Watermelon (*Citrullus lanatus* Thunb) is cultivated throughout the globe in 96 countries. There are around 1200 varieties of watermelon found in different parts of the world. Total global production of watermelon was 108.9 million tons whereas India’s production was 0.4 million tons in 2013 (FAO, 2016). The leading growers were China, Turkey, Iran, Brazil and United. Watermelon is cultivated in hot and dry climate with mean temperature of 22-30ºC and little available water. The shape of fruit varies from globular to oblong. It is harvested in summer months and liked by consumer due to its delicate flavor and attractive color (Tressler & Joslyn, 1971).

2.1. Watermelon Composition

Watermelon is the third most popular fruit (Zhao et al., 2013) in the world containing good quantity of nutrients. Pigment extracted from watermelon acts as functional ingredient and can be incorporated into breakfast cereals, frozen dairy desserts, yoghurts, spreads, candy, carbonated beverages, confectionary, sauces and soups etc (Olempska, 2006).

Chahal & Saini, (1999) analyzed bottled *Indo-American hybrid* watermelon juice and reported 6.4-9.0 g/100g soluble solids, 0.05-0.08g/100g acidity, 5.52g/100g reducing sugars and 7.76g/100g total sugars. Quek et al., (2007) reported 12.1°Brix total soluble solids, 5.5 g/100ml glucose, 6.8 g/100ml fructose and 1.2 g/100ml sucrose in watermelon (*Sugar baby*) juice. The previous studies on physico-chemical analysis of watermelon juice reported 91.82% moisture, 0.09-0.13% acidity, and 5.2 mg/100g ascorbic acid (Tee et al., 1988; Fila et al., 2013).

Pinto et al., (2011) found variations in lycopene content in *Portuguese* watermelon fruits measured by HPLC analysis. Seedless watermelons had higher lycopene content of 6.1 to 11.2 mg/100g fresh weight than seeded type that contained 3.5 to 7.6 mg/100g fresh weight. Davis et al., (2004) evaluated lycopene and total carotenoid content in flesh of watermelon using spectrophotometric method. Lycopene in flesh of watermelon ranged from 1.0-8.1 mg/100g. It was found that yellow and orange watermelon contained 0.3-1.3 mg/100g total carotenoids.
Tadmor et al., (2005) analyzed the carotenoids in red, yellow and orange watermelons. HPLC method to extract carotenoids was used and results were compared with color mutants of tomato. Red watermelon contained high levels of lycopene (4.8 mg/100g) whereas orange watermelon contained an orange pigment called pro-lycopene (0.8 mg/100g). Watermelon was found to be rich source of lycopene as compared to tomato. Perkins-Veazie et al., (2006) determined the lycopene content of 50 commercial cultivars of seeded and seedless red fleshed watermelons. Scanning colorimetric and spectrophotometric assays of total lycopene were used to separate watermelon cultivars on the basis of lycopene content into low (<5mg/100g fresh wt.), average (5-7mg/100g fresh wt.), high (7-9mg/100g fresh wt.), very high (>9mg/100g fresh wt.) cultivars. Cultivars vary greatly in lycopene content ranging from 3.3-10mg/100g. Most of the seeded hybrid cultivars had average lycopene contents with few exceptions such as ‘Summer Flavor 710’ and ‘Ole’ which were high in lycopene having 8.23mg/100g and 7.17mg/100g respectively. The seedless watermelon cultivars such as ‘Extazy’, ‘Hazera 5109’ and ‘Xite’ fruits have high lycopene content ranging from 9.3-9.9 mg/100g. Total carotenoid content varied from 3.7-12.2 mg/100g fresh wt. among red fleshed watermelon cultivars.

Watermelon kernels contained about 14.9-35.7% protein (full fat free basis) and 35-59% on fat free basis (Ige et al., 1984, De-Mello et al., 2000). The lipids were found to be rich in linoleic and oleic acids while the protein was rich in arginine, glutamic acid, aspartic acid and leucine amino acids (El-Adawy et al., 2001). Inuwa et al., (2011) determined nutrient composition of watermelon juice. The moisture, ash, fat, crude fibre, crude protein and carbohydrate content in the three varieties (‘Jaji’, ‘Zaria’, ‘Central Market’) of watermelon fruit varied from 93.4-94.6%, 0.5-0.55%, 0.10-0.15%, 0.30-0.40%, 0.50-0.60% and 4.00-5.00% respectively. The magnesium, calcium and iron content varied from 34.93-38.87, 0.62-0.71 and 0.18-0.33 mg/100g. If watermelon cannot be consumed within shelf life period, it can be dried into powder to use as a supplement food instead of spoiling the fruit.

Tlili et al., (2011b) analyzed the effect of fruit sampling area on bioactive compounds and antioxidant activities of different watermelon cultivars. Lycopene content in different sampling areas like blossom end, stem-end, heart and peripheral reached the highest value in ‘P503’ (10.2 mg/100g fw) and ‘Giza’ (9.7 mg/100g fw) cultivars. Bioactive compounds and antioxidant activities were affected by genotype and sampling area. Choo & Sin, (2012) analyzed lycopene, ascorbic acid and antioxidant activities of
red and yellow fleshed watermelons. The flesh of red-fleshed watermelon had higher ascorbic acid (8.6 mg/100g) and lycopene (0.95 mg/100g) contents compared to the ascorbic acid (5.2 mg/100g) and lycopene (0.04mg/100g) contents of the flesh of yellow-fleshed watermelon. The lower value of lycopene was due to variation in cultivars depending on geno type and environmental conditions.

2.2. Variation of pigment content during ripening

Color of mesocarp is usually white when unripe that changes into red on maturity. Kirk & Tilney-Basset, (1978) showed that lycopene biosynthesis increased dramatically during the ripening process as chloroplast undergoes transformation to chromoplasts. Environmental conditions during production such as light intensity, temperature and irrigation can change the lycopene content by 10-20% (Perkins-Veazie et al., 2001; Leskovar et al., 2004). Synthesis of carotenoids and accumulation of lycopene within the chromoplasts in watermelon fruit results in characteristic red color of flesh (Perkins-Veazie et al., 2006; Grassi et al., 2013).

Pardo et al., (1997) found that the formula 1000 a/(b+L) generated from tristimulus colorimeter values was highly correlated with visual color rankings of watermelon for all red fleshed melons. The colorimeter readings ‘a’ and ‘1000 a/(b+L)’ were best correlated with levels of extracted lycopene from local and commercial cultivars of melon. Perkins-Veazie et al., (2001) reported that average content of lycopene in watermelon was 4.87mg/100g on fresh weight basis. Harvest maturity, day/night temperature, vine health, soil fertility, irrigation and light intensity had an effect on lycopene formation in watermelon. Seedless types samples tended to have higher amounts of lycopene (5.0mg/100g on fresh weight basis) than seeded type. Tristimulus colorimeter a* and chroma values were positively correlated with lycopene values.

Bangalore et al., (2008) studied the ultrastructure of watermelon (cv Hazeraa SW 1) mesocarp of different maturities using transmission electron microscopy. Micrographs from immature fruit showed incompletely formed chromoplasts. The chromoplasts changed from a less organized globular form in immature to symmetrical form in mature and again to an asymmetrical form in over mature watermelons. In over mature fruit, breakdown in ultrastructure leads to exposure of lycopene to action of cyclases that catalyze the lycopene into β-carotene or to oxidation.
Kang et al., (2010) studied the expression of carotenoid-related genes during the development and ripening of five watermelon cultivars namely “Zaohua” (red), “96B41” (pink), “307chaofeng” (yellow), “Unknown” (orange) and “Sanbai” (white). The carotenoid content estimated by HPLC and dot blot hybridization was compared with the expression of standard carotenoid genes like Psy, Pds, Zds, CrtIso, Lycb, Chyb, Nced1, Nced2, Nced3 during fruit development. In red and pink varieties, the decrease of gene expression for Lcyb and Chyb after 30 days of pollination may be consistent with the high accumulation of lycopene and β-carotene. In yellow variety, expression of detected genes increased markedly with the onset of maturation. The expression of all detected genes decreased rapidly in the white color variety upon fruit ripening which may be attributed to reduction in metabolic flux in the carotenoid pathway.

Liu et al., (2010) determined lycopene content in Diploid (2X), Triploid (3X) and Tetraploid (4X) types of red fleshed watermelon. Petroleum ether, ethyl alcohol and methanol were used to extract lycopene from watermelon. The lycopene content of diploid watermelon was 3.3-5.5 mg/100g fruit where as triploid fruit contained 4.1-6.2 mg/100g and tetraploid fruit contained 3.8-5.9 mg/100g. Studies on changes in pigment content during fruit development revealed that lycopene content was low in young fruit, high in fully mature fruit and decreased in over mature fruit.

Tlili et al., (2011a) analyzed the bioactive compounds and antioxidant activity in watermelon cultivars (Crimson sweet, Dumara, Giza, P503 and P403) during development and ripening at white, white-pink, pink and red-ripe stages. Different stages of ripening were identified on the basis of TSS as white stage (≥2ºBrix), white pink stage (4ºBrix), pink stage (6ºBrix) and red ripe stage (≥8ºBrix). The ripening stages significantly influenced lycopene, β-carotene content and lipophillic antioxidant activity. At the red ripe stage, P503 cultivar showed the highest amount of lycopene (6.45 mg/100g fw), whereas the Dumara cultivar showed the highest level of β-carotene (0.21 mg/100g fw). Giza cultivar scored first for total phenol (26 mg GAE/100g fw), flavonoid (26 mg RE/100g fw) and total vitamin C (20.4 mg/100g fw) contents. Lycopene content in five different watermelon cultivars was in the range of 0.02-6.45mg/100g during successive stages of fruit development. β-carotene was not detected at white and white-pink stages of ripening but varied in the range of 0.01-0.21 mg/100g at pink and red ripe stages.

Soumya & Ramana-Rao, (2014) estimated the biochemical composition and antioxidant activity of four watermelon cultivars during development and ripening. The
Ascorbic acid values were in the range of 0.6-6.2 mg/100g at different stages of ripening of watermelon (‘Suman 235’) fruit. Total, reducing and non-reducing sugars were in the range of 1.98-8.14, 0.08-2.87 and 1.90-5.27% respectively in ‘Beauty’ watermelon cultivar which were higher than other cultivars. The highest lycopene content was estimated in the ‘Beauty’ watermelon cultivar during different stages of ripening. A strong positive correlation was observed between total polyphenols and lycopene with antioxidant activity.

2.3. **Storage of fresh watermelon fruit**

Fish & Davis, (2003) investigated effects of frozen storage on lycopene stability in watermelon puree and cubes for 1 year and observed 30-40% losses during storage at -20°C and 5-10% losses at -80°C. Lycopene was more stable in puree as compared to cubes at -20°C whereas no difference was observed in lycopene content of cubes or puree held at -80°C.

Perkins-Veazie & Collins, (2003) studied effect of maturity, storage and minimal processing on lycopene levels of watermelon. Seeded and seedless red fleshed watermelon contained 3.6-7.8mg/100g lycopene whereas orange or yellow fleshed watermelons had less than 0.5mg/100g lycopene. Under ripe and overripe watermelons had about 20% less lycopene than fully ripe watermelons with maturity effects dependent on variety. Lycopene content increased from 3-26% on ripening. ‘Black Diamond’, a light red, heirloom type variety had the largest gain in lycopene content with ripeness. The soluble solids content was low in under ripe as compared with ripe or overripe watermelons. There was loss of 6 to 10% of lycopene content during 2 weeks of storage at 5 to 13°C. About 10% lycopene was lost when held at 2°C for 10 days in darkness. No loss of lycopene in minimally-processed watermelon was found after 4 days storage.

Melons of a seeded and a seedless variety were cut into 5 cm cubes, placed in unvented polystyrene containers, sealed and stored at 2°C for 2, 7 or 10 days (Perkins-Veazie & Collins, 2004). Lycopene content decreased to 6 and 11% after 7 days of storage for *Summer Flavour 800* and *Sugar Shack* melons, respectively. β-carotene and cis lycopene contents were found to be 2 and 6 mg/kg for *Summer Flavor 800* and *Sugar Shack*, respectively and did not change with storage. After 10 days of storage, CIE L* values increased while chroma values decreased, indicating a lightening in color and loss of color saturation. Symptoms of chilling injury, like juice leakage, or lesions...
were not seen on the fresh-cut watermelon after 10 days storage at 2°C. Carbon dioxide levels increased and oxygen levels decreased linearly during storage, creating a modified atmosphere of 10 kPa each of CO\(_2\) and O\(_2\) after 10 days. Fresh-cut watermelon held for 7 or more days at 2°C had a slight loss of soluble solids, color saturation and lycopene which was most likely caused by senescence of fruit.

Perkins-Veazie & Collins, (2006) observed changes in carotenoid content of intact watermelons during storage. Three types of watermelon, open-pollinated seeded, hybrid seeded, and seedless types were stored at 5, 13 and 21°C for 14 days to study the effect of storage on flesh color, composition, and carotenoid content. There was increase in 11-40% lycopene and 50–139% \(\beta\)-carotene in watermelons stored at 21°C whereas little change in carotenoids content was observed in fruit held at 13°C which indicated that carotenoids biosynthesis in watermelons was affected by storage temperature. Radulovic et al., (2007) studied changes in quality parameters in watermelon during storage at 20°C and 85% R.H. for 7 and 14 days. Positive correlation between weight loss and decrease of reducible sugars was highly significant. The reducing sugars decreased by 42.5% after seven days of storage. The changes can be related with the loss of sweetness after first week of storage. In the second week of storage, the predominant changes were in physical properties of watermelon.

Yau et al., (2010) analyzed the size, weight, moisture content, total soluble solids, color, pH, total acidity and sugar content of red seedless watermelon during storage at 28°C and 70-80% RH. The average weight, diameter and length of red seedless watermelon fruit were in the range of 3970-7640g, 20.5-23.5cm and 20.7-24.3cm respectively. The moisture content, total soluble solids, pH, total acidity and fructose content of watermelon were 91.8-94.1%, 9.13-7.43°Brix, 5.10-5.34, 0.09-0.13% and 2.04-2.51% respectively on fresh weight basis during storage. The study concluded that the optimum eating quality of watermelon stored at 28°C and 70-80%RH was within one week after harvest.

2.4. Watermelon juice concentration and powder

Sharma & Maguer, (1996) found that lycopene loss was proportional to the concentration and therefore the degradation rate increased due to both increased lycopene and total solid concentration during heating. Mcglynn, (2001) produced watermelon concentrate and used it as a feedstock for further purification or directly as a food
ingredient or dietary supplement. Lycopene content of the pureed melon ranged from 7.3-8.6 mg/100g (dry weight). Lycopene retention in the dry powder ranged from 33.5-47.9%. Saurez-Quintanilla et al., (2003) studied the rheological behavior of papaya, melon and watermelon concentrates. Power Law model explained the rheological behavior of watermelon concentrates with the coefficient of determination of 0.993. Nature of flow behavior of all the concentrates was pseudoplastic.

Sogi, (2003) studied the effect of concentration (7-50ºBrix) and temperature (5-50ºC) on viscosity of watermelon juice and reported that apparent viscosity of watermelon juice increased with increase in total soluble solids content and decreased with temperature. Results revealed that apparent viscosity of watermelon juice concentrate decreased with increase in spindle speed at selected temperature indicating its non-Newtonian pseudoplastic flow behavior. The value of coefficient of determination for observed and computed values was 0.955 which indicated that exponential model well explained the relationship within the limits.

Perkins-Veazie & Collins, (2006) determined the changes in carotenoid content during concentration of watermelon juice. During extraction of juice, heating and addition of pectinase increased the juice yield by 4% but reduced the recovery of lycopene and total carotenoids. The increase of total soluble solids to 42ºBrix at 50ºC increased the lycopene content fivefold but reduced β-carotene by 40-50%. Results showed that pasteurization had no effect on individual carotenoid content of the juice but may have helped stabilize the color of the juice during storage.

Sogi et al., (2010) used central composite design to analyze the effect of particle size (0.075, 0.15, 0.25, 0.355, 0.425 mm), temperature (1.6, 5, 10, 15, 18.4ºC) and total soluble solids (14.77, 25, 40, 50, 65.23ºB) on the rheological properties of watermelon juice. Experimental values of consistency coefficient k, varied from 0.178-0.628 Pa s^n and flow behavior index n from 0.281 to 0.949. Results revealed that coefficient of determination (R^2) and standard error for consistency coefficient k were 0.84 and 0.043 and for flow behavior index n were 0.42 and 0.102 respectively. Surface graphs showed that k value increased with increase in total soluble solids and particle size while decreased with temperature. Gomes et al., (2011) concentrated watermelon juice by reverse osmosis on a pilot plant unit equipped with polyamide composite membranes at 30ºC, 60 bar trans membrane pressure and 650 h^-1 recycle flow rate. The total solids and total titrable acidity (% T.A.) were increased from 7.07 to 29.6 g/100g and 1.21-3.55% respectively in the watermelon juice with increase in total soluble solids from 8 to 30
g/100g by reverse osmosis process. Lycopene content and antioxidant activity of watermelon juice increased from 3.1-10.1mg/100g and 0.34-0.81 µmol trolox/g respectively with increase in total solids from 8 to 30 g/100g by reverse osmosis process.

Quek et al., (2007) analyzed the physicochemical properties of spray dried watermelon powders. Increase in the maltodextrin (3-5%) and temperature (145, 155, 165 and 175°C) significantly decreased the moisture content and water activity of spray dried watermelon powder. The lycopene content of spray dried watermelon powder decreased from 95.4 to 72.5 mg/100g with change in temperature from 145-175°C. Depending on the inlet temperature lycopene was concentrated approximately 20-30 folds compared with raw fruit by weight basis. Colorimetric analysis showed that the L*, a*, b*, hue and chroma values changed with the inlet temperature. Increase of maltodextrin also affected the pigment content due to dilution of pigment. Correlation coefficient between lycopene and hue angle of spray dried watermelon powder was in the range of 0.946.

Gomes et al., (2014) estimated the lycopene content and antioxidant activity of spray dried watermelon powder prepared using lab spray dryer with experimental conditions of 180°C inlet temperature and 90°C outlet temperature, 7 bar atmospheric pressure, 700L/h air flow rate, 34 ml/min feed flow rate and mixture of Arabic gum and maltodextrin as encapsulating agents. The results showed an improvement of 216 and 192.5% in the lycopene content and antioxidant activity respectively in the watermelon powder when compared to the watermelon juice. Arya et al., (1985) concluded that freeze dried watermelon powder was stable in the water activity (a_w) range of 0.22-0.25 whereas caking started when water activity value increased beyond 0.33.

2.5. Juice Processing and waste generation

The majority of watermelon is consumed in fresh form and negligible quantity is processed. Watermelon juice could be a better alternate to handle surplus produce in peak season and give highly pigmented product for food application. The surplus produce can be utilized for the extraction of juice. The watermelon juice with functional properties can be utilized for the production of mixed juices, nectars, crush and fruit cocktails, concentrate and powder, whereas, the rind for products like pickle, preserve, pectin etc (Lazos, 1986). Watermelon pomace is a concentrated source of lycopene having potential application in food products with health claim. The pomace generated during processing of cull fruit or watermelon damaged during production, processing and marketing can be
extracted for pigment where as the seeds can be used for oil and protein for human consumption. Utilization of lycopene from watermelon waste in different food products would increase their aesthetic and therapeutic value and preventing its disposal into the rivers, canals, and / or soil. Wastes are those end products of food industry that are not recycled or used for other purposes. These wastes have potential use if there are appropriate technical means to handle it and the value of the subsequent products exceeds the cost of reprocessing.

Crandall & Kesterson, (1981) reported 41.5% juice, 7.5% pulp, 1.5% seeds and 49.6% rind. Uddin & Nanjundaswamy, (1982) reported 60% pulp, 31% rind, 5.4% peel and 3.1% seeds. Hayoglu & Fenercioglu, (1990) observed 50% juice yield while Shin et al., (1978) found 56.2% juice from watermelon. Watermelon contained 42% juice, 33.64% rind and 23.59% pomace (including seeds) on wet basis (Sogi, 2003). The waste generation from watermelon is in the form of cull fruits, pomace, seed and rind. Arocho et al. (2012) found that moisture, pH, TSS and lycopene of fresh watermelon pomace were 90.2-91.0%, 5.1-5.2, 8.4-9.7°Brix and 20-24 mg/100g on wet basis respectively. Lycopene content of pomace was about 4.5 times higher as compared to flesh tissues.

2.6. Drying characteristics of watermelon pomace

Higher moisture content of watermelon pomace makes it susceptible to microbial decomposition leading to environment problems (Kerje & Grum, 2003). However, it can be preserved by reducing the moisture to a safe level where microorganisms cannot grow and cause spoilage (Falade et al., 2007). Dehydrated waste can be stored and easily utilized for the extraction of bioactive compounds. Lycopene is one of the most important bioactive compounds having tremendous potential in preventing cancers (Giovannucci, 1999; Bramley, 2000; Weisburger, 2002; Omoni & Aluko, 2005).

Drying is one of the oldest methods of preservation (Mudgal et al., 2009). Drying changes the physical and biochemical form of fruit leading to shrinkage and change in colour, texture, taste etc. At low humidity, the dried product can be kept without special packaging for several months. Drying processes are energy intensive and knowledge about their efficiency and optimum operating conditions is vital for the economical operation of dryers. For heat sensitive materials such as food, the loss of quality relating to color, nutrients, taste, and texture is another important factor to be considered simultaneously with energy conservation.
Various mathematical models used for drying/dehydration of foods, can be categorized as theoretical and empirical. Theoretical models are based on molecular diffusion (Becker & Sallans, 1955; Brooker et al., 1974) while drying kinetics may be represented by Fick’s law of diffusion (Crank, 1975). Empirical models, developed to describe the drying kinetics of cereal grains (Thompson et al., 1986) give best results in predicting their drying behavior. However, the applicability of these equations is restricted to the conditions in which they were derived (Brooker et al., 1974).

Drying of biological material is diffusion controlled process and may be represented by Fick’s law. The simplified solution to the diffusion equation, widely used for describing the drying behavior of biological materials (Brooker et al., 1974; Byler et al., 1987), is also called logarithmic model. However, it has been observed that this model did not adequately explain the drying behavior of many products. Page’s model has also been widely used to describe the drying behavior of a variety of biological materials with better results than the earlier ones (Misra & Young, 1980; Byler et al., 1987; Shivhare et al., 1991). The Arrhenius law can be used to relate the drying rate constant to air temperature. Drying process and subsequent storage of dried product require knowledge of the sorption behavior for designing dryer and/or storage structure as well for predicting changes during drying and storage as a function of temperature and relative humidity.

Choice of drying method depends on the type of food, the quality level to be achieved and the cost that can be justified (Potter, 1996). Sun drying has been the most common and traditional method practiced all over the world. Sun drying is dependent on climate or weather condition and is very slow therefore not suitable for many high quality products. Dehydration or mechanical drying involves moisture removal under controlled conditions of temperature, humidity and airflow rates. The mechanical dryers may vary from simple home set to large commercial units, which may be provided with trolleys, fans, temperature and humidity regulators (Lal et al., 1986).

Falade et al., (2007) studied kinetics of mass transfer during osmotic dehydration of watermelon slices. Mass transfer during osmotic dehydration was modeled using Fick’s second law of diffusion. Water diffusivities for variable thickness of watermelon slices at different temperatures were in the range of 0.1030×10⁻⁹ to 3.549×10⁻⁹ m²/sec. Activation energy for moisture and solids diffusivity ranged from 5.09 to 32.77 kJ/mol and 3.43 to 32.38 kJ/mol, respectively. CIE color parameters of fresh, osmosed and osmo-oven dried watermelon revealed that L*, a*, b*, color intensity and chroma values increased with increase in osmotic solution concentration in osmosed and osmo-oven dried watermelon.
Water diffusivity of watermelon slices increased with the temperature but decreased by increasing the thickness of the samples.

Arocho et al., (2012) studied the effect of drying methods such as cabinet and drum drying and storage time on lycopene content and color of watermelon pomace. The moisture, ash, fat, protein, total dietary fiber and carbohydrates contents of drum dried and cabinet dried watermelon pomace were in the range of 11.92-13.25, 3.46-3.56, 0.38-0.62, 6.51-12.61, 10.27-14.03 and 56.06-67.36% (w.b.) respectively. The average lycopene content of dried samples was 1.49 mg/g which is greater than for fresh watermelon pomace (0.201 mg/g dry basis). Lycopene loss occurred in both the drying methods but drum drying showed more loss that might be due to the fact that samples in the drum dryer were exposed to high heat and light, which caused a higher loss as compared to cabinet dryer. In terms of color, drying resulted in an increase in $L^*$ and $b^*$ but decrease in $a^*$ value. Cabinet drying was found to be the better method for preserving the color and lycopene content of watermelon pomace. Lycopene in dried pomace was stable after one year under frozen storage condition and vacuum-packaging.

2.7. Moisture sorption isotherms of watermelon pomace

The prediction of the moisture exchange between air and foodstuffs is very important since it affects the properties and shelf life of the later. Sorption isotherms which relate the equilibrium moisture content (EMC) and water activity ($a_w$) at a given temperature and pressure provide a way to describe the hygroscopic properties of food stuffs (Sun & Bryne, 1998; Sogi et al., 2002; Shivhare et al., 2004). Information on the sorption isotherms is important in the drying process and for microbiological safety (Rizvi, 1995). The sorption isotherm curve of dried food material was sigmoid in nature (Wani et al., 2006).

Sorption isotherm represents the EMC of hygroscopic food material at changing relative humidity conditions of the surrounding environment at a particular temperature (Sogi et al., 2003; Shivhare et al., 2004). The EMC not only influences the physical, chemical and microbial stability of a food material but is also used as one of the input parameters in drying models. Knowledge of the sorption behavior is required for designing dryers, storage structures, packaging material, as well for predicting changes in food product during drying and storage as a function of temperature and relative humidity.
Various models employed to describe the adsorption/desorption isotherms can be grouped as under based on the parameters involved.

**Two Parameters Models:** Kelvin equation (Kelvin, 1871), Langmuir equation (Langmuir, 1918), BET equation (Brunauer-Emmett & Teller, 1938), Harkins-Jura equation (Harkins & Jura, 1944), Oswin equation (Oswin, 1946), Smith equation (Smith, 1947), Hasley equation (Hasley, 1948), Henderson equation (Henderson, 1952) and Chung-Pfost equation (Chung & Pfost, 1967).

**Three Parameter Models:** Cubic model (Alam & Shove, 1973), Schuchmann-Roy-Peleg equation (Schuchmann et al., 1990).

**Four Parametric Models:** Peleg equation (Peleg, 1992), ISSE equation (Isse et al., 1993).

The accuracy of the EMC equation dictates the successful modeling and optimization of design of a dryer.

Sorption isotherm data also allow determination of the differential heat of sorption by the application of the Clausius-Clapeyron equation on the isosteric equilibrium pressures at different temperatures (Thompson et al., 1986). The net isosteric heat of sorption has been used to estimate the energy requirements for dehydration processes. No literature was found on sorption behavior of watermelon pomace waste. Wani et al., (2006) studied on moisture adsorption isotherms of watermelon seed and kernels from *Citrullus Lanatus Cv Mateera* and *Citrullus vulgaris Cv. Sugar baby* using standard static method with saturated salt solution over a range of water activities from 0.113 to 0.92 at 20-60°C. The adsorption capacity of seeds decreased with increase in temperature at constant water activity. Sorption models were used to explain the adsorption behavior involving water activity and moisture content (Type I) and temperature (Type II). Oswin’s models gave best fit among Type I with coefficient of determination of 0.953-0.995, standard error of 0.031-0.0571, mean relative error of 0.071-0.152 and scattered residual plots. Modified Oswin equation was the best fit model among Type II for the seeds and kernels of both the cultivars with coefficient of determination of 0.997-0.999, standard error of 0.151-0.255, mean relative error of 0.018-0.244 and scattered residual plots. The net isoelectric heat of adsorption, estimated from Clausius-Clapeyron equation decreased from about 27.0 to 0.5 kJ/mol in kernels and 18.0 to 0.5 kJ/mol in seeds of both the cultivars as the moisture content increased from 5 to 25 % (dry basis).
2.8. Pigment Extraction from watermelon

Characteristic red pigmentation of the ripe watermelon, tomato, pink grapefruit, pink guava and rose hip is due to lycopene (Mangels et al., 1993; Scott & Hart, 1995; Holden et al., 1999). It, an acyclic isomer of β-carotene, is a 40-carbon (C_{40}H_{56}) aliphatic compound which is longer than any other carotenoid. It is highly unsaturated molecule containing 11 conjugated double bonds arranged in a linear array and two unconjugated double bonds (Davies, 1976). The long chromophore in the polyene chain accounts for the red color of lycopene and also for its powerful antioxidant activity (Shi & Maguer, 2000). It is devoid of provitamin-A activity due to lacks the β-ionone ring structure. Lycopene can be readily cyclised to β-carotene by the plant enzyme lycopene-β-cyclase (Clinton, 1998; Khachik et al., 2002).

Watermelon pigment is usually extracted with organic solvents such as chloroform, hexane, acetone, benzene, petroleum ether and carbon disulfide. The efficient mechanical grinding of the material can be used to facilitate extraction. Exposure of extracted lycopene to light should be avoided and only gold, yellow or red light should be used (Landers & Olson, 1986). Shi et al., (2002) reported that heating at 60 and 80°C favored the isomerization of lycopene. Heating treatment at 120°C and long time heating treatment at 100°C improved the extraction of lycopene from puree matrix. Exposure to light caused no significant change to total and all-trans lycopene, although significant loss of cis-isomer lycopene was observed.

Fish et al., (2002) used the rapid and inexpensive method for lycopene that is spectrophotometric assay. This method requires 80% less organic solvent for extraction of lycopene. Hexane and 95% ethanol was used for the extraction of lycopene. Extraction yield from these two methods was almost similar. Maximum lycopene content was obtained from variety Tri-X-313i.e 63.0 mg/kg fresh weight. Davis et al., (2003) discussed a rapid and reliable light-absorption method to assay watermelon lycopene content that uses no organic solvents. Results were compared with hexane extraction method. The puree absorbance method gave a precise linear relationship (R^2=0.98) to lycopene content and was independent of lycopene concentrations or watermelon variety within the lycopene concentration measured (24-88mg/g fresh weight).

Supercritical CO₂ fluid extraction of freeze dried watermelon tissue was used to extract lycopene at 60, 70 and 80°C temperature, 3000-4000 psi pressure and 0, 5, 10,
and 15% ethanol as modifier (Vaughn et al., 2003). Studies showed that higher level of ethanol modifier was more effective in extracting lycopene.

Barba et al., (2006) used methanol (100%), ethyl ether (100 %), tetrahydrofuran (100 %), methanol/tetrahydrofuran (92:8 v/v), methanol/ tetrahydrofuran (50:50 v/v) and hexane/aceton/ethanol (50:25:25 v/v/v) for the extraction of lycopene and β-carotene. A mixture of hexane with acetone and ethanol or methanol has been used for lycopene extraction because other components such as diethyl ether and tetrahydrofuran might contain peroxides that react with carotenoids (Sadler et al., 1990; Shi & Maguer, 2000; Van den Berg et al., 2000). The stability of lycopene extracts obtained with hexane/aceton or hexane/ethanol was higher than that of extracts obtained with other organic solvents such as chloroform, methanol, or dichloromethane (Taungbodhitham et al., 1998). Davis et al., (2007) used a rapid method of light absorption to study total carotenoids in yellow fleshe watermelon. This method does not require organic solvent. Results obtained by them were compared with method that uses hexane. Evaluation of 177 samples of watermelon was performed and results showed total carotenoids in range of 0-7μg/gm (fresh weight). Three methods performed were low volume hexane extraction, HPLC analysis and puree absorbance method. In low volume hexane extraction method, 0.05% BHT in acetone, 95% ethanol and hexane were used. In HPLC, three solvent mixtures- 90% methanol, 10% deionized water containing 0.5% triethylamine and 150 m ammonium acetate was used. The second mixture was 99.5% 2-propanal and 0.5% trimethylamine. The third was 99.95% tetrahydrofuran, 0.05% triethylamine. Puree absorbance method require no reagents and this method is improvement over conventional method. Of the three methods, hexane method gave highest estimate of total carotenoids in all samples. Total carotenoids concentration measured was 0-7μg/g fresh weight.

Katherine et al., (2008) studied the effect of extraction conditions such as temperature (70-90°C), pressure (20.7-41.4 MPa) and solvent addition (10-15%) on supercritical extraction of lycopene from watermelon and found that temperature had the most significant effect on lycopene yield. A lycopene yield of 3.8mg/100g of fresh weight basis was obtained at 70°C, 20.7 MPa and 15% ethanol by volume. As another set of experiments the temperature was varied from 60-75°C at an atmospheric pressure of 20.7MPa in the presence of 15% ethanol. Results showed that lycopene yield at 60°C extraction temperature was 14% greater than that obtained at 70°C.
Ai-Guo, (2009) optimized the extraction process of lycopene from watermelon. Fresh mature watermelon was used for the lycopene extraction using different organic solvents. Effect of extraction temperature, extraction time, solid/liquid ratio and pH on extraction of lycopene was studied. Extraction process of lycopene was optimized by the orthogonal test. Ethyl acetate was found to be the optimal solvent for extracting lycopene from watermelon. Maximum extraction of lycopene was found at 30º C temperature, extraction time of 1.5 h, pH of 4.0 and solvent/meal ratio of 1:1.

Liu et al., (2010) determined lycopene using red fleshed watermelon varieties, *Diploid* (2X), *Triploid* (3X) and *Tetraploid* (4X) were determined in mature fruit. Solvent method was used for the extraction of lycopene from watermelon. Petroleum ether, ethyl alcohol, methanol was used to extract lycopene and changes in lycopene during fruit development were also studied. *Diploid* watermelon contained lycopene 33.2-54.8 mg/kg fruit, *Triploid* fruit contained 41.2-61.8mg/kg and *Tetraploid* contained 38.1-59.8 mg/kg. Lycopene content was low in young fruit and high in fully maturity stage.

Shi et al., (2011) optimized the conditions for the extraction of lycopene from watermelon. Response surface methodology was used to study the effect of parameters such as time and temperature of extraction and number of extractions on lycopene extraction. Second order quadratic equation was established. Optimum extraction conditions were hexane (containing 2% dichloromethane) as extraction solvent, solvent/meal ratio 3:1 (ml/g), number of extractions was 2, extraction time of 1.9 h and extraction temperature of 29.8ºC. Under these optimized conditions, lycopene content was found to be 14.71 mg/kg.

2.9. Lycopene Analysis

HPLC analysis of carotenoids is usually done with C18 or C30 RP-columns, operated with isocratic or gradient elution with a wide variety of mixtures of different organic solvents as mobile phases, using UV–visible (λ ≈ 450 nm) or photodiode array or MS detection (Gomez-Prieto et al., 2002; Pichini et al., 2002; Tzouganaki et al., 2002; Lin & Chen, 2003; Burns et al., 2003). Variations in the properties of silica packing material in terms of particle size, porosity, carbon load, end-capping technique, and polymerization can greatly affect the sensitivity and selectivity of lycopene analysis (Sander et al., 1994). Heating the column is sometimes used to improve pigment separation as well as to standardize the separation conditions (Schoefs, 2002). C30 stationary phase is employed
to achieve superior selectivity of lycopene isomers compared to conventional C_{18} reversed-phase and silica normal-phase columns (Sander et al., 1994; Emenhiser et al., 1996).

A polymerically synthesized C_{30} column provides excellent separation of all-trans lycopene isomers from the cis counterpart (Emenhiser et al., 1996; Rouseff et al., 1996). Identification and structure elucidation of isomeric carotenoids have been facilitated with the aid of high-resolution NMR spectroscopy. Hengartner et al., (1992) reported the use of H- and C-NMR, UV/VIS, mass, and IR spectroscopy to fully characterize 15 (E/Z)-isomeric forms of lycopene. Antioxidants such as butylated hydroxyl toluene (BHT) should be employed in extraction and separation solvents to control oxidation and isomerization reaction of lycopene (Nguyen & Schwartz, 1998).

In nature, lycopene exists in all-trans form and seven of these bonds can isomerize from the trans-form to the mono or poly-cis form under the influence of heat, light, or certain chemical reactions. As a result of the 11 conjugated carbon-carbon double bonds in its backbone, lycopene can theoretically be arranged in 2048 different geometrical configurations. Although a large number of geometrical isomers are theoretically possible for all-trans lycopene, but only certain ethylenic groups of a lycopene molecule could participate in cis-trans isomerization because of steric hindrance (Pauling, 1939; Zechmeister et al., 1941).

Interconversion of isomers is thought to take place with exposure to thermo energy, absorption of light, or by involvement in specific chemical reactions. Cis isomers of lycopene have chemical and physical characteristics distinctly different from their all-trans counterparts. Some of the differences observed as a result of a trans-to-cis isomerization reaction include lower melting points, decreased color intensity, a shift in the $\lambda_{\text{max}}$, smaller extinction coefficients, and the appearance of a new maximum in the ultraviolet spectrum (Zechmeister & Polgar, 1943). Stereoisomeric forms of lycopene were described with special reference to the properties of light absorption in relation to their molecular structures (Zechmeister, 1962).

For the extraction of carotenoids from the samples, different systems can be used, like liquid–liquid extraction, solid phase extraction or supercritical fluid extraction (Gomez-Prieto et al., 2002; Rozzi et al., 2002; Tzouganaki et al., 2002). Lycopene is more commonly extracted with organic solvents such as ethyl acetate, ethanol, acetone, petroleum ether, hexane, benzene, chloroform, etc. prior to chemical analysis for quantitative determination (Al-Wandawi, et al., 1985; Sadler et al., 1990; Sharma &

2.10. Stability of pigment

Lycopene appears to be quite stable within the plant matrix but may degrade and isomerizes when solublized in oil or organic solvents (Hackett et al., 2004). Henry et al., (1998) studied the oxidative degradation kinetics of lycopene, lutein, 9-cis and all-trans β-carotene during heating in safflower seed oil at 75, 85 and 95°C for 24, 12 and 5 h respectively. The degradation kinetics followed a first order kinetic model. The rates of degradation were lycopene > all-trans β-carotene = 9-cis β-carotene > lutein. The degradation rate constant of lycopene obtained from first order model varied from 0.109 to 0.518 h⁻¹ with change in temperature from 75 to 95°C. The results concluded that the degradation rate of lycopene was higher than β-carotene at 75, 85 or 95°C whereas lutein had the greatest stability in the model system of the carotenoids tested.

Nguyen & Schwartz, (1999) reported that lycopene was susceptible to chemical changes when exposed to light and heat, and formation of cis isomers of lycopene may decrease its biological activity. As lycopene is present naturally in trans form in food products, the formation of cis forms of lycopene might be due to processing or storage.

The degradation of total amount of lycopene during heating was found to follow a first order model (Lee & Chen, 2002). The degradation rate constant (min⁻¹) of lycopene increased with increasing temperature and activation energy was calculated to be 61 kJ/mol. The kinetics of lycopene degradation was examined by studying the effects of oxygen, temperature and light intensity on the formation of its volatile oxidation products (Cole & Kapur, 1957 a, b).

Under different food processing conditions, lycopene undergoes degradation via isomerization and oxidation, which impact its bioactivity and reduce the functionality for health benefits. Carotenoids are sensitive to isomerization in heat, light, or iodine, and to aerial oxidation (Zechmeister & Tuzson, 1938 a, b; Zechmeister, 1944; Frecknall & Pattenden, 1984). The degradation reactions of lycopene are influenced by factors such as reaction medium, temperature, physical state, and environmental conditions. The most important factors during processing are heat, light, and oxygen. Lycopene isomerization and the amount of cis-isomers increased as a function of processing time during heating of lycopene rich foods.
Lycopene may be expected to undergo changes during processing and storage: isomerization of all-trans to mono-cis or poly-cis forms and oxidation (Cole and Kapur, 1957 a, b). Due to presence of long chain of conjugated C-C double bonds, lycopene is susceptible to chemical changes when exposed to light and heat and the formation of cis-isomers of lycopene may decrease its biological activity (Nguyen & Schwartz, 1999).

2.11. Antioxidant properties of watermelon

Djuric & Powell, (2001) estimated the antioxidant capacity of aqueous and organic extracts of lycopene rich foods like ketchup, fresh tomatoes, tomato paste, tomato sauce, tomato soup, vegetable juice, canned tomatoes and watermelon. The value of lycopene in watermelon was 3.7 mg/100g which was higher than obtained in tomatoes (2.3 mg/100g), tomato juice (2.9 mg/100g) and tomato soup (2.0 mg/100g). The TEAC of food extracts was greater in the aqueous versus organic fractions except for watermelon and tomato sauce where levels were similar in the two fractions. The watermelon TEAC was significantly higher than that of tomato sauce or ketchup.

Tlili et al., (2011a) estimated the hydrophilic and lipophilic antioxidant activities in watermelon cultivars harvested at four different stages by trolox equivalent antioxidant capacity (TEAC) assay. In watermelon varieties Crimson sweet, Giza, P403 and P503, the highest hydrophilic antioxidant activity was detected at red-ripe stage with values ranging from 97.4 to 546.5 µM Trolox/100g on fresh weight basis. A peak in lipophilic antioxidant activity was reached at the red ripe stage of maturity in Crimson sweet, Giza and P503 cultivars with high value of 467.9 µM Trolox/100g fresh weight basis in Crimson sweet variety. Considering the data from all watermelon cultivars good and significant correlations between lipophilic TEAC values and lycopene (r= 0.649) were obtained during ripening.

Soumya & Ramana Rao, (2014) estimated the total antioxidant activity by DPPH method of four icebox cultivars of watermelon fruit during their development and ripening. The total antioxidant activity of ‘F1 Arun’ and ‘Beauty’ watermelon cultivars increased with different stages of ripening (young, pre-mature, mature, pre-ripened and ripened) and values were in the range of 48.8-53.3% and 49.8-60.3% respectively where as decreasing trend in antioxidant activity was observed with ripening in ‘Karina King’ and ‘Suman 235’ cultivars.
2.12. *In vivo* bioavailability of lycopene

The fraction of an oral dose of a parent compound that reaches the systemic circulation refers to bioavailability (Schumann et al., 1997). The bioavailability of *cis*-lycopene isomers is found to be more than in the all *trans*-lycopene (Boileau et al., 2002). Lycopene can be effective in reducing the risk of cancer, if it is bioavailable. Lycopene was found to possess moderate curative effects by increasing the survival rate of X-radiated mice (Forssberg et al., 1959). *In vivo* studies have shown a tumor-suppressive activity of lycopene (Stahl & Sies, 1996). Lycopene reduces the low-density lipoprotein oxidation and helps to reduce cholesterol levels in the blood (Rao & Agarwal, 1999). Lycopene was superior to α- and β-carotene in inhibiting cell proliferation in various human epithelial cell lines (Levy et al., 1995).

Edwards et al., (2003) examined the bioavailability of lycopene from fresh frozen watermelon juice in healthy, non smoking adults (36-69 years) for 19-week crossover study. The subjects were given the different treatments like controlled diet, first treatment including 20.1 mg/day lycopene, 2.5 mg/day β-carotene and second treatment included 40.2 mg/day lycopene, 5 mg/day β-carotene obtained from watermelon juice. After 3 week of treatment, plasma lycopene concentration were 272, 1078 and 1182 nmol/L for controlled, first treatment and second treatment diets. Lycopene was bioavailable from fresh-frozen watermelon juice. However, dose–response effect was not apparent in plasma when the watermelon dose was doubled.

Collins et al., (2006) compared the artificially sweetened watermelon with the conventional melons in all quantitative and qualitative factors including taste acceptability, carotenoids, pH and level of sugar content. The average soluble solid content and total sugars of low-sugar watermelon was 5% and 635mg/g on dry weight compared to conventional watermelons containing 9% and 760 mg/g on dry weight respectively. The pH, lycopene, β-carotene and total carotenoid levels were similar in both fruits. Results demonstrated that a low sugar watermelon is a palatable fruit choice to individuals who must restrict their sugar intake with added benefits of lycopene and acceptability.

2.13. Lycopene application in food
Color is one of the most important quality characteristics of food products. Natural and synthetic food colors are used worldwide to improve the acceptability of the food products. Natural colors are more expensive, less stable and less potent than their synthetic counterparts. But advances in technology have narrowed the gap in all the three shortcomings. Nutraceutical and functional foods have triggered the use of natural colors not only for appearance, but also for the health. The use of natural colors in food is an ancient practice, but currently gaining importance because consumers want to avoid synthetic colors.

The FAO/WHO Joint Expert Committee on Food Additives (JECFA) recommended that more attention should be given to methods to reduce the trace element impurities in food colors (Singh, 1997), therefore, food industry has turned to suitable natural alternatives. Demand for natural food coloring has been growing although most of the natural colors are costlier than their corresponding synthetic colors. Natural colors are generally extracted from fruits, vegetables, seeds, roots and microorganisms and are also called ‘biocolors’ because of their biological origin (Pattnaik et al., 1997).

Plant pigments, by virtue of their natural occurrence in edible plants, are generally considered to be harmless. Nature produces a variety of brilliant pigments having commercial value as food colorings, e.g. water-soluble natural colorants such as anthocyanins, betalains etc. and oil soluble colorants such as carotenoids, curcumin, etc. Epidemiological studies strongly suggest that high intakes of vegetables and fruits reduce the risk of some diseases such as atherosclerosis and cancer (Ames et al., 1995; Steinmetz & Potter, 1996; Ness & Powles, 1997; Lampe, 1999).

Lycopene is receiving growing attention from the food processing industry. It is proving to be an excellent natural food color which, at the same time, serves as an important health-boosting phytochemical that plays a major role in the human natural defense system against degenerative diseases.

Lycopene is effective in low concentrations, free of off-flavors and capable of imparting color ranging from yellow through orange to deep red. Addition of lycopene as a food color depends on the formulation, method of food preparation and the manufacturing techniques involved. Council Directive permits the use of the extract as a color in foodstuffs at levels up to 500mg/kg (expressed as lycopene) but this approval does not extend to the use of lycopene as a food ingredient (Anon, 1995).

Lyc-O-Mato® is a lycopene based colourant which is used in beverages, powdered beverages, dairy foods, surimi, confectionery, bakery, breakfast cereals, nutritional bars,
soups, meal replacement, sauces salsas, pastas, chips and snacks, dips and spreads (Anon, 1997).