

CHAPTER 2

Literature Review

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2.1 Introduction

In this chapter, a brief review of the citrus fruits, its bitterness, methods for detection and debittering and various sensors for analyte detections are presented. The chemical information of phytochemicals, limonin and naringin responsible for bitterness in citrus fruit juices are described. Various conventional methods and techniques used for the detection and debittering of limonin are explored in this chapter. Finally, from the literature, the potential of nanostructures-based capacitive sensor is explored. The issues with processing citrus fruit juices such as the bitter principles, detection of bitter chemicals, debittering techniques, possible inclusions of electronic devices for detection, etc are the topics of the current review study.

2.2 Citrus fruits

Citrus fruit juice holds a significant position as the primary component product of the juice and food industries. For over 4000 years, citrus fruits belonging to the family Rutaceae have been cultivated and found to be the most produced fruit crops in the world (FAOSTAT) [1] in which the flowers clamp an disk of annular shape and the leaves have

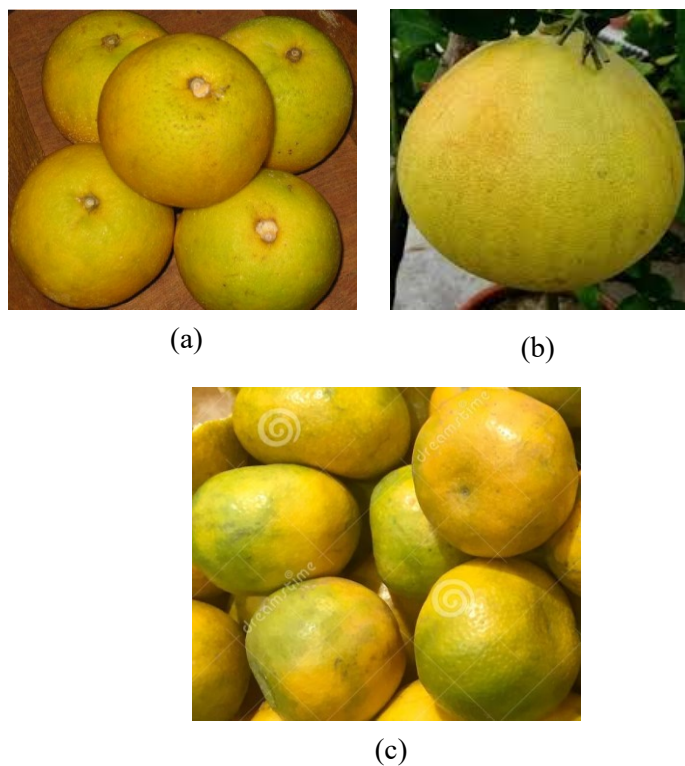


Figure 2.1: The citrus fruits (a) Citrus Limetta (mosambi) (b) Citrus grandis (pomelo) (c) Citrus sinensis (orange) [dreamstimes.com]

transparent oil glands [2]. Citrus fruits are thought to have originated in southeast Asia and were later introduced to the middle East and southern Europe. Following the paths of civilization, the fruits were scattered to other countries with the support of travelers and missionaries [3]. Most of the citrus fruit that belongs to the Rutaceae family grown by Indian farmers are kinnow, mosambi, orange, pomelo, lemon, galgal, tangerine, grapefruit, etc. Fig. 2.1 presents the commonly and locally available (India) images of citrus fruits mosambi, orange, pomelo fruits showing their colour, texture, etc. Certain vitamins, minerals, and bioactive substances are abundant in citrus fruits which exhibit anti-inflammatory, antioxidant, antiviral and antifungal activities [4]. These fruits are consumed by consumers in the form of fresh juice and processed fruit products or directly. The fruits have specific aromas, tastes and oils for which they are well known [5].

2.3 Bitterness in citrus fruits

Packing fruit juices and products could be a substitute for their seasonal availability to make them available all year round. Food materials can be transported to far-off locations in the simplest manner possible by being packed. Citrus juice's bitterness, however, may cause issues when it is kept for a long period. The consumer's acceptance of citrus fruit juice is also affected by the bitterness of the juice. The fruits' chemical nature reveals the existence of a number of chemically bitter metabolites (Naringin, tangeretin, nobiletin, sinensetin, quercetin, limonin, nomilin, and neohesperidin) [6]. Yet, mostly a small number of properly identified metabolites—limonin and naringin—play a substantial part in producing bitterness. The ratio of other bitter components nomilin to limonin is considerably low in fruit [7]. The main compounds in kinnow that cause bitterness are limonin and naringin (Limonoid aglycones). Based on the specific part, maturation stage, growth conditions, and kind of fruit, there may be a difference in the type and concentration of chemicals that produce bitterness.

Naringin (Fig. 2.2a). is a bio-molecule of the flavonoid phenolic group [8] that causes fast bitterness in citrus fruit juice obtained during its preparation whereas, a white, crystalline biomolecule termed as limonin of the limonoid group causes delayed bitterness in fruit juice generated after its preparation. The triterpene derivative limonin, that contains a furan ring and an epoxide group, is highly oxygenated in nature [9] (Fig. 2.2b).

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An essential disaccharide derivative is naringin ($C_{27}H_{32}O_{14}$) with Molecular weight (Molar Wt.= 580.50 g per mol). It is 2-O-(alpha-L-rhamnopyranosyl)-beta-D-glucopyranosyl moiety substituted into (S)-naringenin in the seventh position via glycosidic linkage [10]. It is composed of naringenin-7-[alpha-L-rhamnopyranosyl-(1 \rightarrow 2)-beta-D-glucopyranoside] [11] (Fig. 2.2a). The amount of bitter chemicals varies among the various portions of a single fruit. Naringin was found to be present in grapefruit in multiple parts, including the juice (30-75 mg/100 g), flavedo (270.00-431 mg per 100 g), albedo (130.00-1558.9 mg per 100 g), pith (1328-1760 mg per 100 g), and seeds (29.0-267.0 mg per 100 g) [12, 13] [14]. Sweet oranges contain 1.73 mg of naringin per 100 gm, while sour oranges contain 6.34 mg and Tangelo has 33.73 mg of naringin per 100 gm [15, 16].

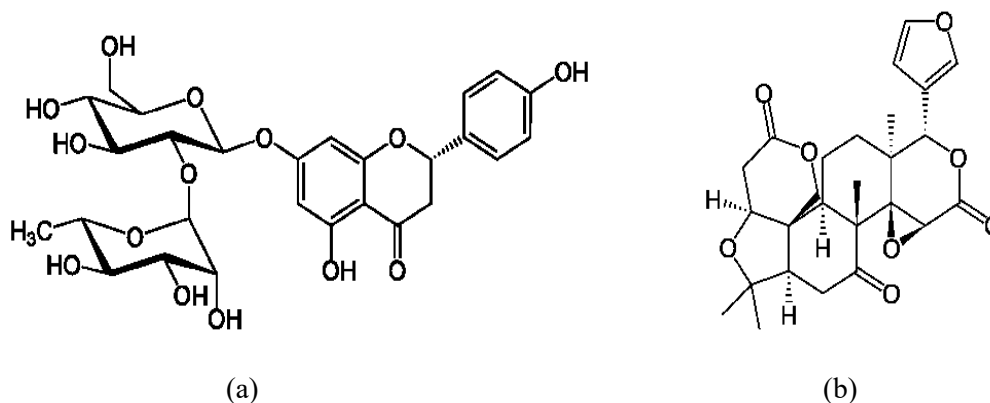


Figure 2.2: Chemical structure of (a) naringin and (b) limonin

A highly oxygenated metabolite linked to triterpene derivatives called limonoid aglycones is the source of limonin. These chemicals can be found in fruits of Meliaceae and Rutaceae families [17, 18]. There are two main categories of limonoids: the first category comprises aglycones, while the second category includes the glucosides associated with them. Limonoids include ichangin, nomilin, limonin glucoside, and nomilinic acid, among others [19, 20]. Fig. 2.2b shows the whitish substance limonin ($C_{26}H_{30}O_8$, Mol .Wt. 470.52 g per mol) which is a white-colored compound present in citrus fruits. Chemically, limonin (IUPAC name: 7,16-Dioxo-7,16-dideoxylimondiol) belongs to furanolactones which contains 8 hydrogen bond acceptors, 1 rotatable bond with topological polar surface area 105 \AA^2 and 1 covalently bonded unit. Limonin is also termed as limonoic acid di-delta-lactone. Another name of limonin is limonoate D-ring-lactone, and it is soluble in ethanol and glacial acetic acid. Limonin is slightly soluble in

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water. Citrus fruits and their hybrid varieties contain more than 30 distinct limonoids [21] [22]. Hasegawa and Miyake (1996) showed that the terpenoid biosynthesis path, that initiates with the cyclization of squalene through cytoplasmatic acetate mevalonate (CAM). This is the route by which limonoids are generated in citrus fruits [23]. There are many oxygenated compounds with a furan ring connected to a D ring. Based on their structural structure and oxidative responses, further limonoids are categorized [24].

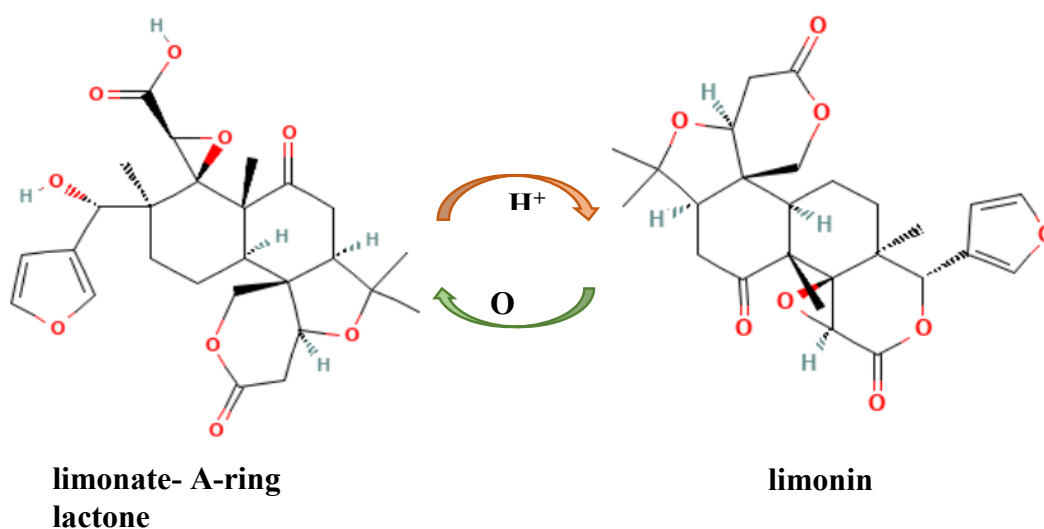


Figure 2.3: limonate- A-ring lactone (LARL) being converted to limonin in acidic medium and its reverse process

Lemon juice (12.0 mg L^{-1}), grapefruit juice (11.40 mg L^{-1}), orange (4.70 mg per L), pomelo (18 mg per L^1) and tangerine (34 mg L^{-1}) used to have the strongest limonin concentrations [25]. To check for the presence of limonin, Baswal et al. (2018) investigated the seeds, peel, and juice of kinnow [26]. The limonin is found to be present at $8 \text{ mg}/100\text{g}$ in the peel, $0.25 \text{ mg}/100\text{g}$ in the seeds, and $1.5 \text{ mg}/100\text{g}$ in the juice. According to reports, the grapefruit's flavedo (6.00 mg per kg), albedo (11.00 mg per kg), pith ($10.30 \text{ mg per } 100\text{g}$), and seeds ($118.80 \text{ mg}/100\text{g}$) are found to contain varying amounts of limonin. The concentration of the other bitter glycosides, nomilin, was found to range from 0.1 to 0.60 mg per L , $0.4 - 0.79 \text{ mg per L}$ and $0.90 - 1.80 \text{ mg per L}$ of grapefruit juice, oroblanco, and melogold, respectively [25]. Nomilin concentration in juice decreases in mature fruit as compared to immature fruits [7].

According to McIntosh et al. (1982), there are two different ways that bitterness can occur in fruit juice [27] (for both bitter and non-bitter fruits): 1) fruits' content of flavonoids along with the derivatives of them cause bitterness (bitter orange and

grapefruit) 2) bitterness brought on by a compound's transformation from its non-bitter form into a bitter one. Juice's bitter taste is caused by the transformation of limonin glucoside, a non-bitter component, into limonin, a bitter chemical, through the processes of deglycosylation and cyclization. [28, 29]. The bitterness in citrus fruit juice that originates from limonin usually results from physical and freezing damage to the fruit. The reaction begins with the mechanical shattering of juice-containing sacs, which leads LARL (limonate A-ring monolactone), which is not bitter, to change into a bitter form (limonin) (Fig. 2.3). The conversion of tasteless, non-bitter forms into bitter forms is an enzyme-catalyzed reaction (limonin D-ring lactone hydrolase) that takes place in an acidic environment and depends on the availability of LARL [30]. A decrease in the concentration of LARL was observed with the maturation stage [31].

2.4. Assessment of delayed bitterness: methods and techniques

Limonin in citrus juices can be measured and found using a variety of analytical methods and procedures. A versatile tool for the detection of bittering chemicals is thin-layer chromatography (TLC). Limonin is more accurately and thoroughly measured utilising spectrophotometry, gas chromatography (GC), radioimmunoassay (RIA), enzyme-linked-immunoadsorbent assay (EIA), High performance liquid chromatography (HPLC), and reverse-phase HPLC.

Many scientific and industrial applications demand high-performance on-site detection of limonin content in citrus juices. Few reported methods for the development of sensors include the mechanism of amperometric microbial biosensors and Organic Electrochemical Transistor [32, 33]. Table 2.1 shows the previously reported method/techniques for limonin measurement.

Limonin was twice isolated from navel orange juice using dichloromethane [34]. The alumina-treated mixed extracts were filtered and treated with acid to wash alumina using chloroform. Extracts made from a mixture of dichloromethane and chloroform were evaporated, and the leftover material was partitioned between acetonitrile and petroleum ether. Limonin in the acetonitrile layer was found by alkaline hydroxylamine treatment, acid ferric perchlorate solution addition, and measurement of the solution's absorbance at 510 mp. The results of this approach were accurate in measuring limonin in the 5 to 40 p.p.m. range, and they were in good agreement with reports of navel orange juice's bitterness. Due to interference from coumarins, it proved unsatisfactory for grapefruit juice, orange peel, twigs, leaves, and roots.

Maier and Grant, 1970 reported the detection of limonin using a Specific thin-layer chromatography assay. Using two chloroform extractions method limonin was extracted from the citrus juices or in acidified tissue suspensions once it is formed. Using acetonitrile limonin was measured where limonin was dissolved after the evaporation of chloroform. In thin layer chromatogram, the acetonitrile along with limonin was marked where benzene: ethanol: water: acetic acid (200; 47:15; 1, upper phase) solution was used for development. It was then dried, sprayed with Ehrlich's reagent and reacted with gaseous HCl. Limonin was measured by comparison of standard and unknown limonin by observing the visual or spectro-densitometric results. A sensitivity of 0.5 ppm was observed and varieties of citrus fruit juices were used for testing [35].

Tatum and Berry introduced a concise TLC method for limonin quantification in 1973 which was quicker than any prior procedure because it required no extraction or preparation when used with commercial single-strength or reconstituted juices [36].

Mansell and Weiler established an I- radioimmunoassay method in 1980 for the triterpenoid bitter component known as limonin. The limonin-bovine serum albumin conjugate's synthesis as well as that of the iodinated tracer were both reported. The assay had a detection limit of 0.07 ng or 0.7 ppb and the antibody had a high affinity (K_d , 1.1×10^9 l/mol) and selectivity for limonin [37].

In 1980, Rouseff and Fisher reported measuring limonin using the High-Performance Liquid Chromatography (HPLC) method. Using a ternary solvent solution and a nitrile (CN) column in the normal phase mode, four important citrus limonoids were isolated in less than 15 minutes. The separation of limonin from similar juice limonoids using HPLC was reported for the first time. For limonin or nomilin, the detection limit at 207 nm was 10 ng. At 40 °C, the optimum column efficiency was noted. At 1.0 mL/min, the maximum column efficiency and detector response per unit of time was achieved. With a relative standard deviation, RSD, of 2.2% ($n = 5$), limonin in 5.0 ppm grapefruit juice can be estimated. The limonin RSD in orange juice with low limonin content ($X = 0.75$ ppm) is 3.2% ($n = 5$) [38].

A solid-phase enzyme immunoassay for the quantitative determination of the bitter triterpene lactone, limonin, in citrus juice samples was described by Jourdan et al. in 1984 [39]. The presence of limonin can be determined as 0.1 ppm. After the entire assay time, quantitative findings were obtained in 1 h. The assay employs an antibody-coated polystyrene micro cuvette, a vertical light path photometer, and a forced air microplate incubator. It also uses a limonin-alkaline phosphatase tracer with strong

immunoreactivity. Radioactivity required expensive counting apparatus, and the assay's user needed to have the necessary general facilities to handle radioisotopes. Furthermore, even in locations where it would be beneficial to determine limonin, the use of radioactivity is often restricted [39].

T. Van Beek and A. Blaakmeer (1991) performed high-performance liquid chromatography on a C18 column with UV detection at 210 nm to measure the limonin content. The specimen was cleaned up using centrifugation, filtering, and a C2 solid-phase extraction column for a specific, quick, and reproducible purification. From 0.0 to 45 ppm limonin, a linear response was achieved. There was a 2 ng minimum detectable level. The lowest concentration that could be accurately and successfully detected without concentration was 0.1 ppm [40].

A technique for limonin extraction from citrus juices employing solid-phase extraction (SPE) and reversed-phase analysis was described. The method offered a better separation of limonin from other constituents than previously published reversed-phase methods, had a quick sample preparation process, and did not prematurely deteriorate the analytical column. For improved sensitivity with UV detection at 214 nm, the SPE technique achieved 95-108% recovery and 2-4 fold concentrations of limonin in extracts. When stored at -4 °C, limonin extracts were stable for 30 days after being extracted into 70% methanol. White and pink grapefruit, navel, Valencia, Hamlin, and sour orange juices were all examined for limonin. However, the stationary phase was prone to contamination by components found in citrus juices [41].

The development of limonin detection sensors has attracted a lot of attention from scientists. In 2012, Puri R., et al. [32] demonstrated a limonin-selective amperometric microbial biosensor that could use kinnow mandarin juice as a carbon source while other sugars were present. This stable, lim⁺ auxotrophic mutant's respiratory activity in the presence of the analyte, limonin, was used as the basis for the analytical determination. The relationship between dissolved oxygen (DO) and limonin concentrations of 20, 25, and 30 ppm were established. For both the steady-state method and the initial slope method, response times of around 20 and 12 mins, respectively, were reported. In the 15–50 ppm range, the calibration curve for limonin was linear [32]. The biosensor's performance was repeatable and unaffected by intermittent storage and usage for at least a month.

In 2015, Rathore et al. explored how an electronic tongue system responded to the primary compounds in orange juice that affect flavour and health benefits and are also

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affected by Huanglongbing (HLB) disease [42].

Table 2.1: Few reported methods / techniques for limonin assessment

Authors & year	Methodology used	Major findings	key Points/limitations	Ref
Wilson and Crutchfield, 1968	Spectrophotometric determination	Detection range 5- to 40-p.p.m.	Not satisfactory for orange peel, twigs, leaves, roots, or for grapefruit juice, not on site detection, time consuming.	[34]
Maier and Grant 1970	Specific thin-layer chromatography assay	sensitive to at least 0.5 p.p.m	not on site detection, time consuming, expensive	[35]
Tatum and Berry 1973	Thin-layer chromatogram	limonin concentration can be determined on six juices in 1.5 hr	not on site detection, time consuming, expensive	[36]
Mansell and Weiler 1980	I- radioimmunoassay technique	detection limit of the assay was 0.07 ng	Not on-site detection, time-consuming, expensive	[37]
Rouseff and Fisher 1980	High Performance Liquid Chromatography (HPLC) technique.	Limonin in a 5.0 ppm can be determined	Use of toxic materials, long data analysis, not on-site detection, time-consuming, expensive	[38]
Jourdan et al. in 1984	Solid-phase enzyme immunoassay	As little as 0.1 ppm of limonin can be detected	Not on site detection, required costly counting equipment, users of the assay must be well equipped with the general facilities to handle radioisotopes, time-consuming, expensive	[39]
Puri, R. et al. (2012)	Amperometric microbial biosensor using a mutant (lim ⁺) of a strain <i>Pseudomonas putida</i> G7,	Correlation between limonin concentrations and the dissolved oxygen (DO) was established Reproducible, intermittent storage and reuse for at least 1 month. Response times: approx 20 min	Larger response time, intermittent storage and reuse for at least 1 month, not a direct measurement of analyte from the juice as the limonin was extracted from juice using chloroform and other reagents.	[32]
Nileshi, S., et al., 2018	The electrochemical interaction between CNPs and limonin has been exploited.	detection limit of 10nM , selective with a range of interfering species	Costly, not ease in fabrication, reusable with the replacement of the sensing layer	[43]
Nileshi, S., et al. (2019)	Organic electrochemical transistor (OECT).	Selective, (detection limit: 10 nM), Early detection of citrus greening disease	Costly, Long and complex fabrication process, Multiple uses with the replacement of sensing layer	[33]

Ceria nanoparticles (CNPs) were revealed to be useful as a transducer incorporated in silk fibroins that was combined with an organic electrochemical transistor to detect limonin by Saraf et al. in 2018 [33]. Due to the redox nature of the dual oxidation states, Ce^{3+} and Ce^{4+} , switching on the surface, CNPs were found to have antioxidant characteristics. In order to target electroactive substances like limonin, oxygen vacancies are created on the surface as a result of the surface's continuous switching between oxidation states. Therefore, limonin has been detected employing a transistor platform by exploiting of the electrochemical interaction between CNPs and limonin. With a steady increase in the ID current with limonin content, the OECT developed during this research showed a detection limit of 10nM. The organic electrochemical transistor (OECT) working with nanoparticles of cerium (CNPs) was presented by Nileshi, S., et al. [43] in 2019 as a transducer to detect an ultralow concentration of limonin. The created sensor had a response time of a few seconds and displayed selectivity for limonin with a detection limit of 10 nM.

2.5 Debitting methods

Researchers are concentrating on the scientific techniques that could be used for fruit juice debittering to extend the life of fruit juices and improve customer acceptance. Globally, physical, chemical, and biological techniques based on microorganisms are being evaluated for their effectiveness in reducing citrus fruit bitterness. To reduce the bitterness and enhance the flavour, artificial sweeteners, resins, and enzymes are also applied. Removal of bitter chemicals, removal of physical barriers like pith, use of flavour enhancers and bitter compound scavengers (salt, sugar, florisil), and enzymatic reduction of bitter components are all part of the basic mechanism for reducing bitterness. The main issues in citrus fruit juice like debittering techniques, and future prospects, are reviewed below in this section.

2.5.1 Biochemical Basis for debittering

Vaks & Lifshitz, in 1981 introduced the limonin degradation process in Orange juice that was trapped in a dialysis sac. It was debittered using a soil bacteria (*Acinetobacter* sp.) which was purified by enrichment culture, where it grew using limonin as a carbon source. In the limonin degradation process, the molecules deoxylimonin and deoxylimonic acid are separated. 1L of bitter orange juice was

debittered using the immobilized bacteria of 120 mg in the dialysis sac. Limonin can be broken down into its non-bitter components in three different ways (Fig. 2.4) during fruit ripening, during enzyme catabolism, and depending on the fruit [44].

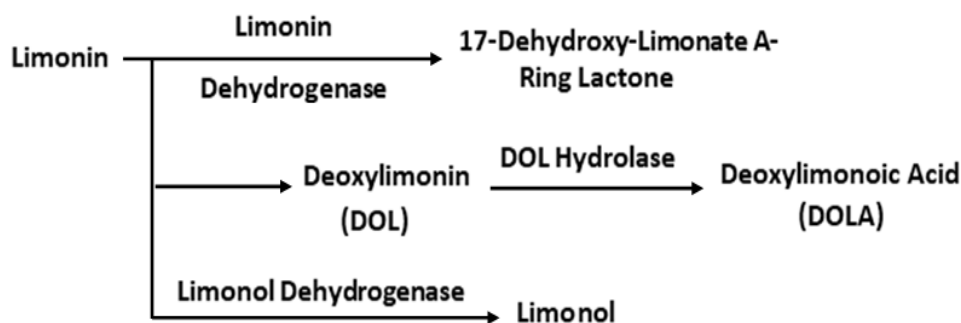


Figure 2.4: Degradation of limonin

2.5.2 Physical methods

The physical methods using resins are a combination of diverse fatty acids, waxes, resin acids, and resinenes ($C_{20}H_{30}O_2$). Resins are mostly taken from trees in the Pinaceae and Dipterocarpaceae families for commercial use. Both non-woody and woody plants have unique surface glands and interior ducts where resin is produced. They are plant metabolic wastes that can be removed through infection or excision [45]. The resins are water-insoluble with soluble in an organic solvent. It is a metabolic byproduct with inert nature.

According to Mishra and Kar (2003), amberlite IR 400 and IR 120 have the ability to reduce the bitterness of grapefruit juice. There was a noticeable difference in the debittering potential of IR 400 and IR 120, with IR 400 removing naringin by 69.23% and IR 120 reducing the naringin level by 9% [46].

Dowex Optipore L285 and Amberlite XAD-16HP are used by Kola et al. (2010) to remove the limonin-based bitterness from orange juice. They observed that whereas Amberlite XAD-16HP treatment does not represent any risk to change in nutritional quality, Dowex Optipore L285 application causes a fall in titrable acidity in oranges [47].

Nas and Karatas (2017) introduced Amberlite XAD-7HP to lower the bitterness of orange juice. Their findings showed the efficiency of Amberlite XAD-7HP application as the employed technique reduces limonin from orange juice by 90–96% [48].

2.5.3 Chemical method

Fruits are treated with sodium hydroxide at 82–83°C for 40–60 s to debitter fruit juices using lye treatment as reported by Kore and Chakraborty in 2015. The fruits are then rinsed in citric acid with a defined quantity and washed with running water removing any remaining NaOH [49]. Lye treatment for debittering can be used on a range of fruits of various ages. The creamy-white portion in outer layer of fruit (peeled) reacts with carboxylic and hydroxyl groups during the lye treatment, which causes the hydrophilic derivative to be removed during water washing.

According to Sogi and Singh (2001), the amount of sodium hydroxide employed in lye dealing affects debittering [50]. Since NaOH causes debittering up to a certain concentration has negative effects beyond that concentration. Anand et al. (2012) investigated the effects of various methods to debitter kinnow juice. They established that lye treatment was the best approach for juice debittering among many techniques (florisil, and their combinations) [51]. As per Scientific reports of debittering juice propose that during lye treatment the reduction of white papery segments from kinnow fruits outcomes in utmost debittering of juice [52].

Florisil is an odourless, white substance known as activated magnesium silicate. Fruit juices' shelf life is increased by using florisil, a significant debittering agent. According to Barmore et al. (1986), florisil was used to debitter grapefruit juice. Different florisil concentrations (5–20%) were employed in their analysis. The amount of substances in grapefruit juice that cause bitterness is significantly impacted by florisil concentration. By using florisil at a 20% concentration, limonin content is reduced from 8.80 to 1.70 ppm and naringin from 326 ppm to 159 ppm. Grapefruit juice's percentage of total acid decreased from 0.81 to 0.33% [53].

The impact of florisil on the ascorbic acid and decreasing sugar of kinnow juice was reported by Kashyap and Anand (2017). The usage of florisil was found to reduce the amounts of reducing sugar (3.53%) and ascorbic acid (18.14 mg/100 g) [54]. According to research investigations, Beta-cyclodextrin can take the bitterness out of fruit juices. According to Deshaware et al. (2018), bitter gourd juice can be debittered using -cyclodextrin[55]. They employed a concentration of 0.25 to 2% of -cyclodextrin, of which 1.5% showed success in eliminating the bitterness from bitter gourd.

According to Mongkolkul et al. (2006), 5% -cyclodextrin at 30°C for 60 mins causes a reduction of 80.71% in the limonin level of tangerine juice [56].

2.5.4 Biological methods

Hasegawa et al., reported the microbial mass immobilized for debittering, when grown on sodium-limonate-rich media, an *Arthrobacter globiformis* isolate developed intracellular limonate dehydrogenase. It facilitates the reversible conversion of limonate to 17-dehydrolimonoate. These investigators effectively extended the use of two other bacterial isolates, *Pseudomonas* 321 - 18 and *Bacterium* 342-152-1 to lower limonin in grapefruit juice [57].

Early season (more bitter) juice was debittered using a pure bacteria from soil called *Acinetobacter* sp. as reported by Vaks and Lifshitz, in 1981. On a dry basis, it was observed that 120 mg of bacterial mass was sufficient for optimum debittering of early-season bitter orange juice to the drinkable condition [44]. For *Pseudomonas* sp. and *Arthrobacter globiformis* II and its variations isolated from the soil, the same method of debittering was proposed by Hasegawa in 1983. These organisms formed the non-bitter metabolites 17-dehydroxylimonoate-A-ring lactone and limonol from the limonin in orange juice when packed in a column [58]. The same researchers reported another bacterium, *Corynebacterium fascians*, isolated from soil, that converts limonin to limonol with the help of enzyme, limonol dehydrogenase. These cells were immobilised in acrylamide gel and used for the conversion, which resulted in debittered citrus juice with minimal impact on the contents of citric, maleic, and ascorbic acids, fructose, glucose, and sucrose. This process significantly reduced limonin and almost all nomilin. Continuous limonin degradation is a function of pH and the degradation is optimal when pH was changed from 4.5 to 5. In contradiction of pH changes, increased in resistance is shown by the immobilized cells, the system improved nearly complete action when the pH was re-established to 7.0 after being functioned for extensive periods at pH 4.0.

2.6 Drawbacks

The drawbacks of using such traditional analytical methods/ techniques for the detection and debittering of limonin in citrus fruit juices are as follows:

- Destructive to its test sample: the samples used in such methods are damaged irreversibly due to chemical and physical treatment on the samples before evaluation.
- Time-consuming: some of the methods and techniques require many hours to complete for the analysis.

- Complex sample preparation and data analysis: sample preparation for analysis is complex as it requires chemical and physical treatment. Moreover, the analysis of the raw data demands the experts from the given field.
- Expensive: acquiring instruments, setup, chemicals, etc. for such analysis makes it expensive.
- Tedious: as it requires many hours to complete the debittering and involves many steps, working on such methods and techniques becomes laborious and tedious.
- Requirement of skilled persons to operate: due to the sophistication of instruments and steps involved, such traditional methods and techniques require skilled persons to operate.

2.7 Sensors

A sensor is a device that detects inputs from the physical world and reacts to them. Sensors are classified into different categories based on different parameters. Based on the measurand, the sensors are classified as acoustic sensors, optical sensors, electrical, mechanical, biological, etc. Based on energy/power, active and passive sensors are there. There are three basic categories of sensors based on the materials and signal conversions- firstly, physical sensors, which provide data about a system's physical properties (such as distance, mass, temperature, and pressure); secondly, Chemical sensors that transform chemical data from a system into an analytically meaningful signal and third, biosensors (biological) that use a biological sensing component to quantify chemical compounds. These devices are coupled with transducers to produce a response that can be observed. In our research work, the chemical sensors have been focused on as the measurand is a chemical input that provides bitterness in citrus fruit juices. The emphasis has been given to the capacitive devices based on planar digitated structures for their various advantages.

2.7.1 Chemical Sensors

In chemical sensors, the receptor (sensing film) interacts with the target analytes in certain chemical reactions when the sensor is exposed to them. The chemical/ physical information carried by the reaction transforms into energy that can be evaluated by the transducer [59]. The ion exchange, adsorption, and partition equilibrium processes between the analytes and the receptor take place at the interface.

Fig. 2.5 shows a typical electrochemical sensor and its processing of physical information.

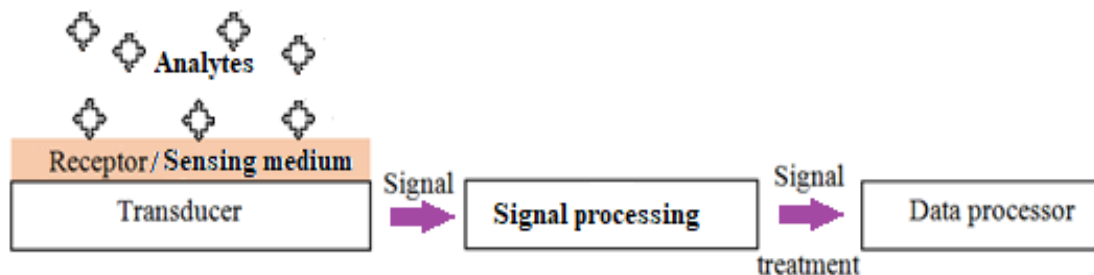


Figure 2.5: Working of an electro-chemical sensor with different components

In a chemical sensor, the chemical sensing phenomena might occur on the sensing layer's surface or over the entire sensitive film. In a volume interaction the analytes are adsorbed and distributed throughout the sample phase and the bulk of the sensitive material and in a surface interaction the active species are adsorbed at the surface/interface. During the sensing process, physisorption can range from extremely weak to very powerful. With an interaction energy of 30 KJ/mol, the chemical is physically absorbed or adsorbed during physisorption [60] but with an interaction energy of 120 KJ/mol, the chemical binds to the surface and forms a covalent bond during chemisorption.

2.7.2 Resistive sensors/ chemiresistors

A chemiresistor is a type of chemical sensor that modifies its electrical resistance as the chemically reactive environment changes. It depends on the direct chemical reaction of the analyte and the detecting substance [61]. The Covalent, hydrogen, or molecular recognition bonds can be formed between the detecting substance and the analyte to cause interaction. Metal-oxide semiconductors, certain conductive polymers and nanomaterials like graphene, carbon nanotubes, and nanoparticles are a few examples of materials that have chemiresistor characteristics. Usually, gadgets like electronic tongues or electronic noses use these materials as partially selective sensors.

A simple chemiresistor is made up of a sensing substance that covers a group of interdigitated electrodes or fills the gap between two electrodes. It is simple to measure the resistance between the electrodes. The presence or absence of the analyte can change the resistance that is inherent in the sensing material. Analytes interact with the sensing material during exposure. The resistance reading changes as a result of these interactions.

Some chemical resistors simply show analyte presence when the resistance changes. It is possible to determine the amount of analyte present in some cases when the resistance variations are proportional to the analyte concentration.

Chemical warfare agents and gases such NH_3 , H_2 , HCl , NO_2 , H_2S , CO , CO_2 , SO_2 , LPG, (CWAs) and vapour of volatile organic compounds (VOCs) were sensed by chemiresistors using polyaniline (PANI) nanocomposite based materials [62]. It has been successfully tested that PANI-based sensors, which transform a chemical interaction into an electrical signal and cover a wide variety of applications, are effective sensors for monitoring both organic and inorganic substances. In the development of chemiresistor based on conductive polymer Lange U., et al. reported the application of two, four and six electrodes measurement configuration in overcoming artifacts and other effects caused by contact resistance and others. This regeneration of chemiresistive sensors performs speedy and reversible measurements [63]. Due to the distinctive structure and remarkable properties, two-dimensional materials (2DMs), have proven to be desirable for fabrication of chemiresistor gas sensors [64]. The 2DMs such as graphene, transition metal dichalcogenides (TMDs), graphitic carbon nitride (g-C₃N₄), metal-organic frameworks (MOFs), MXenes, black phosphorus (BP), boron nitride (BN), etc are used for fabrication of chemiresistors.

2.7.3 Capacitive Sensors

A detailed analysis of the past, present and future of capacitive sensing is explained by Ghafar et al. [65]. Fig. 2.6 shows a parallel plate capacitor whose concept can be used for different sensing purposes as a capacitive sensor. The prime advantage of capacitive

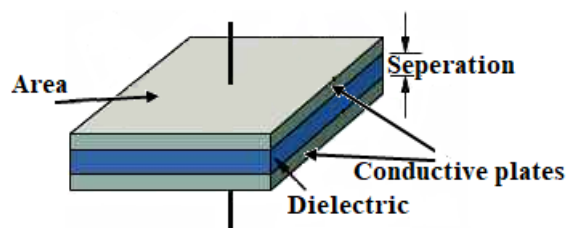


Figure 2.6: Parallel plate capacitor

sensing is that sensing can be done at very high speeds down to the ns range. Some of the advantages of capacitive sensing over the alternate existing sensing technologies are its increased sensitivity, power saving, increased signal to noise ratio (SNR) and easy-to-fabricate properties. All the major applications using capacitive substrates detect the capacitive changes by functionalizing the electrode or dielectric layer. By altering the functional group of the material, specific detection of analytes is achieved.

2.7.4 Optical sensors

In the middle of the 1960s, it was first proposed to employ optical fibers for sensing purposes. Since then, numerous analyte-detection fiber-optic chemical sensors have been developed. Analytical data are investigated by optical sensors and assays using optical transduction techniques like absorbance, reflectance, luminescence, etc. These fiber-optic technologies have produced high-quality and affordable optical fibers that can be used for chemical sensing applications. Optical fibers are surprisingly robust, adaptable, and long-lasting. Since its small size enables *in vivo* sensing, eliminating the need for sample collection, fiber-optic chemical sensors are also widely used in the clinical field. Due to the integration of high specificity (from molecularly imprinted polymers (MIPs)) and flexible sensing ability, the optical fiber (OF) sensors based on MIPs are able to have consideration globally [66].

Sultangazin A., et al. in 2017 reported hydrogen sulfide detection using the chemical sensor that uses smartphone having made of plastic optical fiber (POF) [67]. A smartphone flashlight is used as the sensor's source, while a camera serves as its detector. A 3-D printed connector is employed to connect the source and detector sides of the POF to the smartphone. Through the deposition of silver on the POF's outer surface, the sensor is made functional for the detection of H₂S. Experiments show the sensor system's viability because they successfully detect the presence of H₂S by increasing optical losses across the POF link. Distributed optical fiber sensors (OFS), including OTDR and OFDR, can sense temperature or acoustic signals to monitor pipeline leaks. Many specific applications in the fields of agricultural, civil, and petroleum engineering are investigated using OFS [68].

2.7.5 Electrochemical sensors

For the investigation of water, and food quality great attention has been paid to the fabrication of analytical sensors. In overcoming the limitations of different analytical methods, the focus has been given to the electrochemical sensors. Broadly there are two categories of electrochemical sensors-i) the potentiometric sensor that changes its potential with respect to the analyte and ii) voltametric and amperometric sensor where the conductivity changes due to redox reaction in the electrode structure [69]. This amperometric sensor has now been established for a wide variety of analytes, including CO, nitrogen oxides, H₂S, O₂, glucose, unusual gases like hydrazine, and many more vapors, in a wide variety of geometries. A triple potential-step

chronoamperometric technique was created by Amatore et al. to allow for the simultaneous measurement of reactive oxygen and nitrogen species produced by immunostimulating macrophages [70]. Because it combines small size, low power, high sensitivity, and a relatively low price, the amperometric gas sensor has an advantage over many other types of sensors and is ideal for portable toxic and explosive gas instrumentation. Low oxidation signal and high over potential are the limitations of electrochemical sensors [71]. Recently, electrochemical sensors for quick monitoring and detection of SARS-CoV-2 from patient biologic fluid samples have been established [72]. Because of their great reactivity and selectivity, optical and electrochemical sensors and biosensors have recently been utilized to estimate antioxidant activity [73].

2.7.6 IDE capacitive sensor

The capacitive sensor exhibits a revolutionary change in the nanosensing world making a huge impact in the fields of healthcare, defence, electronics and environmental sensing fields. In a capacitive sensor, the stray capacitance of the leads (conductors that connect the electrodes with the electrical excitation source) (Fig 2.6) is equivalent to the capacitance between two coplanar strips. Therefore, the coplanar strip pattern may be repeated numerous times to create an interdigitated electrodes (IDE) configuration that is easy to measure [74]. Compared to signals produced by a single pair of electrodes, those obtained by the repeated nature of the electrode fingers were stronger. Owing to its advantages, planar interdigital sensors have been widely used in a variety of applications during the past few decades due to compactness, quick response times, lack of radiation, and lower manufacturing costs, etc [75] [76]. It has a low-cost mass-fabrication process and the ability to use them for many different applications without having to make notable changes in the design [77]. Research has been going on in the improvement of the performance of the IDE capacitive sensors. Igreja et al. in 2004 examined the problems with designing the capacitance of the interdigital electrodes for a multi-layer construction. To investigate the non destructive testing (NDT) and material characterization of this kind of sensor construction, they used an analytical tool [78]. Li et al. offered a thorough examination of the impacts of interdigital sensor design factors and geometry, such as electrode width and substrate thickness, on their performance [79]. The type of substrates used to create the electrodes is what distinguishes magnetic and capacitive sensors operating on the same interdigital transducers [80]. varying the

geometry of the sensors the sensitivity of these sensors can be improved [81]. There hasn't been much research done so far on how interdigital sensors' geometric parameters affect their performance [81, 82].

In this dissertation, the concept of capacitive sensing has been expanded to a novel development of chemical sensors for the interest of monitoring the phytochemical of fruit juices which causes delayed bitterness in it. Furthermore, a dielectric changing technique using specific functional groups has been implemented. The use of a single passive electronic device to create multiple low-cost, portable, flexible and disposable chemical sensors has been achieved using the principles of capacitive sensing.

2.8 Summary

This chapter has given a brief introduction to citrus fruits and the phytochemicals present in citrus fruits that cause bitterness. The biomolecule limonin is responsible for delayed bitterness which can be used as an indicator for bitterness assessment in citrus fruit juices. Various conventional methods and techniques used to quantify limonin were reviewed. The limitations associated with the techniques were noted such as destructive to its test sample, time-consuming, requiring complex sample preparation and data analysis, expensive, laborious and requiring skilled persons to operate, etc. Debittering methodologies such as Lye treatment, the addition of sugar, florisil, naringinase, enzyme treatment, etc were reviewed. Further, no work has been reported for the detection as well as reduction measurement of bitter compound limonin using the same device. Therefore, there is a huge scope of research on the development of devices to overcome the present limitations. Different sensor systems used for the assessment of different analytes were reviewed. The Interdigitated Electrodes based (IDE) capacitive sensor has immense potential for overcoming the present limitations and can be implemented for on-site detection as well as measurement in the reduction of limonin content in citrus juices with fast, low cost, high selectivity and sensitivity. The succeeding chapters accompanies the development of sensors based on the IDE structure.

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