

Different methods for extracting lycopene from Industrial waste tomato paste

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Abstract

Tomato (*Solanum lycopersicum* L.) is the second most important vegetable worldwide. It is valued for its low calories and abundance of bioactive compounds. Carotenoids, especially lycopene, are very valuable compounds that it contains. Lycopene is responsible for its red hue and many health benefits.

About 30% of tomatoes produced each year are lost during processing or harvesting.

Extracting crucial components like lycopene from discarded vegetables, such as skin, pulp or seeds, is an efficient food processing method due to the nutritional benefits.

A variety of methods have been developed to improve the randomization and detection of biological compounds in plant materials. The purpose of these methods is to investigate and re-evaluate the waste and by-products of the tomato, with special attention to the lycopene content, as well as to identify the current technical barriers and possible uses in the food industry. However, challenges related to quality, economic access, industrial replication and environmental safety still exist.

Key words: tomato, lycopene, extraction, efficiency, solutions, enzymes, innovative technologies, waste

Introduction

The properties and financial benefits of the tomato

Tomato, (*Solanum lycopersicum* L.), is the second most important, widely consumed and popular vegetable in the world, but with a Mediterranean appeal, which is due to its low

calorie content and bioactive compounds and a rich source of antioxidants and valuable biomolecules such as alpha carotene. Beta-carotene, lycopene, lutein, soluble and insoluble fibers such as cellulose, hemicellulose and pectin are used in various industries ((Catalkaya and Kahveci, 2019) and (Ali et al, 2020) and (Méndez-Carmona et al, 2022) and (Imran et al., 2020).

The article authored by Ali et al. highlights that tomatoes contain 23 diverse minerals, with more information on their sources.

Tomato also has high nutrients and antioxidant-rich phytochemicals and contains essential amino acids, monounsaturated fatty acids, ascorbic acid, tocopherol, phytosterols and contains phenolic compounds such as quercetin, kaempferol, naringenin, caffeic acid and lutein. Which have antioxidant activity (Méndez-Carmona et al, 2022). Antioxidant compounds such as carotenoids, vitamin C, vitamin E, and its phenolics neutralize reactive oxygen species and protect cell membranes against lipid peroxidation (Claye et al, 1996).

Essential fatty acids, such as linoleic and polyunsaturated fatty acids in tomatoes, are important for maintaining plasma membrane integrity, cell growth and disease prevention (Freitas et al, 2018).

Essential amino acids are required for body functions such as maintaining cell structure, transporting nutrients, wound healing, and tissue repair.

Tomato contains 17 amino acids, essential amino acids make up 39.75% of the total protein.

Carotenoids, including lycopene and tomato beta-carotenoids, protect plants against photo-oxidative stress processes and are antioxidants. They improve vision, prevent cardiovascular disease, protect sperm health, and prevent cancer. Lycopene, also a type of carotenoid, is useful for the prevention of liver, lung, prostate, breast and colon cancer ((Navarro-González et al, 2018) and Ali et al, 2020).

Sterols found in plants, animals and microorganisms are essential for human health. Plant sterols or phytosterols prevent the absorption of cholesterol. They reduce LDL-C and prevent CVD.

They also have anti-cancer effects, act as antioxidants, stimulate the Immune system, and have anti-inflammatory properties. Tomato is a rich source of phytosterols, of which beta-sitosterol and stigmasterol are the main ones (Ali et al, 2020 and Ostlund Jr et al, 2003).

Antioxidants beta-carotene, ascorbic acid and flavonoids in tomatoes delay the oxidation of free radicals or prevent it. And they help prevent various human degenerative diseases caused by normal metabolic reactions, diet and lifestyle activities such as cardiovascular diseases, diabetes, cancer, neurological diseases and aging (Vallverdu-Queralt et al, 2011).

The content and amount of nutritional value of tomatoes are different based on the variety, extraction methods and environmental conditions. Tomatoes are classified as canned, dried tomatoes, paste and tomato-based processed foods. The ripeness of tomatoes is related to the quality of the fruit, as the water content varies from 93 to 95 percent and the dry matter content varies from 5.5 to 9.5 percent.

They are classified into four commercial types: round, Irregular, elongated, cherry (Méndez-Carmona et al, 2022).

Tomato production in the world is 170 million tons. i.e. 127.5 million tons for fresh consumption and 42.5 million tons for industrial processing (Coelho et al, 2019).

About 180 million tons of tomatoes are produced annually. 70-80% of which is converted into products such as peeled tomatoes, paste, fruit juice, sauce and ketchup. All kinds of Industrial processing of tomatoes, from steam peeling to the production of tomato paste, produce many by-products.

20-30% of fresh tomato crops are lost or wasted, which indirectly leads to economic loss and loss of natural resources. Furthermore, 2-5% of processed tomatoes are processed waste.

The content of by-products depends on the final product and the process method, so that canned tomatoes only produce skins. While other crops may produce a mixture of skin, seeds and pulp. By-products of tomato processing with low added value such as animal feed, compost or waste disposal create important environmental problems.

By-products of this mixture can also be used in the meat industry. However, research shows that as mentioned, these by-products contain natural carotenoid compounds with high antioxidant activity which can resist industrial processing methods and bring significant economic and environmental benefits (Kelebek et al, 2017) and (Paulino et al, 2020) and (Pataro et al, 2020).

These wastes have the potential to be reused to recover compounds such as lycopene, dietary fiber, pectin, proteins and oil. Management strategies and use of these compounds with high added value, natural and cheap as additives, natural antioxidants and edible oils are very important in the food industry (Catalkaya and Kahveci, 2019) and (Grassino et al, 2020) and (Coelho et al, 2019) and (Méndez-Carmona et al, 2022).

Several technologies have been proposed to improve the efficiency and quality of recovery of bioactive compounds in plant materials.

This review of the performance of lycopene extraction and recovery methods from tomato waste, including the use of solvents or enzymes or modern technologies such as high pressure and supercritical fluids or the use of new methods such as ultrasound, microwave, pulsed electric field and provides heating.

The aim of these methods is to analyze and re-evaluate tomato waste and by-products with a focus on lycopene content and existing technological challenges and potential applications in the food industry. However, challenges related to quality, economic access, industrial reproducibility and environmental safety still exist (Méndez-Carmona et al, 2022).

Carotenoids

Carotenoids, natural tetraterpene pigments, are lipophilic pigments responsible for yellow, orange, red, and purple colors. They are classified into carotenes (non-oxygenated molecules such as lycopene) and xanthophylls (oxygenated molecules). Morphology, micro and nanostructure of carotenoids are studied using optical microscope and confocal Raman microscope.

Lycopene-based carotenoids have unique microstructural features that make them useful in food and pharmaceutical applications.

Studies of crystalline properties of lycopene and agglomerates show pseudo-spherical morphology in nanometer form.

Tomato processing can cause significant structural damage to particles, and dried vegetables have complex membrane and crystal structures associated with carotenoids. The ability to absorb carotenoids in the body is influenced by factors such as compounds and bonds in the food, the type of processing, their instability and low solubility in digestive fluids.

Most of the carotenoids are found in tomato skin, which accumulate in chloroplasts and chromoplasts during fruit ripening. Carotenoids are sensitive to high temperatures, light and oxygen, causing changes in their chemical structure and instability. Identification and quantification of carotenoids requires specialized methods ((Méndez-Carmona et al, 2022) and (Amorim-Carrilho et al, 2014 and (Campestrini et al, 2019)).

Carotenoids deactivate singlet oxygen and peroxy radicals. DPPH method is used to measure antioxidant activity.

DPPH solution is prepared by mixing methanol with DPPH reagent, and then the extracts are mixed with the solution and incubated, and the absorbance will be measured.

Antioxidant activity Is expressed as percentage change in absorbance compared to TBARS and FRAP control ((Sharma and Bhat, 2009) and (Stahl and Sies, 2003)).Lycopene is the dominant carotenoid and strong antioxidant responsible for the red color In tomatoes, which constitutes more than 85% of Its total carotenoids.

Tomato skin, whichh contains about five times more lycopene than the whole pulp of tomatoes, can be a useful source of lycopene ((Catalkaya and Kahveci, 2019) and (Pandya et al, 2017)).

Lycopene

Lycopene, found in fruits and vegetables such as tomato, carrot, watermelon and papaya, has many applications In the food, pharmaceutical

and human health industries (Kunthakudee et al, 2020).

Red fruits have higher lycopene. Environmental factors such as sunlight intensity, temperature, greenhouse culture, humidity and fruit ripening time affect the concentration of lycopene.

Lycopene, derived from isoprene, has a tetraterpene structure consisting of carbon and hydrogen atoms, a central carbon chain with 13 double bonds, and Is commonly known as Ψ , Ψ -carotene.

Lycopene is one of the 600 carotenoid compounds in the group of antioxidants, and consumption between 1.85 mg per day and 9.81 mg per day reduces the risk of cardiovascular diseases due to its antioxidant properties and the reduction of reactive oxygen species and inflammation.

Lycopene helps convert low-density lipoprotein (LDL) into oxidized LDL (OxLDL), which Is removed by macrophages.

Lycopene can reduce the activity of myeloperoxidase (MPO) in the vascular wall, which produces hydrogen peroxide and superoxide. Lycopene is also a better singlet oxygen scavenger than other carotenoids.

Phytoene (PT) and phytofluene (PTF) are colorless carotenoids with 9-10 double bonds of tomato, which are different in terms of dissolution, stability, absorption, metabolism and transport (Hatami and Ciftci, 2023).

Studies show that 83% of prostate cancer can be cured in patients with higher lycopene levels. Lycopene and vitamin E also have protective effects on prostate tumor growth. More clinical trials are needed to evaluate long-term effects (Amorim-Carrilho et al, 2014).

Different techniques of lycopene extraction

Extraction with solvents and oils

The extraction of lycopene from tomatoes is an attractive method because of its cost-effectiveness, efficiency and simplicity. Metal extraction has many uses in the food industry, but the extraction of lycopene is difficult because it is mainly found in the chromatophores of the skin.

However, due to its hydrophobicity, chromoplast structure, and difficult bioavailability, it is often difficult to recover from tomato skin, and conventional solvent extraction methods often require complex pretreatments and excessive use of toxic organic solvents. (Pataro et al., 2020).

By adding methanol, ethanol, or acetone to common organic solvents, it can be extracted with inorganic solvents such as acetone, petroleum ether, hexane, benzene, and chloroform, ethyl acetate, acetonitrile, and dichloromethane (Kunthakudee et al, 2020).

Adsorption of macroporous resin is also useful for purifying lycopene and beta-carotene. High performance liquid chromatography (HPLC) is the most widely used technique for the purification of carotenoids (Méndez-Carmona et al, 2022).

Solvent systems are the preferred method for extracting carotenoid pigments from tomatoes due to their simplicity and low cost. The optimal conditions include a mixture of polar and non-polar solvents. Which enables the solubility of non-polar carotenoids such as lycopene and β -carotene.

However, some non-polar and organic solvents make it unsuitable for use in food due to long-term and toxic effects including leukemia, kidney cancer, neurotoxicity and cardiovascular system disorders.

Current extraction methods, such as solvents, can cause degradation, toxicity and decrease biological properties and hinder their added

value ((Coelho et al, 2019) and (Méndez-Carmona et al, 2022)).

Vegetable oil is an environmentally friendly solvent because it is edible, safe for human use, and acts as a barrier against oxygen, reducing oxidation time and degradation rate.

Another alternative is extraction with vegetable oil. Studies have shown that vegetable oils are suitable solvents for the extraction of food compounds, such as carotenoids obtained from pomegranate waste and tomatoes cooked in olive oil (Kunthakudee et al, 2020).

Also, coconut oil is more efficient in extracting lycopene from tomato paste waste. More research is needed for repeatable and sustainable alternatives ((Méndez-Carmona et al, 2022) and (Kunthakudee et al, 2020)).

Also, a 2020 study focused on the extraction of lycopene from tomatoes using environmentally friendly solvents such as coconut oil, olive oil, soybean oil, and palm oil. Instead of hydrocarbon solvent (Kunthakudee et al, 2020).

Extraction with the help of enzymes

Enzymes that hydrolyze polysaccharide compounds can help to recover bioactive compounds including lycopene from tomato and its products (Catalkaya and Kahveci, 2019).

Enzyme-assisted extraction is a sustainable alternative to conventional methods that use enzymes from fungi, bacteria, fruits, vegetables, and animal organs to extract bioactive compounds.

The main enzymes used are cellulases, hemicelluloses and pectinases. Studies have shown that enzymes can effectively extract lycopene from tomato processing wastes, and optimal results are obtained at 30°C, 3.18 hours, and 0.16 kg/kg enzyme yield. However, the high costs of using enzymes create challenges (Méndez-Carmona et al, 2022).

Catalkaya & Kahveci (in 2019), conducted a study with the aim of optimizing the recovery of lycopene from tomato waste using solvent extraction with the help of cellulolytic and pectinolytic enzymes and using the response

surface method (RSM), and found that solvent polarity significantly affects the recovery of lycopene extraction.

Extraction with the help of these enzymes significantly increases the concentration of lycopene in the final oleoresin. They also determined the optimal solvent and enzyme concentration conditions for lycopene extraction with lower extraction temperature and time for maximum lycopene recovery (Catalkaya and Kahveci, 2019).

A study by Azabou et al. in 2016 found that the production of *Fusarium solani* pisi enzymes through solid substrate fermentation can increase the amount of lycopene obtained from processed tomatoes compared to preparation with cellulase and pectinase. This increase in lycopene concentration is associated with cells that promote polyphenol synthesis (Azabou et al, 2016)

Extraction with new technologies

Several extraction methods improve experimental conditions to increase the quantity and quality of bioactive compounds found in plant residues, such as lycopene in tomato waste. These methods provide better recycled bioactive compounds at low operating costs. Although Méndez-Carmona et al., 2022 considers environmental protection.

Extraction with the help of ultrasound

Extraction with the help of ultrasound provides greater extraction efficiency due to its action mechanisms such as fragmentation, erosion, capillarity, denaturation and sonoporation and diffusion throughout the plant cell wall and the leakage of cell contents after breaking the wall. And it is an efficient method to extract compounds from food waste.

Sample origin, chemical structure and process parameters such as extraction temperature, type of solvent, time, power and frequency affect the efficiency of the method.

Due to its efficiency and simplicity, ultrasound is considered one of the best techniques for extracting sensitive compounds from food waste ((Méndez-Carmona et al, 2022) and (Grassino et al, 2020))

In a study by HO et al. In 2015, using ultrasound on tomato waste, they obtained 1.3348 mg/g of lycopene, which shows the importance of cavitation and thermal effects (Ho et al, 2015).

Microwave extraction

Microwave-assisted extraction (MAE) is an effective method for extracting bioactive compounds from tomato waste

Increases access to extracted compounds in less time and with less solvent. The extraction process depends on factors such as extraction time, temperature, solvent type, solvent ratio and MAE source strength.

This method has been used to extract lycopene from tomato peel residue and polyphenols from tomato peel waste. It is a low-cost, environmentally friendly and simple-to-use technology that reduces environmental pollution and time (Méndez-Carmona et al, 2022).

High pressure extraction

High-pressure processing (HPP) is a method that involves subjecting solid-liquid foods to pressures between 100 and 800 MPa, which cause damage to cell membranes. This process reduces extraction time and improves efficiency (Méndez-Carmona et al, 2022). High hydrostatic pressure extraction (HHPE) has also been introduced to separate pectin from orange and potato peel wastes (Grassino et al, 2020).

HPP was first used to extract lycopene from tomato paste waste, with optimal conditions such as 500 MPa pressure, 75% ethanol concentration in water and 1:5 solid to liquid ratio. Extraction using high pressure processing was 17% higher than other technologies, without affecting yield (Xi, 2006)

Recent studies have also investigated the optimization of HPP-assisted extraction for

polyphenols, flavonoids and lycopene from tomato pulp with optimal conditions of 450 MPa with 60% hexane In the solvent mixture (Briones-Labarca, 2019).

Grassino et al. 2020 study used high pressure processing (HHPE) and high pressure extraction (assisted by ultrasound) to isolate pectin and polyphenols from tomato peel waste. The researchers confirmed the efficiency of HHPE in terms of pectin yield and quality and compared it with conventional extraction methods.

They also confirmed the efficiency of ultrasound as a combined method In polyphenol recovery from residues obtained after HHPE. The main goals were to create a new and value-added method to increase their efficiency and reduce extraction time and energy consumption (Grassino et al, 2020).

As said; Extraction of lycopene from tomato waste is usually done using organic solvents, but this method is not practical due to low yield, long processing time, high consumption of solvent, and the toxicity of organic solvents. Innovative methods such as ultrasound-assisted, microwave-assisted, enzyme-assisted, and high-pressure extraction have been investigated, but these methods require drying of the waste material, potentially causing loss of lycopene and increasing processing costs (Andreou et al., 2020).

Therefore, other methods with higher efficiency and less limitations have been introduced.

Extraction with the help of supercritical fluid

The case for "natural" lycopene has influenced the acceptance of synthetics in food and pharmaceutical products
 Supercritical carbon dioxide (SC-CO₂) extraction has been used as a clean alternative to traditional solvents, which offers advantages such as non-toxicity, cost-effectiveness and flexibility of the process (Hatami and Ciftci, 2023)(

Supercritical fluids with CO₂ (SFE) is a non-thermal technology that has a significant impact in the food and pharmaceutical industries due to its green and environmentally friendly nature.

This method provides the possibility of extracting the active components of a food composition. which results in the production of CO₂ that can be reused or released safely. This method Is a preferred method due to milder temperatures, shorter extraction time and avoidance of toxic solvents (Méndez-Carmona et al, 2022).(

In 2020, Margotta and De Simone used SFE to extract lycopene from dried tomatoes and produced up to 60% lycopene (Margotta and De Simone, 2020).

In 2019, de Andrade Lima et al. used SFE to extract carotenoids from tomato waste and by-products and obtained a total of 0.046 mg/g of carotenoids (de Andrade Lima et al, 2019).

A study using SC-CO₂ of TPBP yielded a cis-lycopene-rich oleoresin with a maximum cis-lycopene content of 67%.

A mathematical model was developed to optimize the process, which resulted in the highest yield of 0.32 mg lycopene/kg feed.

A recent review article on SC-CO₂ extraction shows the effect of extractable components, pretreatments, and the effect factors of solvent type, time, pressure, temperature, and solvent flow rate on performance.

The main target component in this study was lycopene and pretreatments such as drying, grinding and enzymatic digestion were applied (Hatami and Ciftci, 2023).

Extraction with the help of pulsed electric field:

.Pulsed electric field (PEF) is a non-thermal method used to extract bioactive compounds from plant cells

It Increases the porosity of the cell membrane and allows the exit of intracellular compounds and facilitates the entry of solvent (Méndez-Carmona et al, 2022).

Pulsed electric field (PEF) processing is a non-thermal food processing technology that enhances the extractability of intracellular compounds by disrupting plant and microbial cells.

Its non-thermal nature allows foods to retain their nutritional and quality characteristics. PEF can be used In the production of tomato industry to improve productivity, especially at the peeling stage.

Studies have shown that PEF can increase the water extraction efficiency of plant materials such as carrot, grape, potato or apple tissues. Extraction of carotenoids from tomato waste with the help of PEF has also been investigated. Research shows that PEF technology can effectively reduce energy consumption, increase productivity and effectively value waste by increasing electric field strength and processing time (Andreou et al, 2020).

Pretreatment by PEF with high electric field and low absorption power improves the permeability of plant cell membranes and recovers intracellular compounds from residues and by-products of food processing (Pataro et al, 2020).

Of course, the use of these methods depends on the conditions of the industrial process, the index of the tomato and the characteristics of the method used. However, sometimes a combination of methods shows good results (Méndez-Carmona et al, 2022, Pataro et al, 2018).

Extraction with ohmic heating

Ohmic heating is a new extraction method, based on alternating electric current that passes through semi-conducting materials and creates internal heat due to the electrical resistance of the product. This method has the potential for rapid, uniform and accurate heating of foods and offers a wide range of food processing applications.

However, there is a black point about the relationship between electric fields and the

amount of bioactive compounds and it is not applicable in non-conductive food compounds or inhomogeneous food systems (Coelho et al, 2019).

For this reason, based on the type and characteristics of each material, there is a need for optimization to find the best and most efficient conditions leading to the highest efficiency.

Coelho et al in 2019 conducted a study on the effect of ohmic heating (OH) and medium electric fields (MEF) on the extraction of bioactive compounds (BC) from tomato by-products for economic valuation in a sustainable industrial system.

This study shows that ohmic heating is an effective method for the extraction of polyphenols and carotenoids from tomato by-products with a yield 58% higher than conventional methods. This method offers the possibility of extracting these compounds without the use of organic solvents , but the efficiency is lower than with traditional methods (Coelho et al, 2019). We have to repeat the methods to fix the conditions.

Conclusion

Various extraction methods can be used to achieve optimal conditions to increase the quantity and quality of bioactive compounds from various plant residues. In this case, the low price of lycopene in tomato plants is interesting because it has a lot of food, medicine and decoration.

Looking at the results of various studies in this area, we can see that the expansion of the field of knowledge has given rise to an impressive push of new methods to Increase the quality and efficiency of the extraction of biological compounds.

The advantage of using new thermal and non-thermal methods when extracting biomolecules is that they consume less organic solvents and are more environmentally friendly.

It is said to increase extraction efficiency, increase the quality of extracted compounds, reduce energy consumption and shorten processing times, thereby maintaining the

nutritional value of neutral and temperate compounds.

There are many additional studies related to the choice of method or the combination of different methods, which should be optimized depending on the nature and conditions of product processing, the cost and availability of the method, and the consumer's expectation.

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