Post-Harvest Operations and Processing of Fruits, Vegetables, Spices and Plantation Crop Products

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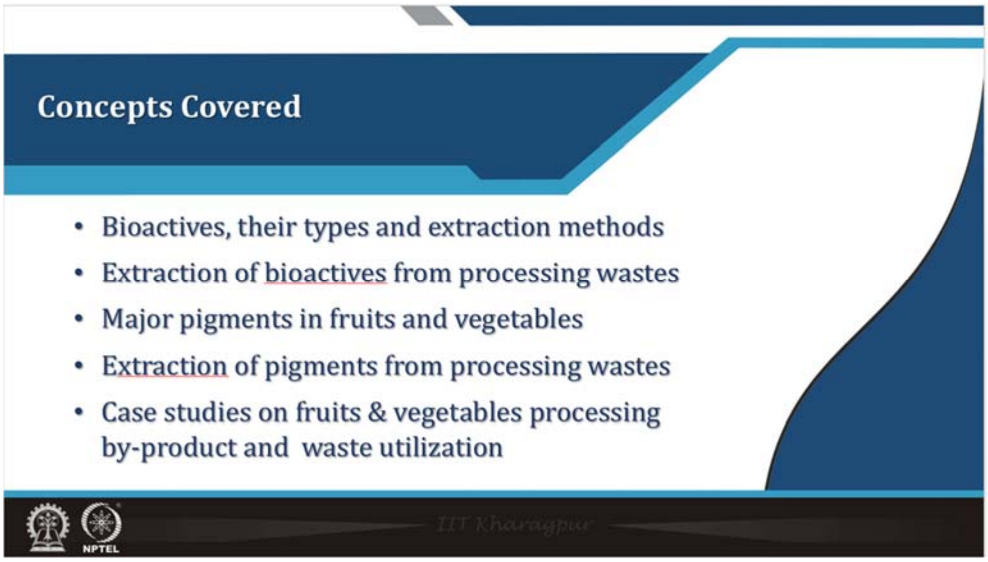
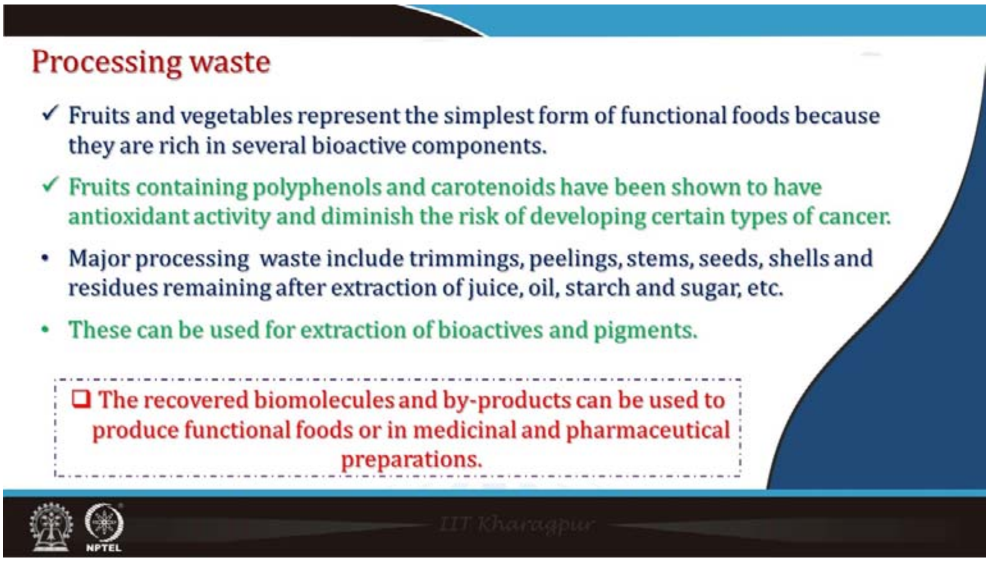
Lecture 57
Extraction of Bio-active and Pigments from Processing Waste

This lecture is about extraction of bioactives and pigments from processing waste.

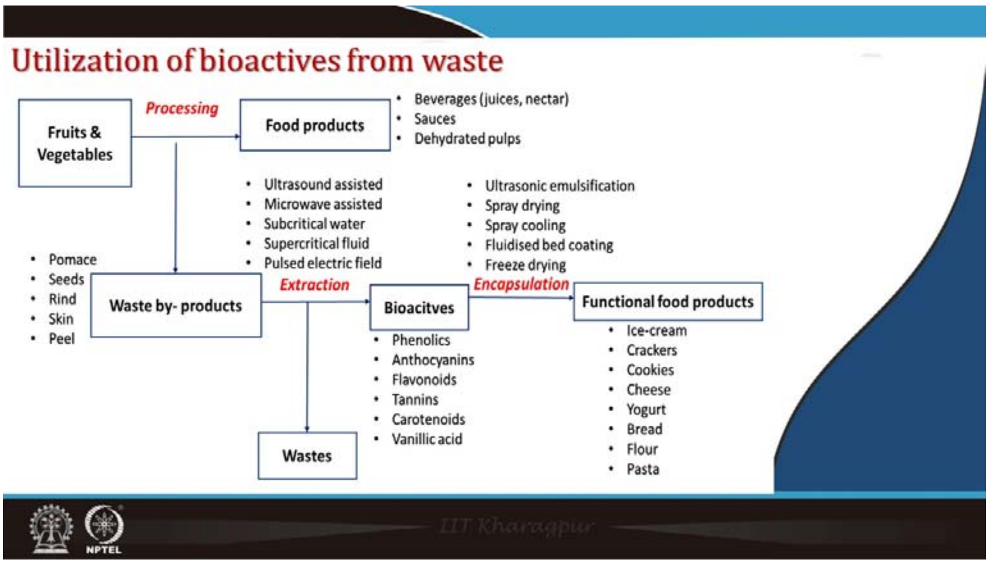


The concepts covered in this lecture include bioactives, their types and extraction methods, extraction of bio-actives from food processing wastes, major pigments in fruits and vegetables and their extraction of pigments from processing wastes, and in the end, a few case studies related to the fruits and vegetables processing by-products and waste utilization.



Processing waste

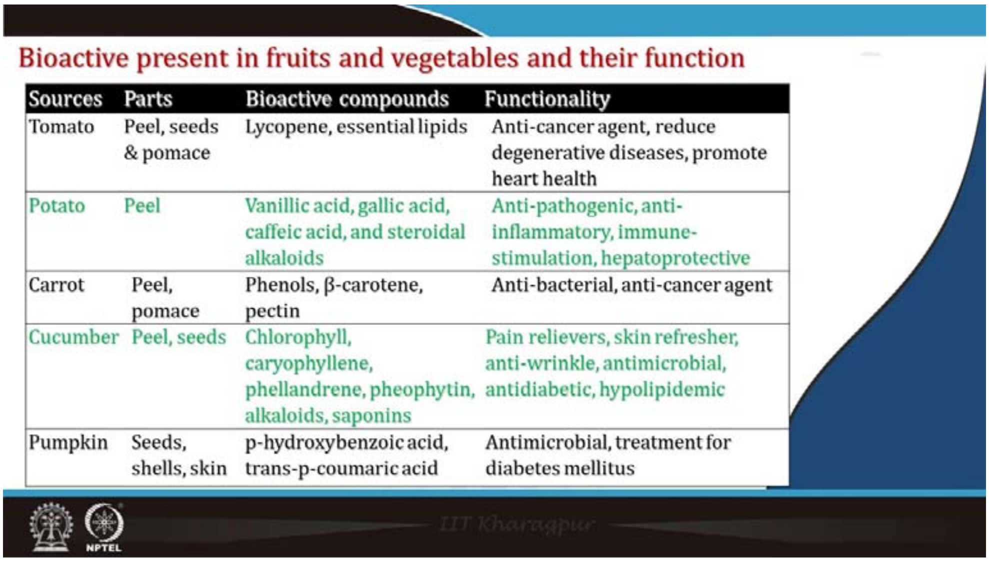
Fruits and vegetables represent the simplest form of functional foods because they are rich in several bio-active components. Fruits containing polyphenols and carotenoids have been shown to have antioxidant activities and they diminish the risk of developing certain types of cancer. Major processing waste includes trimmings, peelings, stems, seeds, shells, even residues remaining after the extraction of juice, oil, starch and sugar, etc. These are a huge amount of waste and by-products is generated particularly from the fruits and vegetables processing industry. So, these wastes can be used for extraction of bio-active components and pigments, etc., because they contain a huge amount of these valuable materials. The recovered biomolecules and by-products can be used to produce functional foods or in medicinal and pharmaceutical preparations.



Utilization of bioactives from waste

The fruits and vegetables can be utilized in various products through processing such as juice, nectar, sauces, dehydrated products etc. After processing various waste by-products like pomace, seeds, rind, skin, peel etc. are produced. So, these by-products can be subjected to appropriate technologies to extract bioactives either by conventional method or by novel extraction techniques and the bio-actives like phenolic, anthocyanins, flavonoids, tannins, etc. can be extracted from them.

These extracted bio-actives can further be encapsulated so as to increase the stability during processing. So, the encapsulation methods such as spray drying, ultrasonic emulsification, spray cooling, fluidized bed coating, and freeze drying. These encapsulated bio-actives can be used in the preparation of various functional foods, as an ingredient in ice cream, crackers, cookies, cheese etc.


Bioactive present in fruits and vegetables and their function

Sources	Parts	Bioactive compounds	Functionality
Tomato	Peel, seeds & pomace	Lycopene, essential lipids	Anti-cancer agent, reduce degenerative diseases, promote heart health
Potato	Peel	Vanillic acid, gallic acid, caffeic acid, and steroidal alkaloids	Anti-pathogenic, anti-inflammatory, immune-stimulation, hepatoprotective
Carrot	Peel, pomace	Phenols, β-carotene, pectin	Anti-bacterial, anti-cancer agent
Cucumber	Peel, seeds	Chlorophyll, caryophyllene, phellandrene, pheophytin, alkaloids, saponins	Pain relievers, skin refresher, anti-wrinkle, antimicrobial, antidiabetic, hypolipidemic
Pumpkin	Seeds, shells, skin	p-hydroxybenzoic acid, trans-p-coumaric acid	Antimicrobial, treatment for diabetes mellitus

Bioactive present in fruits and vegetables and their function

The bio-actives present in fruits and vegetables and their functionality is shown in the table. For example, when the tomato is processed for juice or ketchup or such other things, then its peels, seeds and pomace were emerged as a waste but they contain substantial amount of lycopene and essential lipids and these lycopene, essential lipids, etc. have very good anti-cancer agent. They reduce degenerative diseases, promote heart health.

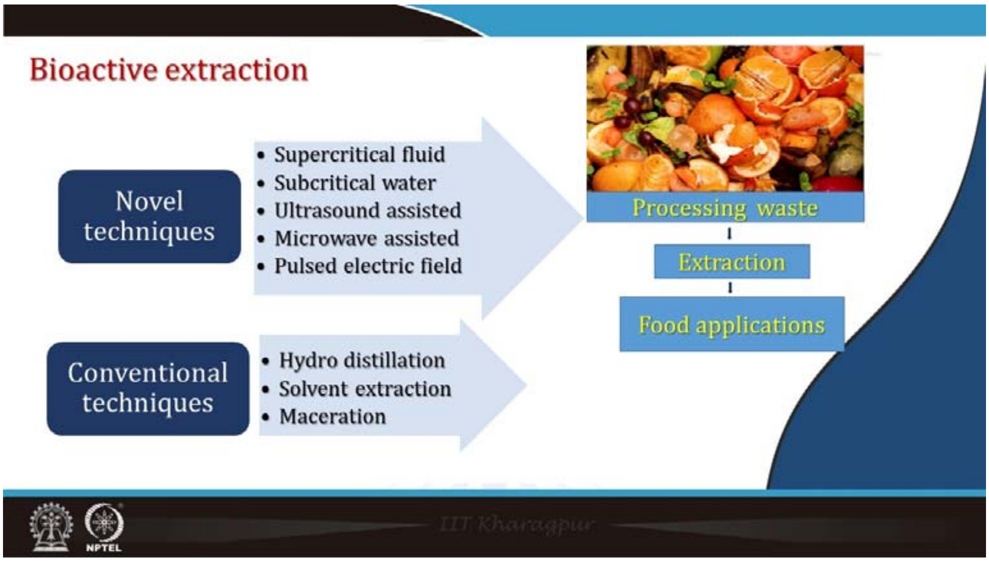
Potato peel contains vanillic acid, gallic acid, caffeic acid, steroids alkaloids etc and have various health promoting functions like anti-pathogenic, anti-inflammatory, immune stimulation. Carrot peel and pomace contain phenols, beta-carotene, pectin which has antibacterial activity, they are also anti-cancer agent. Even pumpkin seeds, skins, shells have p-hydroxybenzoic acid, trans-p-coumaric acid, which are anti-microbial and used for diabetes treatment.

Bioactive present in fruits and vegetables and their function (contd...)

Apple	Pomace, peel	Epicatechin, anthocyanins, phloretin, quercitin glycosides	Blood pressure reduction, anti-inflammatory properties, modifications of plasma lipids
Grapes	Skin, seeds, stem	Caffeic, ferulic, coumaric & chlorogenic acids, proanthocyanidins	Cardio protective, anti-ageing, anti-cancer, enhancement of gut health, anti-microbial potential
Pomegranate	Seeds, peels, pericarp	Gallic acid, delphinidin-3,5-diglucoside, cyaniding diglucoside,	Reduce LDL, inhibit melanogenesis, anti-cancer activity, dietary supplements
Citrus fruits	Peel, seeds	Naringin, eriocitrin, hesperidin, narirutin	Mucoprotective agent, anti-stress, anti-carcinogenic, improve gastro-intestinal health
Mango	Kernel, peel	Anthocyanins, ellagic acid, quercetin, tannins, mangiferin, etc.	Hypocholesterolemic, extension of oil stability, anti-cancer, anti-microbial

The apple pomace and peel contain epicatechin, anthocyanins, quercetin or other glycosides which helps in the reduction of blood pressure, has anti-inflammatory properties etc. Grape skin, seeds and stem have caffeic acid, ferulic acid, carbonic acid, chlorogenic acid and proanthocyanidins and have various health promoting activities like they are cardio protective, anti-aging agent, anti-cancer, and have enhancement of gut health.

Pomegranate, citrus fruits, even mango, all their waste i.e. whether seed, peel, pericarp, kernel, pulp have good valuable components like mango kernel and peel contain anthocyanins, ellagic acid, quercetin, tannins, mangiferin etc., which have hypocholesterolemic, extension of oil stability, they have anti-cancer, anti-microbial activities and so on.



Bioactive extraction

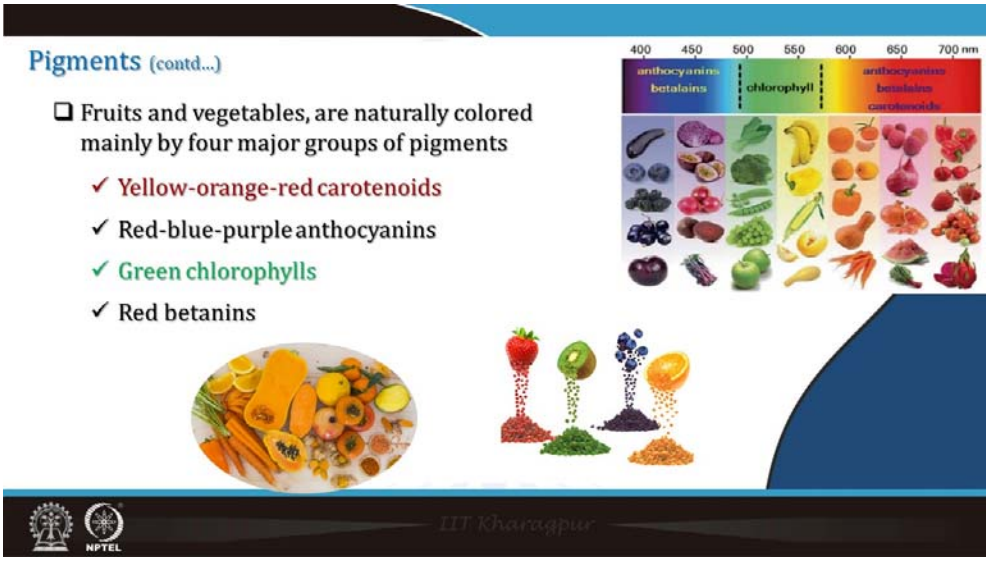
The bioactives from the waste can be extracted either using novel technologies or conventional technologies. Novel technologies include supercritical fluid extraction, subcritical water extraction, ultrasound-assisted, microwave-assisted, and PEF-assisted techniques. Conventional technology includes hydro distillation, solvent extraction, maceration and so on.

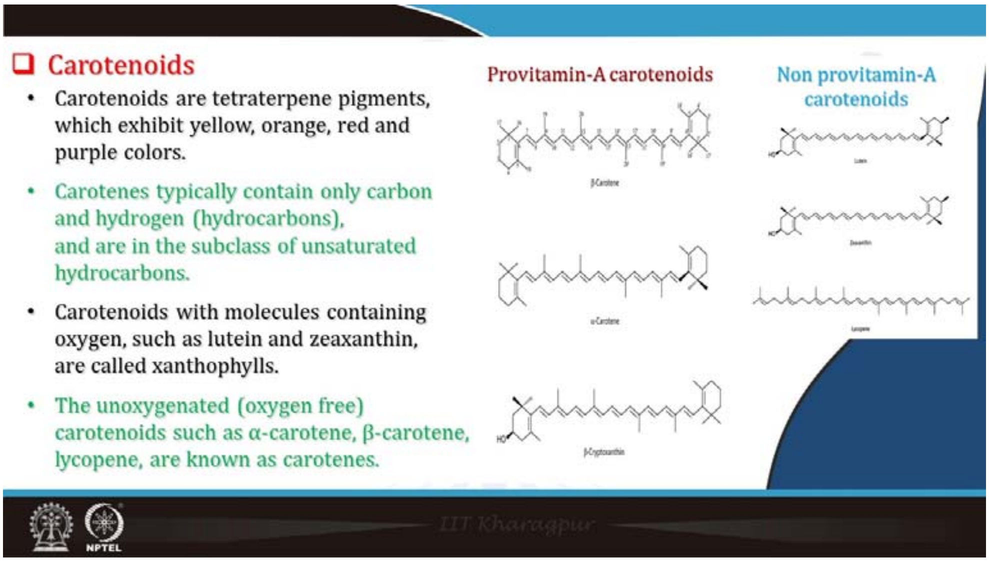
The details of all these technologies had been discussed in earlier classes. The adjustment of the process parameters might be required, but the same technology can be used and then extracted materials can be applied used as an ingredient in food processing.

Pigments-Natural colors

Pigments are present in fruits and vegetables, they are very good source of food color. This natural food color is any dye, pigment or any other substance obtained from fruits, vegetables. They are multicolored because of the presence of various organic compounds which are known as pigments and they contribute to the color of this commodity. The color comes from variety of sources like seeds, fruits, their peels, vegetables, even algae, insect, grass, all these things contain these coloring components and these coloring components can be extracted i.e. the color can be extracted from these components.

The fruits and vegetables, are naturally colored in the form of 4 major groups of pigments. These are either yellow-orange-red carotenoids, red-blue-purple anthocyanins, green chlorophylls, or red betanins. Betanins is the major group of color compounds or pigments present in most of the fruits and vegetables.

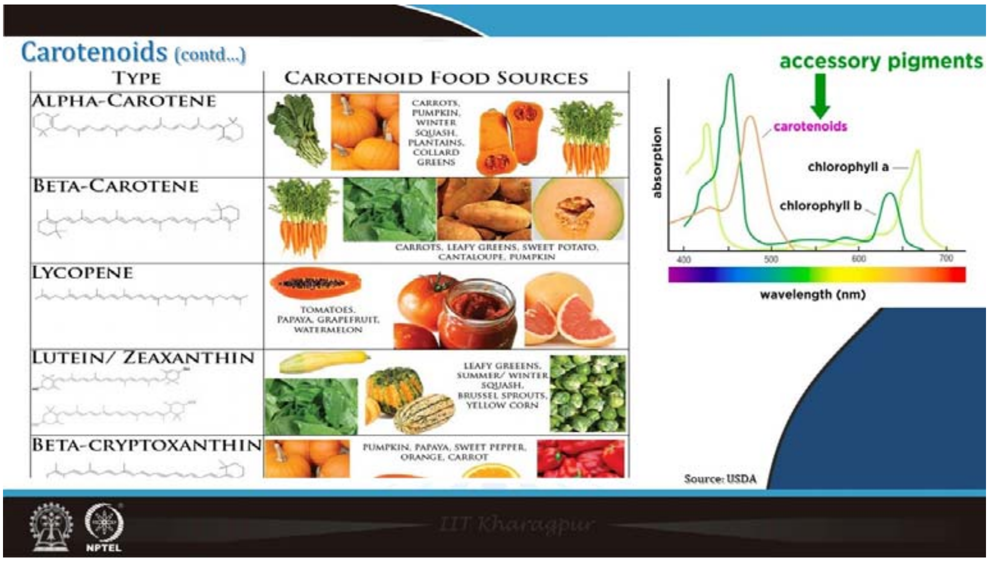




Carotenoids

The carotenoids are tetraterpene pigments, which exhibit yellow, orange, red, and purple colors. Carotenoids typically contain only carbon and hydrogen, so they are basically hydrocarbons and particularly belong to the subclass of unsaturated hydrocarbon, as can be seen in the restructure, they have high degree upon saturated bonds and it is these unsaturated bonds that is the compound they have jagged the colors of different intensity depending on different unsaturated bonds and accordingly, they are color compounds.

Carotenoids with molecules containing oxygen such as lutein and zeaxanthin, are called xanthophylls. In many fruits, the color is present in the form of xanthophylls. The unoxygenated i.e. oxygen free carotenoids, such as beta carotene, alpha carotene, lycopene, are all known as carotenoids or carotenes. The carotenes are a precursor of vitamin A also called pro-vitamin A. When these carotenoids are present in plant foods, they have the pro-vitamin A activity like beta carotene, alpha carotene, beta-cryptoxanthin and so on. When the pro-vitamin A is consumed in body, these are converted into vitamin A. There are certain carotenoids like lutein, zeaxanthin, lycopene etc., lycopene is the color of the tomato. They do not have any pro-vitamin A activity. So, they are known as non-pro-vitamin A carotenoids.

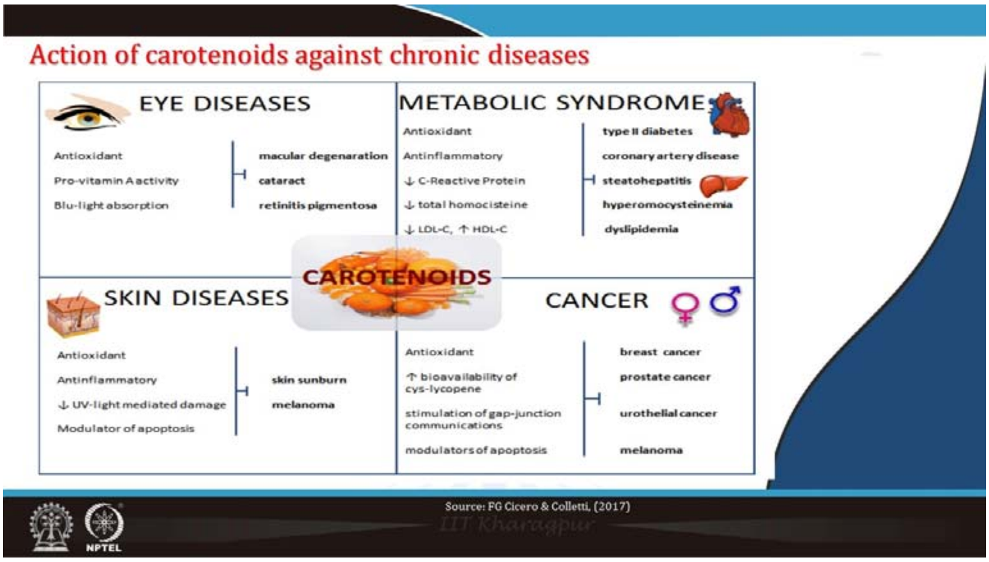


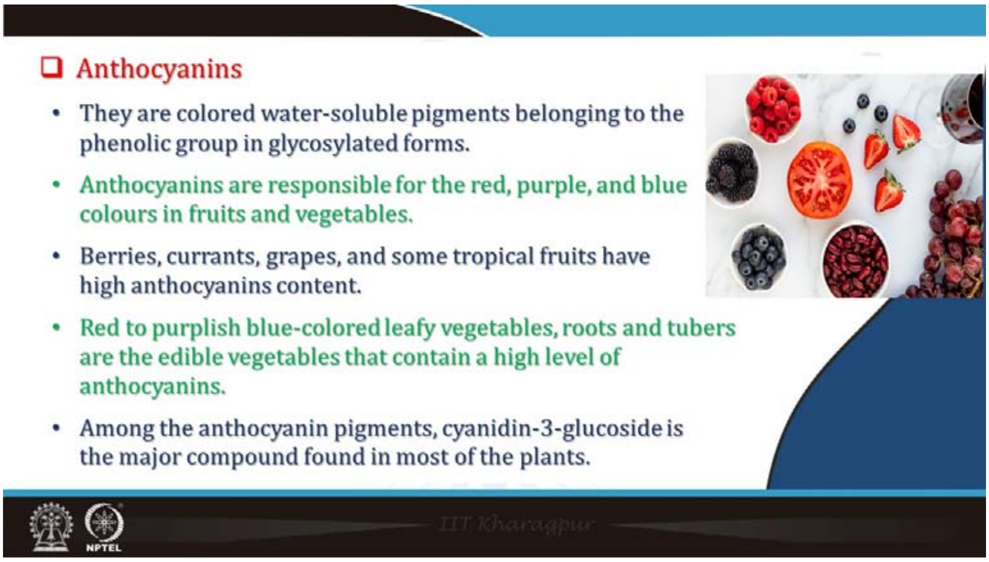
The carotenoids types and their major sources like alpha-carotene is found in carrots, pumpkin, winter squash, plantains, collard greens, etc. Beta-carotene major sources include carrot, leafy greens, sweet potato, and pumpkin. Lutein and zeaxanthin are found in leafy greens, summer / winter squash, brussel sprouts, and yellow corn. Beta-cryptoxanthin is found in pumpkin, papaya, sweet pepper, orange, carrot and so on.

Here in the figure, it can be seen that absorbents they have these compounds like carotenes, they have absorption spectra somewhere around 475 or 480 nm. Chlorophyll A and chlorophyll B, have somewhere around in between 600 to 700 nm. So, these various compounds have different absorption spectra i.e. at different wavelengths, they get the peak and that is how they are normally characterized.

Action of carotenoids against chronic diseases

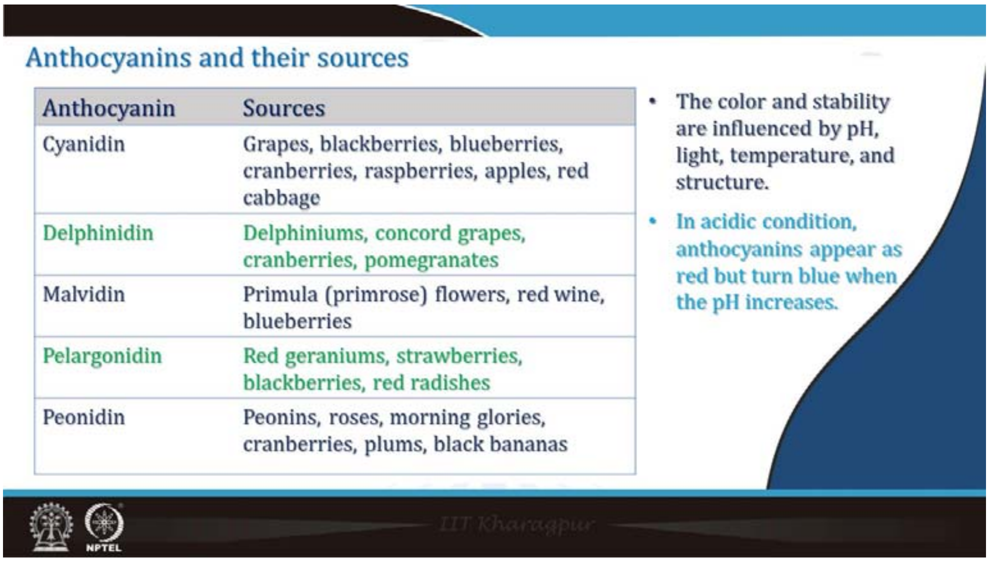
These carotenoids are very useful against various chronic diseases. For example, the carotenoids that contains antioxidant, pro-vitamin A activity, and have blue light absorption effect are beneficial against the macular degeneration, cataract, retinitis pigmentosa. Similarly, in the skin disease i.e. these antioxidant property or anti-inflammatory property or lower down the UV light mediated damages give useful effects on skin sunburn, melanoma etc. So, these carotenoids have their full potential in the whole fruits and vegetables i.e. when we take raw fruits and vegetables, we get these carotenoids. If these fruits & vegetables are bit lukewarm, their potential to fight against the diseases is improved.





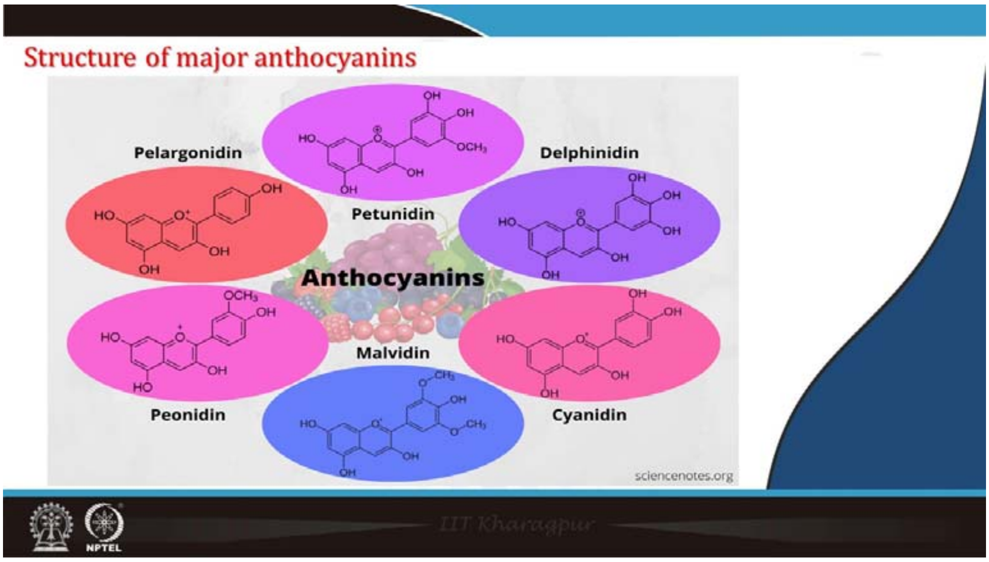
Anthocyanins

Anthocyanins are colored water-soluble pigments belonging to the phenolic group in glycosylated forms. Anthocyanins are responsible for red, purple and blue color in fruits and vegetables. Berries, currants, grapes, and even some tropical fruits have high anthocyanin content. They have red to purplish blue color, even leafy vegetables, root, tubers are the edible sources that contain high level of anthocyanins. Among the anthocyanin pigment, cyanidin-3-glucoside is the major compound found in most of these plants.



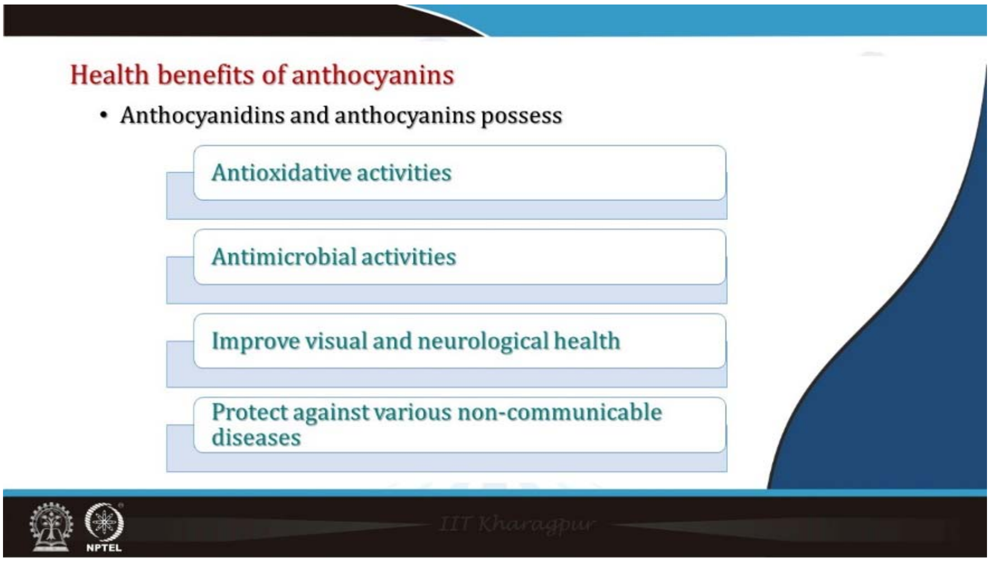
Anthocyanins and their sources

Anthocyanins are grouped in five types like cyanidin, delphindin, malvidin, pelargonidin, and peonidin. They have sources like malvidin is found in the flowers, red wine, blueberry etc. Cyanidin is found in grapes, blackberries, blueberries, cranberries, raspberries, apples and so on. The major portion of these color remains are in the peel or the pomace. So, they can be used to extract. The color and stability of these carotenoids are influenced by pH, light, temperature and structure. In acidic condition, anthocyanins appear as red, but turns blue when the pH increases. The colored nature of these carotenoids may be influenced during processing, but the health value may of course remain intact or it may in some cases may get improved.



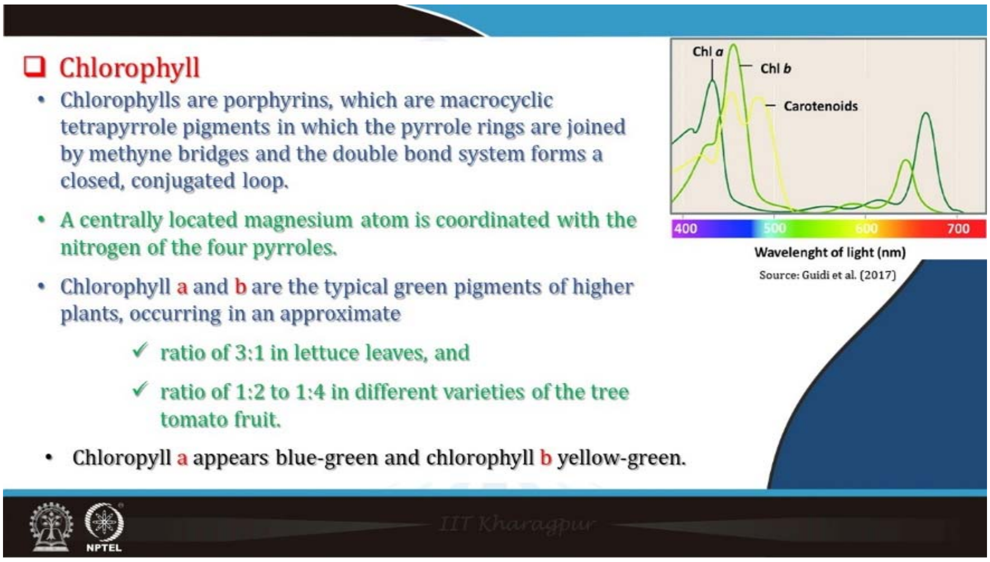
Structure of major anthocyanins

The structure of major anthocyanins are basically phenolic compounds, they have been changing in the structure, and are highly unsaturated. There is a little difference in the structure, compound with each other due which, sometimes have different colors intensity, a color hue and also their health value.



Health benefits of anthocyanins

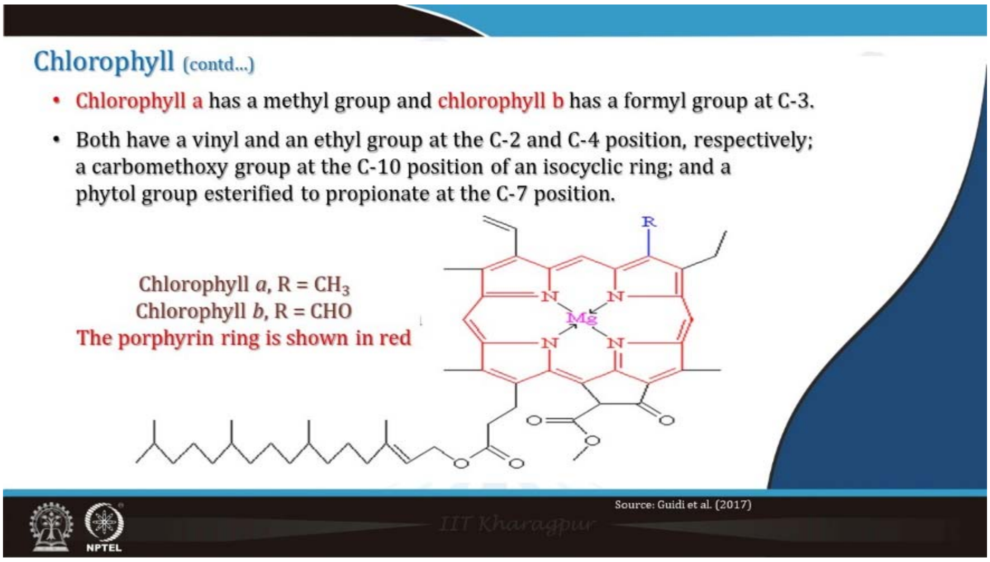
The health benefits of anthocyanins include anti-oxidative activity, anti-microbial activity, they improve visual and neurological health, and protect against various non-communicable diseases.



Chlorophyll

Chlorophyll is another major color compound that is green in color and found in most of the plants. Chlorophylls are porphyrins, which are macrocyclic tetrapyrrole pigments in which the pyrrole rings are joined by methyne bridges and the double bond systems forms a closed, conjugated loop. There is a centrally located magnesium. These all pyrrole rings are joined by the magnesium atom and coordinated with the nitrogen.

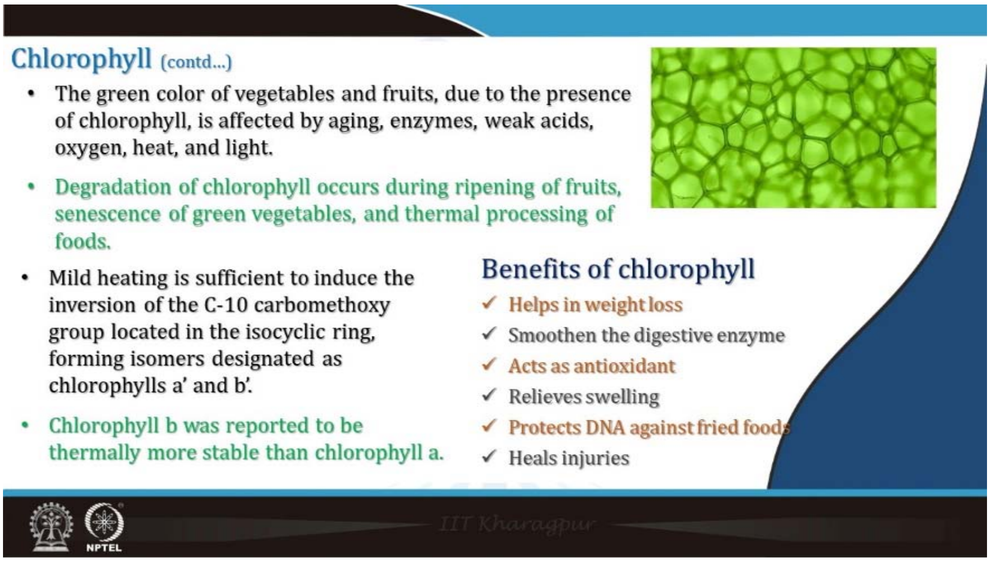
There are 2 types of chlorophyll i.e. chlorophyll A as well as chlorophyll B. Chlorophyll A and B are both typical green pigments of higher plants. They occur in various proportions, for example, they are found in 3:1 ratio in lettuce leave or 1:2 to 1:4 ratio in different varieties of tree tomato fruit. Chlorophyll A appears blue-green in color whereas the chlorophyll B is yellow-green.

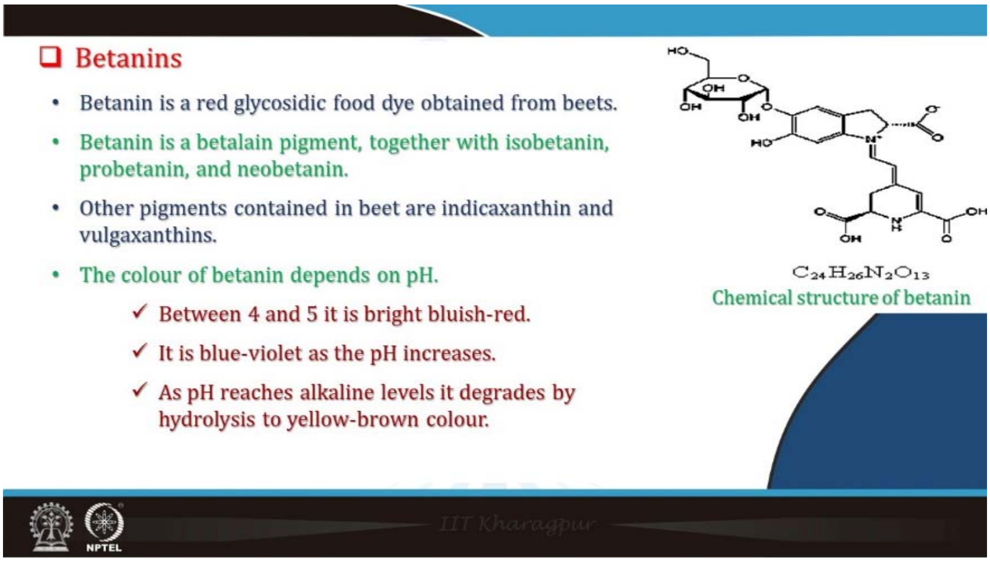


Chlorophyll A has a methyl group and chlorophyll B has a formyl group at third carbon (C-3). i.e R in the figure. So, R group in the A is methyl and in the B is the formyl group and both have a vinyl and ethyl group at C-2 and C-4 position, respectively. There is a carbomethoxy group at C-10 position of an isocyclic ring, and a phytol group esterified to the propionate at the C-7 position. When the green chlorophyll containing vegetables etc. are processed, sometimes these phytol group is removed that central magnesium is removed and accordingly that chlorophylls are converted into pheophytins or pheophorbides and color will change. So, particularly the green vegetables during cooking and processing undergoes various reactions resulted in change in color.

The green color of vegetables and fruits, due to the presence of chlorophylls, is affected by aging, enzymes, weak acids, oxygen, heat, and light. The degradation of the chlorophyll occurs during ripening of fruits, senescence of green vegetables, and thermal processing of foods.

The chlorophyll B was reported to be thermally more stable than the chlorophyll A and these both form of chlorophylls have immense health benefits like they helps in weight loss, smoothen the digestive system, acts as antioxidant, relieves swelling, protects DNA against fried foods etc. and they heals the injuries, wounds and injuries.



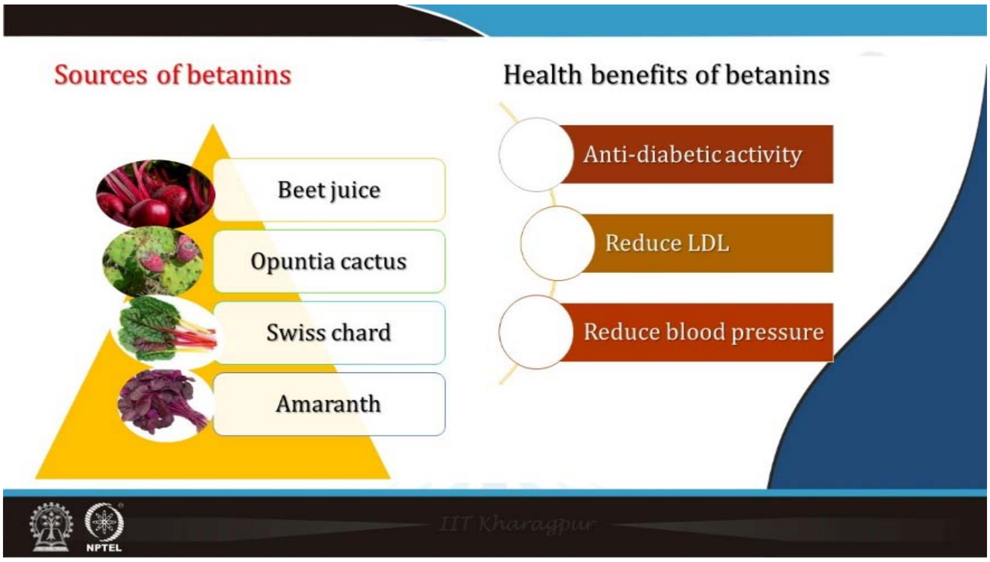


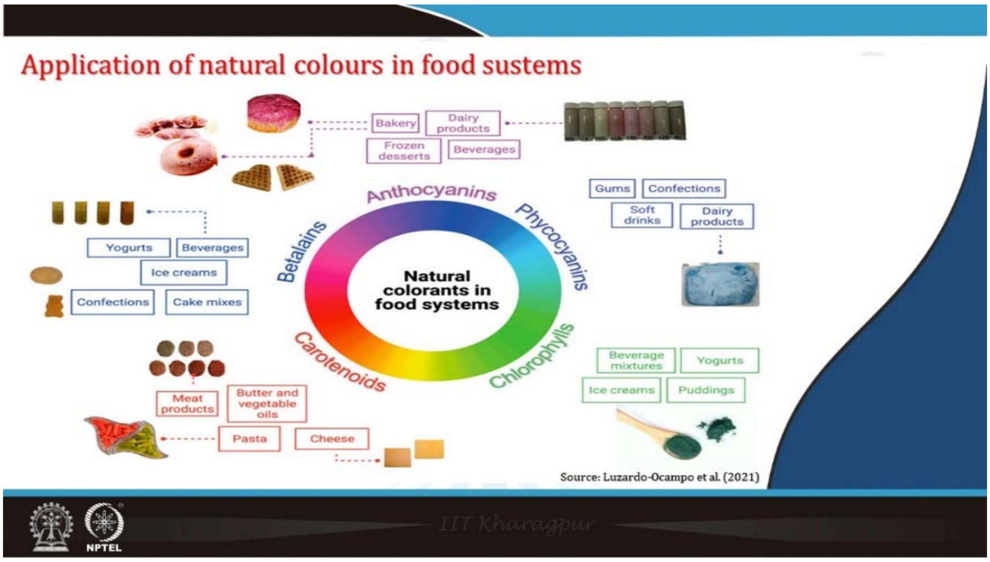
Betanins

Betanin is a red glycosidic food dye obtained from the beet roots. It is a betalain pigment together with isobetanin, probetanin, and neobetanin. Other pigments contained in the beet are indicaxanthin and vulgaxanthin. The color of betanin pigment depends upon the pH. So, when the pH is between 4 and 5, it is bright blueish-red in color, it is blue-violet as the pH increases and as the pH reaches alkaline level, it degrades by hydrolysis to yellow-brown color.

Sources of betanins

The sources of betanins include beet juice, opuntia cactus, swiss chard, amaranth etc. They have various health benefits like they are anti-diabetic, they reduce LDL, they reduce blood pressure and many more.

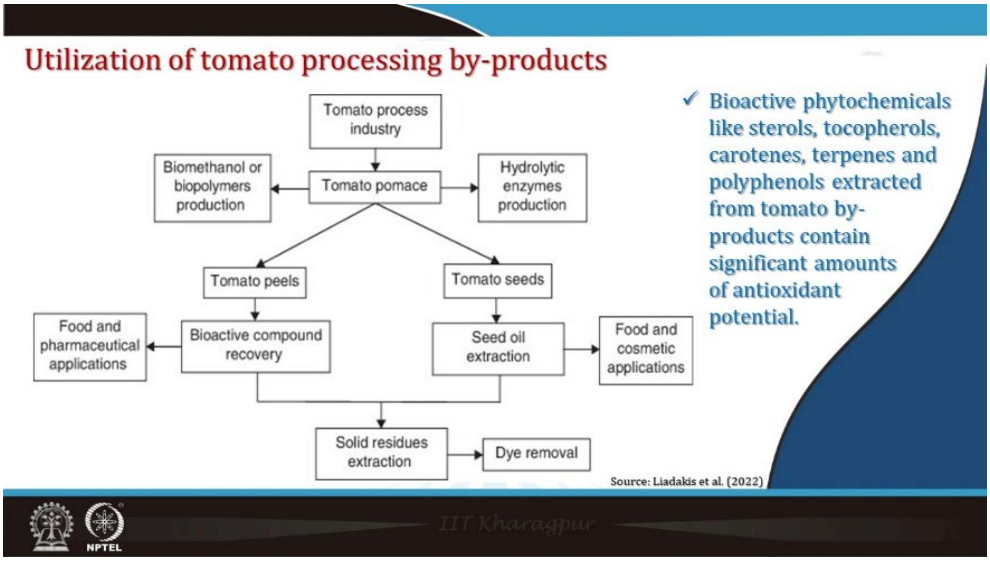




Application of natural colors in food systems

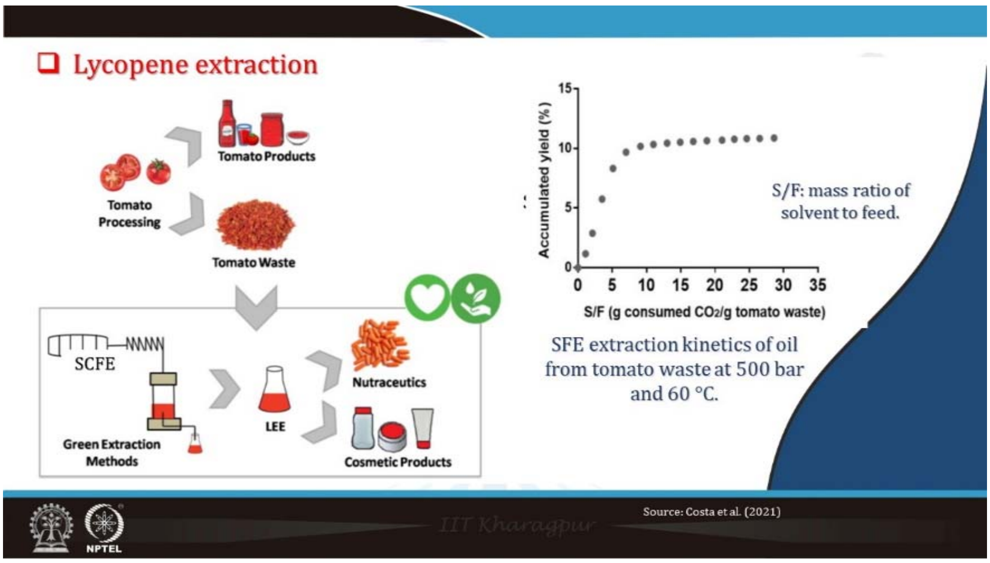
The application of natural colors in the food systems include anthocyanins, phycocyanins, chlorophylls, carotenoids, and betalains. These are the major groups of coloring compounds present in the various plant material and in the waste also. So, they can be accordingly used like betalains can be used in the manufacture of yogurt, beverage, ice cream, confections, cake mixes, etc.

Anthocyanins may be better incorporated into the bakery product, dairy product, frozen dessert, beverages. Phycocyanins in gums, confections, soft drinks, dairy products etc. Carotenoids can be used in meat products, in butter and vegetable oils, cheese, paste and so on. Chlorophylls can be used in the beverage mixtures, yogurt, puddings, ice creams. Overall, these colorants can be used or incorporated into the various food products.



Utilization of tomato processing by-products

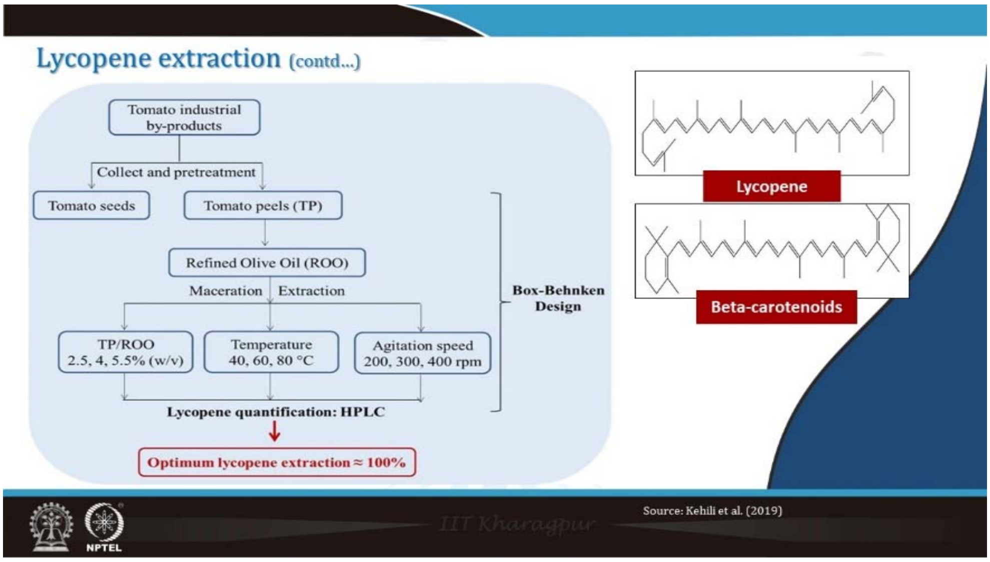
The tomato, when it is processed for juice, concentrate puree etc. to get the tomato pomace and this tomato pomace can be used for production of bio-methanol or biopolymers production or even hydraulic enzymes production can also be done. These tomato pomace include tomato peels and tomato seeds, this peel can be used for bioactive compound recovery and these bioactives can be used in pharmaceutical industry and from tomato seeds, oil extraction is carried out which is used in food and cosmetic industries. The residue from tomato peel and tomato seeds can be used for extraction and then dye removal etc. is done. In fact bio-actives phytochemicals like sterols, tocopherols, carotenes, terpenes, they are all present in the tomato by-products and they have good antioxidant potential.



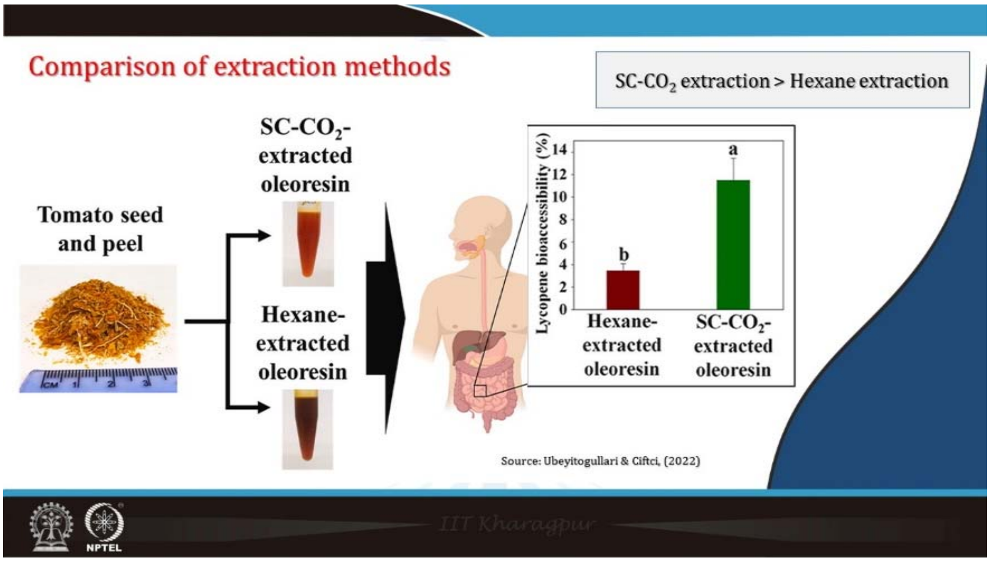
Lycopene extraction

Lycopene is the major color pigment found in the tomato. After the extraction of juice, these colors majority of it retains in the peel or in the pulp residue. After processing of tomato, these wastes can be used to extract lycopene or other compounds. The color can be extracted and used in nutraceuticals and in the cosmetic products.

In this figure, the SFE extraction kinetics of oil from tomato waste at 500 bar and at 60 °C temperature. So, as S to F ratio i.e. the mass ratio of solvent to feed increases, extraction efficiency or accumulated yield of the lycopene increased. It can be seen that from 0 to 5 S/F, yield increases rapidly and after that it is almost stabilized. It can be concluded that proper S/F ratio is required for better recovery.

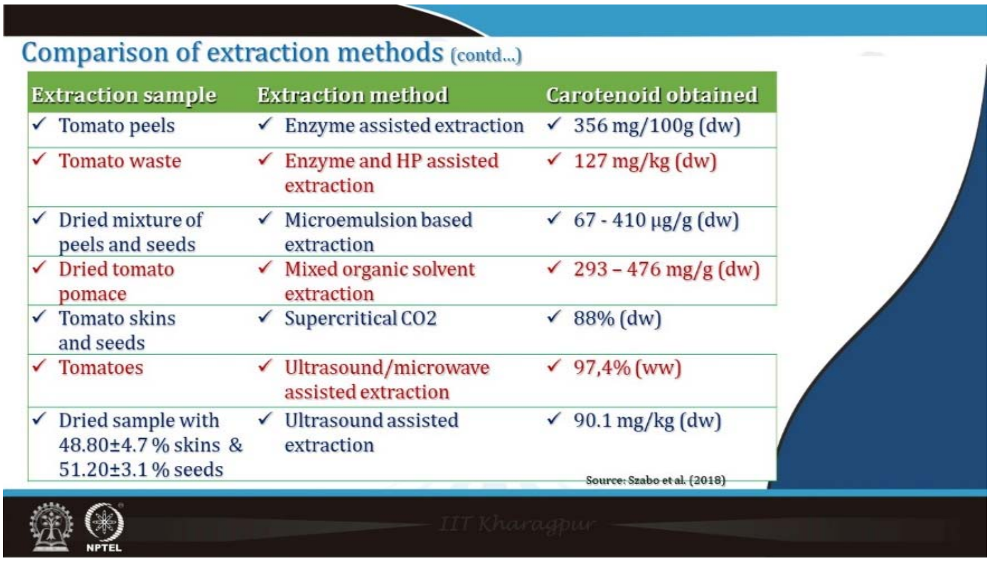


The lycopene extraction process flowchart is shown in the figure. Tomato industrial by-products were collected and pretreatment was given to get tomato seeds (TS) and tomato peels (TP). These peels were mixed with refined olive oil (ROO) and then macerated and extracted were carried out in different proportions of TP and ROO using Box-Behnken design. Finally, the process parameters were optimized for better recovery and yield of the lycopene extraction and the optimum lycopene extraction was almost 100 %. These are the structure of lycopene and beta carotene, they both have almost similar structure with a little difference in the left benzene ring open and closed resulted in change in color.



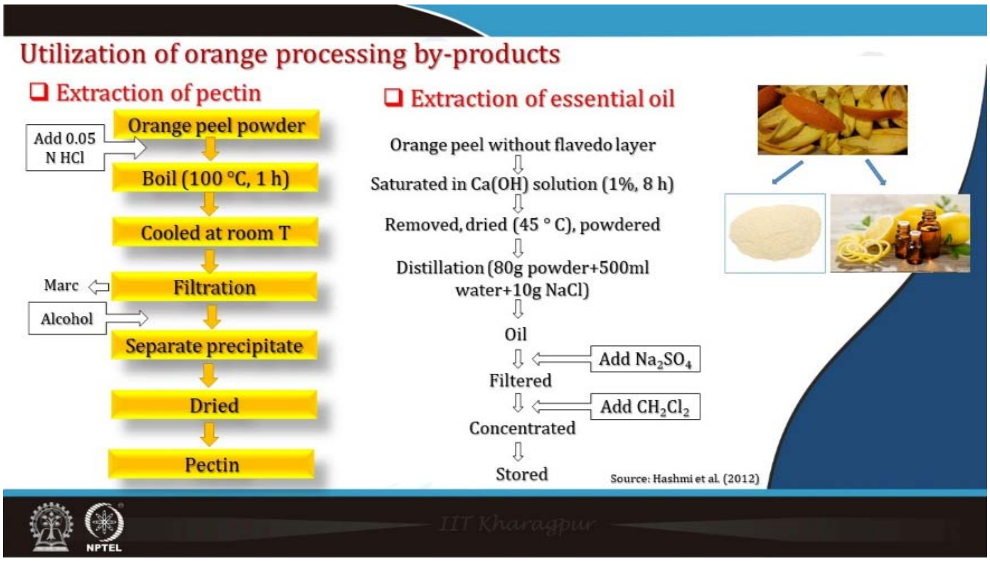
Comparison of extraction methods

Researchers have compared the bio accessibility of lycopene of the supercritical carbon dioxide (SC-CO_2) extracted oleoresin from the tomato seed and peel with the hexane extracted oleoresin. It was found that SC-CO_2 extraction is more biologically accessible than hexane extraction.



Extraction sample	Extraction method	Carotenoid obtained
✓ Tomato peels	✓ Enzyme assisted extraction	✓ 356 mg/100g (dw)
✓ Tomato waste	✓ Enzyme and HP assisted extraction	✓ 127 mg/kg (dw)
✓ Dried mixture of peels and seeds	✓ Microemulsion based extraction	✓ 67 - 410 µg/g (dw)
✓ Dried tomato pomace	✓ Mixed organic solvent extraction	✓ 293 – 476 mg/g (dw)
✓ Tomato skins and seeds	✓ Supercritical CO2	✓ 88% (dw)
✓ Tomatoes	✓ Ultrasound/microwave assisted extraction	✓ 97,4% (ww)
✓ Dried sample with 48.80±4.7 % skins & 51.20±3.1 % seeds	✓ Ultrasound assisted extraction	✓ 90.1 mg/kg (dw)

The table showed extraction sample, their extraction method used and the carotenoid content obtained in the sample. For example, for tomato peel, the enzyme assisted extraction got 356 mg/100 g (dw) of carotenoid content. It can also be seen that novel extraction technologies probably gives better yield. Different components of tomato were used by combinations and permutations and even different extraction methods were tried to find the best method for each combination or component.



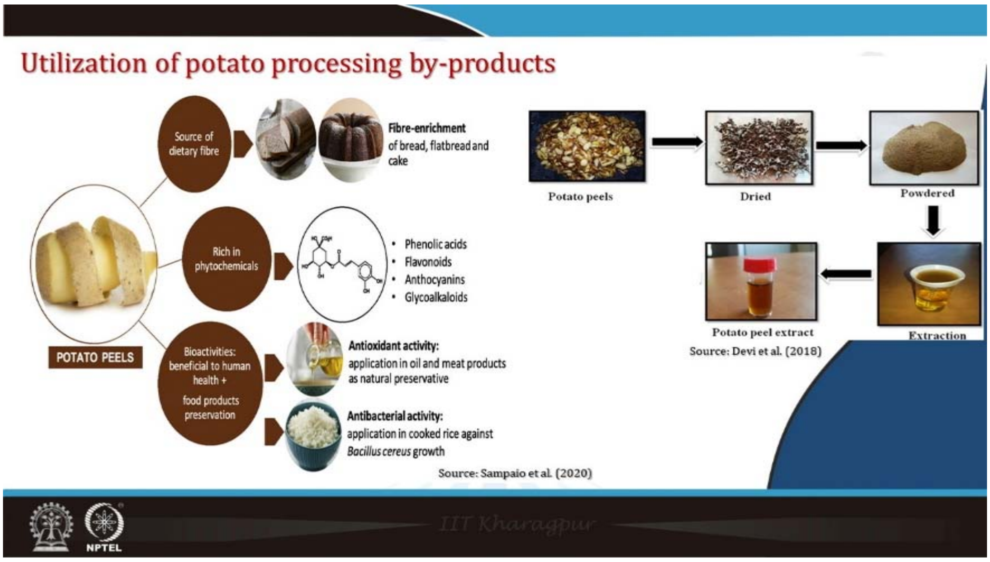
Utilization of orange processing by-products

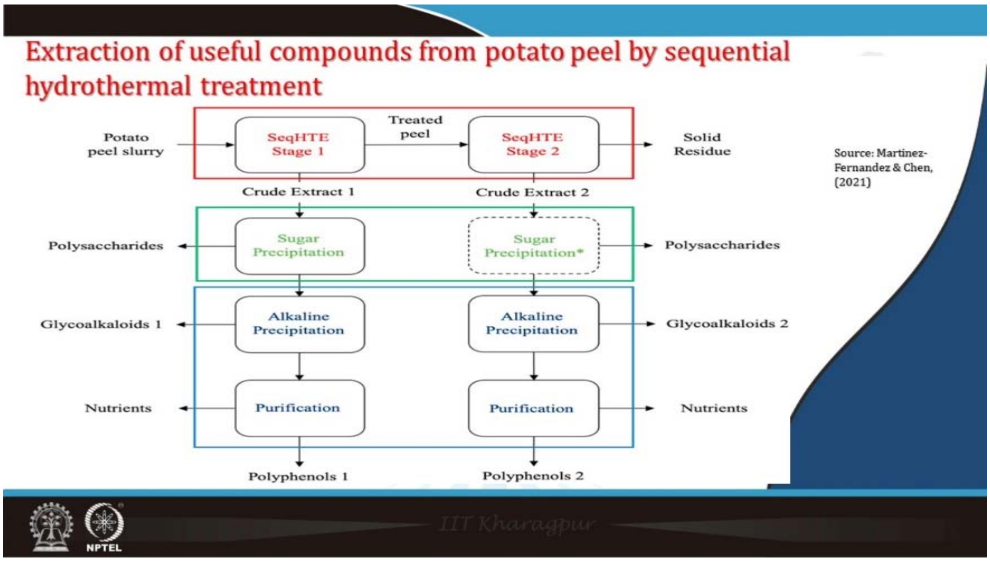
These are the technology reported in the literature for the utilization of orange processing by-products i.e. for the extraction of pectin and extraction of essential oil. For pectin, orange peel is converted into powder using appropriate technology then it is treated with 0.05 N HCl, boiled at 100 °C for 1 h and cooled to room temperature. After that, it is filtered and solid is separated. The liquid portion is obtained or the residue is obtained. It is treated with alcohol and precipitate is separated which is dried to get the pectin powder. Pectin can be further purified and characterized.

For extraction of essential oils, orange peel without the flavedo layer is taken. It is saturated in calcium hydroxide solution (1%, 8 h) and then this is removed from the solution, dried at 45 °C and powdered. This powder is then distilled using either soxhlet apparatus or such other apparatus (80 g powder + 500 ml water + 10 g NaCl) to get oil and sodium sulfate is added to oil and filtered in which ethyl chloride is added, concentrated, and stored.

Utilization of potato processing by-products

A schematic of the utilization of potato processing by-products is shown here. When the potato is processed for chips or other products, it gives the peel which is a source of dietary fiber, and rich in phytochemicals and various bioactives, it is beneficial to human health. So, conversion of these waste peels into various products can be done. The potato peel is dried and powdered, then it is extracted and the potato peel extract can be used in various beverage or other such products.

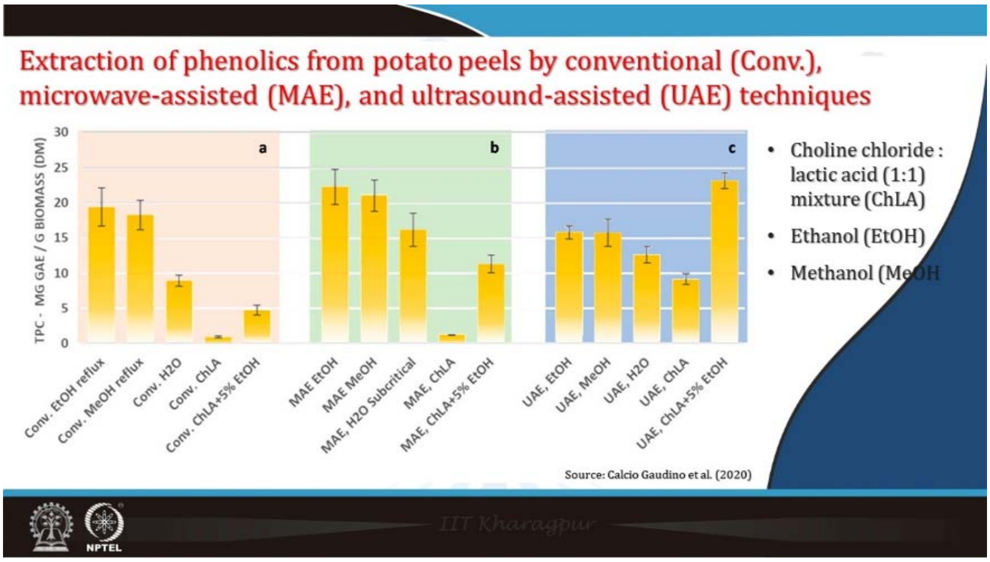




Extraction of useful compounds from potato peel by sequential hydrothermal treatment

The potato peel slurry is treated in two stages. In stage1 & 2, crude extract 1 & 2 are extracted and then sugar precipitation, alkaline precipitation & purification are carried out. During sugar precipitation, polysaccharides are separated. In alkaline precipitation, glycoalkaloids 1 and glycoalkaloids 2 are separated, and finally, by purification, nutrients and polyphenols 1 and polyphenols 2 are separated. Of course, the author has given so there are some other, if you are interested, you can further read to this paper and get more about it.

With the appropriate method, processing technology and optimum process parameters, these valuable components can be obtained from these peels and waste.

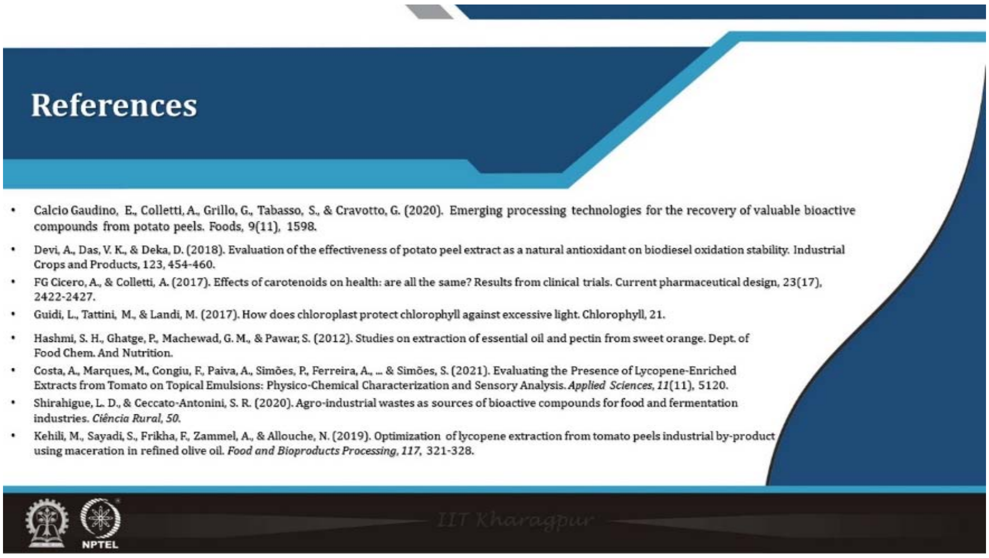


Extraction of phenolics from potato peels

The extraction of phenolics from potato peel by conventional (Conv.), microwave-assisted (MAE), and ultrasound-assisted (UAE) methods has been shown in the figure. Different solvents and their combinations were used to identify the best method and combination and it was found that conventional method with choline chloride and lactic (ChLA, 1:1) gives least TPC, and combination of ChLA & 5% ethanol increases the TPC. Similarly, when the same solvent is used in combination with either microwave or ultrasound, the yield is substantially higher. So, it is better to go for either microwave-assisted extraction or ultrasound-assistant extraction.

Summary

These fruits and vegetables when they are processed generate a huge amount of waste stream or by-products. All these wastes and by-products were almost 50 to 60 %, but these waste is a very valuable source of bioactives and other nutrients. If this waste is left unattended, this will create environmental and many other such problems. But, if there is a proper mechanism in place for their collection especially in poor processing industries like tomato processing industry, it is there responsibility to make some arrangement that whatever wastage being produced, it is properly treated and even if they cannot use, they should have some networking arrangement with some startup and other companies who can utilize these into various value-added products for the extraction of color pigments or bioactives etc. These colorants or bioactives can be used in various food industry, cosmetic industry or pharmaceutical industry depending on their usage. So, proper management of organic by-products is required which will flourish environmental as well as economic benefits by reducing the food waste. The manufacturer will also get the economic advantage along with environmental impact. It is already a win-win situation but the one has to take care that yes waste foods have a proper approach for utilization of these valuable by-products or waste products of horticultural and plantation crop industry.



These are the references used in this lecture.

Thank you very much.