic acid and Nizip sumac contains 32.83% malic and 8.56% gallic acid.

3.13.2. Identification of organic acids in sumac concentrates by Fourier transform spectroscopy (FT-IR).

Fourier transform spectroscopy was used in order to characterize and identify the organic acids found in sumac powder and sumac concentrate. Results were compared to HPLC analysis results.

Fourier transform spectroscopy is a measurement technique whereby spectra collected are based on the measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation. It can be applied to variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy, nucleic magnetic resonance, and electron spin resonance spectroscopy (http://www.wcaslab.com/tech/tbftir.htm).

FTIR offers quantitative and qualitative analysis for organic and inorganic samples. It identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The resulting spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to easily screen and scan samples for different components (http://www.intertek-cb.com/newsitetest7news/ftirlabs.shtml).

Fig.3.65 - Fig.3.67 show the FTIR spectra of sumac powder and sumac concentrate. FTIR spectra show the % Transmittance vs. wave length. Major component found in sumac by this method is again malic acid confirmed with HPLC results. When compared with the spectra of standard L-malic acid (Fig.3.69), similar appearance was obtained in spectra. First chemical bond was detected at 3377.89, whereas standard malic acid gave at the wave of 3636. Second chemical bond was detected at 1936.14 corresponding standard indicated at 1710. All other points detected in figures are so close the standard matter.

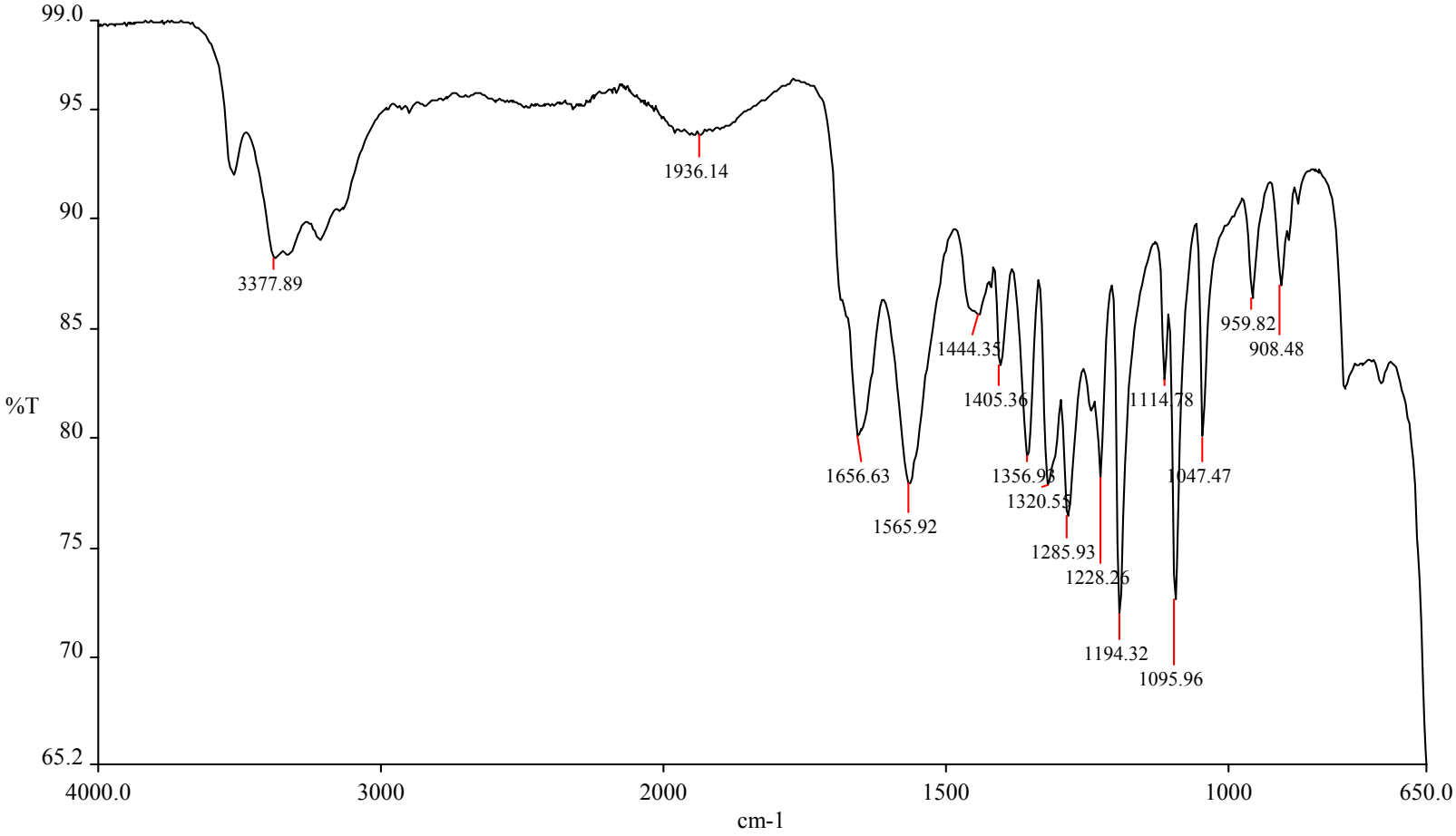

Figure 3.65. FT-IR spectra of sumac powder

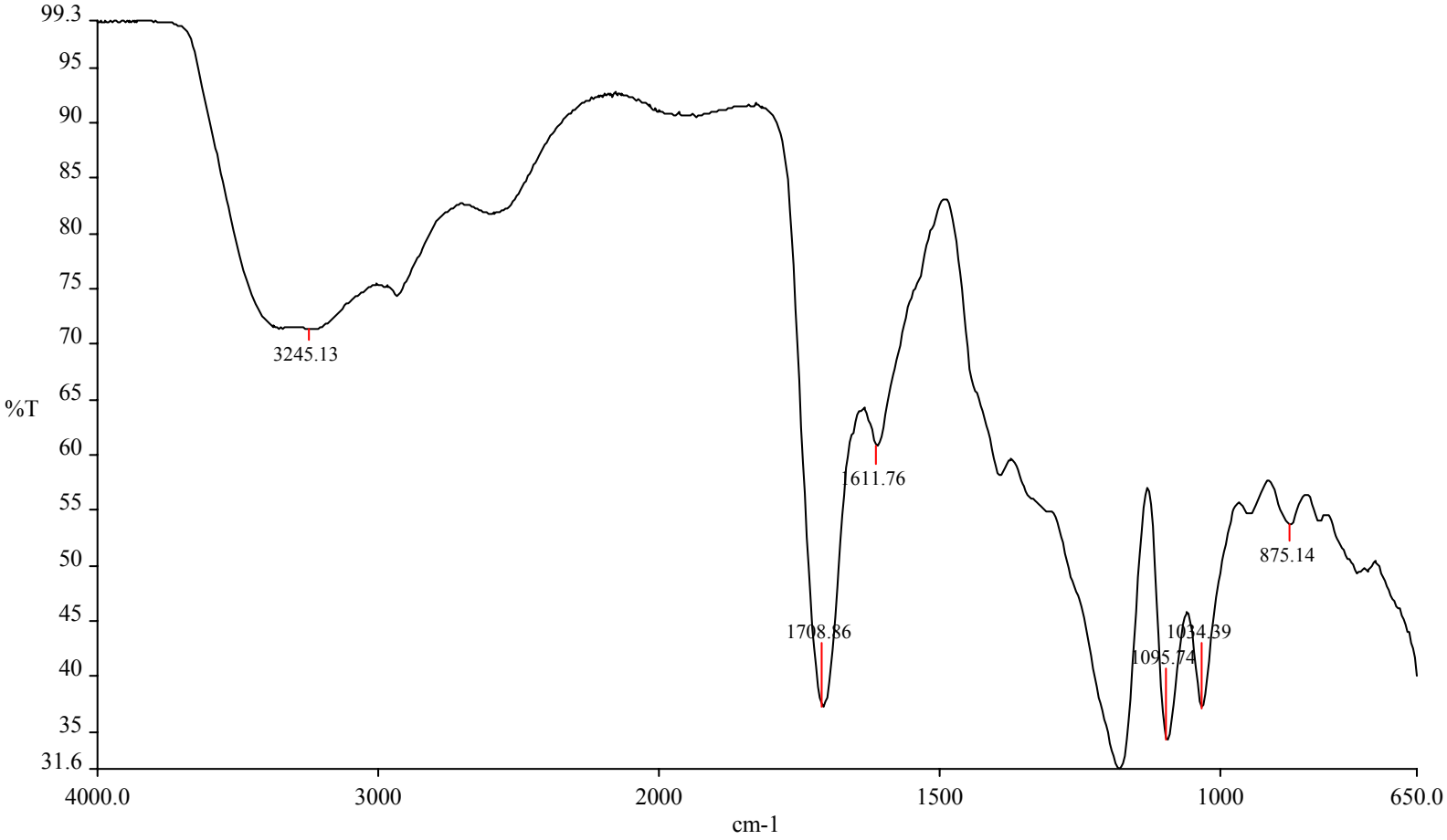

Figure 3.66. FT-IR spectra of sumac concentrate

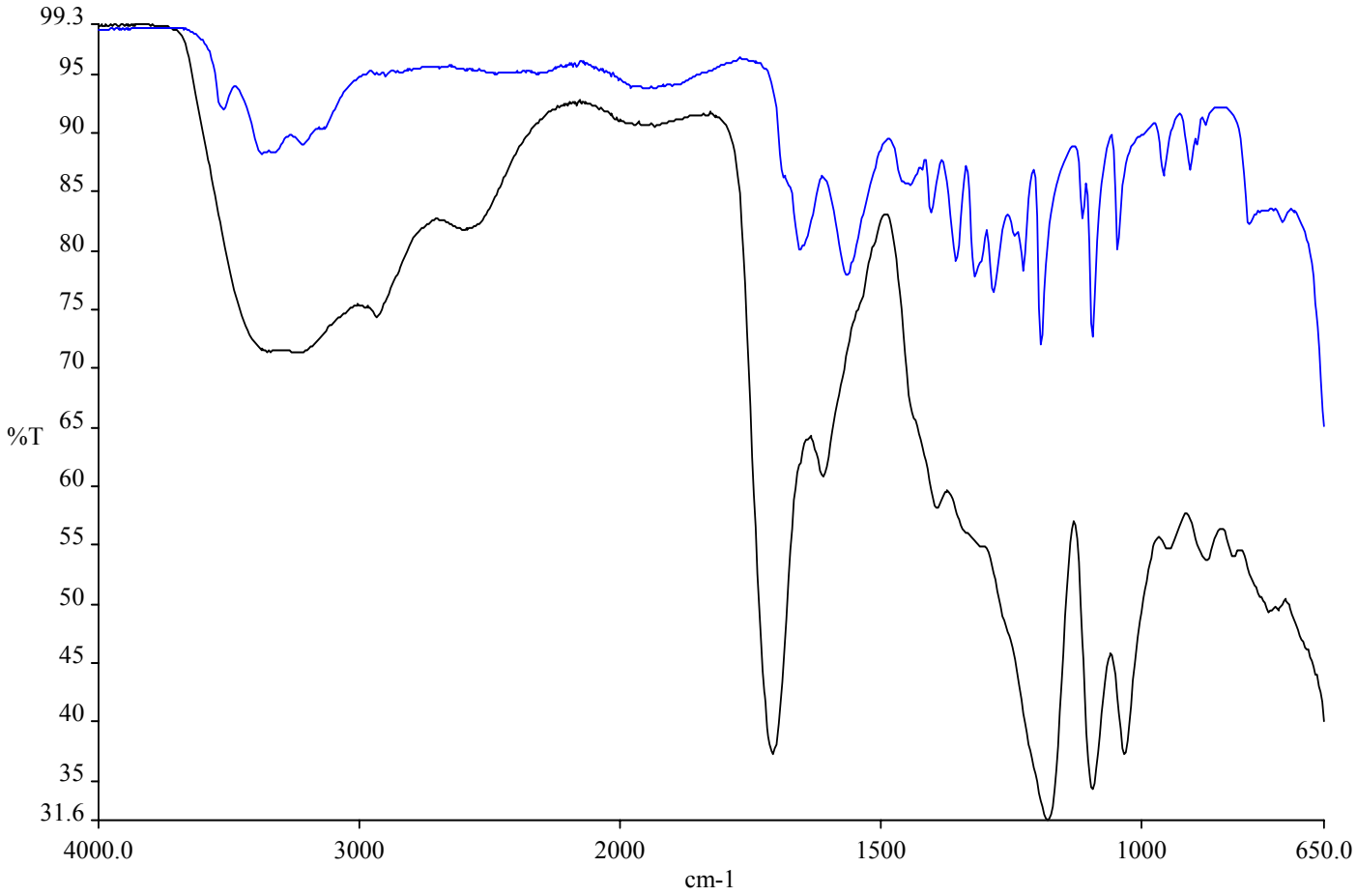

Figure 3.67. FT-IR spectra of sumac powder and concentrate

Figure 3.68. FT-IR spectra of standard malic acid

3.14. Heat Transfer Property of Sumac Concentrate on Rising Film Evaporator

To investigate the variation of the rate of evaporation of water with steam pressure, an experiment was done. The temperature of steam and the temperature of the evaporated vapor were recorded from the reading panel of the rising film evaporator.

Table 3.22 shows all readings on rising film evaporator at a constant vacuum of 0.72 bar and a feed rate of 16 l/h during whole operation. Average rate of cooling water was 8.0 liter/hour.

Table 3.22. Experimental results of measurements on rising film evaporator at constant vacuum, variable steam pressure

Exp. No	Steam pressure (bar)	Rate of evaporation (ml/min)	Ts (^oC)	Tv (^oC)	Temperatures (^oC)	
1	0.25	198.29	65	60	T_1=16.9	T_4=58
					T_2=29.6	T_5=32
					T_3=60.0	T_6=59.5
2	0.42	212.00	77	63	T_1=16.9	T_4=63.6
					T_2=31.5	T_5=23.6
					T_3=66.2	T_6=66.2
3	0.66	213.00	88	65	T_1=16.9	T_4=66.3
					T_2=33.3	T_5=24.0
					T_3=69.0	T_6=68.8
4	0.82	224	94	66	T_1=16.9	T_4=66.7
					T_2=32.9	T_5=35.6
					T_3=71.1	T_6=68.5
5	1.10	240.5	102	68	T_1=16.9	T_4=68.7
					T_2=34.2	T_5=27.3
					T_3=71.8	T_6=71.5
6	1.28	224.6	101	69	T_1=16.9	T_4=68.4
					T_2=34.1	T_5=26.9
					T_3=72.6	T_6=72.4
7	1.50	231.25	111	68	T_1=16.8	T_4=67.8
					T_2=33.3	T_5=48.3
					T_3=71.6	T_6=71.5
8	1.67	232.96	114	69	T_1=16.8	T_4=67.9
					T_2=33.7	T_5=52.7
					T_3=72.3	T_6=72.5

Using the experimental results in Table 3.23, rate of evaporation was determined depending on the temperature difference (ΔT).

The rate of evaporation, E is given by, E=Q/H

where E = rate of evaporation, kg/h

Q = rate of heat transfer, kj/hr

H = latent heat of vaporization of water at system pressure, kj/kg.

The rate of heat transfer, Q is given by, $Q = U_E . A_E . \Delta T_E$

where U_E = heat transfer coefficient, $kj/m^2.hr.^oC$

A_E = surface area for heat transfer, m^2

ΔT_E = temperature difference, ^oC.

The temperature difference, T_E is given by, $T_E = T_S - T_V$.

where T_S = temperature of the steam at pressure, ^oC

T_V= boiling point of water at system pressure, ^oC

In this study, A_E and H are constant, and so;

$E = K_1 . U_E . \Delta T_E$ where K_1 is a constant.

The heat transfer coefficient, U_E, will, in turn depend on the temperature difference, ΔT_E, so;

$U_E \propto (\Delta T_E)$

$E = K_2 . (\Delta T_E)^{n+1}$

where K_2 is a constant and n varies from 0.5 to 2.0.

The rate of evaporation can be increased by increasing the temperature difference, ΔT_E. In this study this was done by increasing the steam pressure, and hence the steam temperature, T_S.

when $E = K_2 . (\Delta T_E)^{n+1}$ equation was converted to linear form as follows:

$$\ln E = [\ln K_2 + (n+1).\ln(\Delta T_E)]$$

Therefore intercept of plot of ln(E) against $\ln(\Delta T_E)$, Fig.3.69 should give the constant K_2.

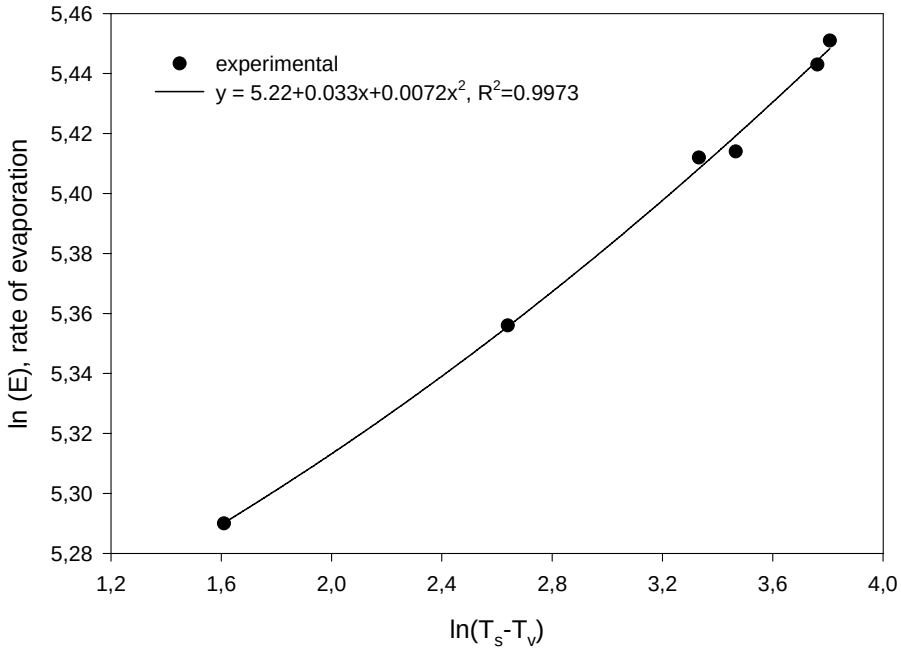

Figure 3.69. Variation of rate of evaporation vs. temperature difference of sumac concentrates during concentration in rising film evaporator.

Intercept of this equation was found as 5.22. This means that; $\ln K_2 = 5.22$.

Therefore, from all calculations above, rate of evaporation was determined in terms of temperature differences. This variation was explained as in Equation (3.20).

$$\ln(E) = 5.22 + 0.033\ (\ln(\Delta T_E) + 0.0072(\Delta T_E)^2 \qquad (3.20)$$

Then, this developed model (Equation. 3.20) can be used for the calculation of the evaporation rate of sumac concentrate during the concentration in rising film evaporator.

CHAPTER 4

4. CONCLUSIONS

The present study investigates the evaluation of quality parameters of sumac berries and concentrate. The physico-chemical properties of sumac berries were determined and different mathematical models were applied for the fittings of density and soaking characteristics.

The sorption isotherms of sumac berries and concentrates were determined. Yield of harvesting time of sumac berries affected their sorption isotherms. Oswin model was observed to be the most suitable mathematical expression to determine the sorption isotherms of both sumac berries and concentrate.

The sumac concentrate indicated Newtonian behavior. Increase in concentration caused a slight deviation from Newtonian behavior. This deviation was evident when Hershel-Bulkey model was applied. Parameters of this model (viscosity coefficient, K and flow behavior index, n) were determined.

Color was observes to be an important parameter for the quality of sumac concentrate. Zero and first-order kinetics were applied to color value variations of sumac concentrates at different temperatures and their activation energies were determined.

The outcomes of this study can be summarized as follows:

1. Non-processed new crop sumac extract has the highest quantity of anthocyanin when compared with new crop sumac concentrate which was concentrated in rising film evaporator. As a result, evaporation process reduced the anthocyanin content approximately to half.
2. Application of heat during extraction decreased the phenolic matter content.

3. Extract of sumac with stems has highest phenolic matter. This high value comes from stem characteristics.
4. There are several reasons in the variations in quantity of phenolic matter content. These were type of extraction, region of harvesting, type of harvesting.
5. Major organic acids of sumac concentrate were malic acid and gallic acid. Malic acid is the main fruit acid but gallic acid is important for the antioxidant property of sumac concentrate.
6. The rates of change of color parameters increased with temperature and concentration.
7. The variation of L, a, and b values were described by both the zero- and the first-order kinetics. However, the zero-order kinetic model was preferred because of the better fit. At low temperature and concentration, the kinetic constants were also low.
8. The Oswin model was the best fitted model for 1-year old crop whole sumac berry, whereas for new crop whole sumac berry, Halsey was the best one. For old crop sumac skin, BET linear and for new crop sumac skin, Halsey were determined as the best fitted models.
9. Sumac concentrate seems to exhibit a slight yield stress with shear-thinning behavior corresponding to the most concentrate (70^{o}Brix) sample at the lowest temperature (20^{o}C) studied. As expected, dilution gave rise to conform to the Newtonian behavior.
10. The exponential model was observed to give a slightly better fit than the power law as at each temperature. For the determination of effect of total soluble solids on rheological behavior of sumac concentrate.
11. The increasing activation energy values with increasing total soluble solid indicated that viscosity was more sensitive to temperature for samples having higher total soluble solids.

4.1. Suggestion for future work

Some quality parameters and physico-chemical properties of both sumac berries and sumac concentrate were evaluated in this study. Although the phenolic matter content with respect to aging was studied, this was inadequate and therefore further studies related with stability evaluation of both berries and concentrates should be carried out. The microbial deterioration of the concentrate below a certain brix should also be investigated in detail together with storage conditions of both berries and concentrate.

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3. PRINTED PAPERS
A. INTERNATIONAL JOURNALS

1) Özkanlı, O. and Tekin, A.R. Rheological behavior of sumac concentrate. *International Journal of Food Properties* (accepted manuscript).
2) Özkanlı, O. and Kaya, A. (2005). Storage stability of butter oils produced from sheep's non-pasteurized and pasteurized milk. *Food Chemistry*. 100, 1026-1031.

B. CONGRESS

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C. PROJECTS

1) TEKİN Ali Rıza, BOZKURT Hüseyin, BAYRAM, Mustafa, ÖZKANLI, Oya. 'GAP tarımsal ürünlerinde Pestisit ve PAH kalıntılarının araştırılması, Avrupa Birliği Standartlarına uygunluğunun tespiti' DPT Projesi, Proje Kodu: 2003 K 120490-3.