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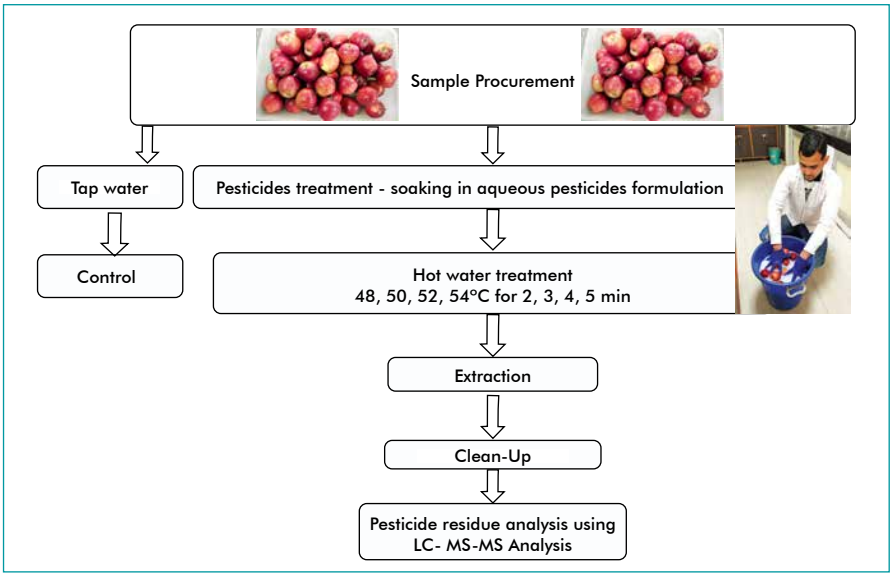
Hot water treatment in apple for pesticide residues degradation

Among the temperate fruit crops, apple is one of the major fruits with a high nutritional profile, which includes vitamins, minerals, antioxidants, and phytochemicals. It is the staple fresh fruit in temperate parts of India as well in the world. Consumption of apples is beneficial for protection against various chronic diseases. Although it is a popular table fruit, its several varieties can also be canned or it can be used for juice, wine, vinegar, and cider making. The changing climate and thereby increased pest-disease incidence has surged the indiscriminate use of pesticides in apple orchards leading to bioaccumulation of residue which is a major concern for consumers. Hence, hot water treatment could be one of the alternative approaches which is safe and ecofriendly.

APPLE is a premier temperate fruit crop in India as well as in the world and is known as the 'king of temperate fruits'. In India, the total area under apple cultivation in 2022 was around 0.313 million hectares yielding 2.437 metric tons. Apple belongs to the genus *Malus* of the Rosaceae family and it originated in Central Asia from its wild ancestor, *Malus sieversi* L. The old proverb 'an apple a day keeps the doctors away' fits well as apples contain high bioactive compounds such as vitamins, antioxidants, dietary fibers, minerals, and other phytochemicals. Moreover, medical studies have shown that the consumption of apples is beneficial for protection against various chronic diseases, owing to their anti-inflammatory and antioxidant properties. However, in comparison to other countries, the yield and productivity is dismally low (8.1 MT/ha), due to emerging insect-pest infestations such as San Jose scale, *Quadraspidiotus perniciosus* (Comstock); woolly apple aphid, *Erioso malanigerum* (Hausmann) and diseases such as powdery mildew, *Podosphaera leucotricha* (Ell. and Ev.) Salm; and scab, *Venturia inaequalis* Cooke (Wint) during the production period. Similarly, some disorders such as bitter pit, brown core and water core can occur during storage, which also contributes towards severe postharvest losses. For control of these pests, diseases and/or storage disorders, several management strategies and pesticides are used by the orchardists. For example, the incidence of woolly apple aphid can be reduced by spraying fenitrothion, dichlorvos, demeton-methyl, phosophamidon or dimethoate during autumn season or by spraying spirotetramat @ 0.015% (~68% control). For San Jose scale management, sprays of superior miscible oils like Hindustan Petroleum spray oil or chlorpyriphos are effective. For control of apple scab, a spray schedule consisting of several fungicides has been standardized in India and powdery mildew can be controlled by spraying myclobutanil, hexaconazole or fluquinconazole. Similarly, for the reduction of storage disorders, pre-harvest calcium sprays are usually recommended and widely used. Therefore, producers practice indiscriminate use of pesticides to control these problems. Although these management strategies provide satisfactory control of pests, diseases, and/or disorders, they are expensive and unfriendly to the environment. Moreover, if pesticides are not applied as per good agricultural practice (GAP) norms during fruit production, their residues may be toxic to consumers. Furthermore, it has come in the news several times that our export consignments are usually rejected at international trade primarily due to pesticide residues. Pesticide residues can be reduced by using a variety of post-harvest techniques, including physical treatments like modified atmosphere packaging, ozone treatment and UV- pretreatments, as well as chemical treatments like 1-methylcyclopropene, salicylic acid and methyl jasmonate. Furthermore, chlorination and various other processing techniques are also used to bring the pesticide residue below the maximum residue limit (MRL) for human consumption. Apart from this, some non-thermal technologies including high-pressure processing, pulsed electric fields and advanced oxidation processes (AOPs) such as ozone, ultrasound, free radical reactions, ionizing radiation and non-thermal plasma have been used for the dissipation of pesticide residues. But these techniques are not cost-effective and are not easily accessible for marginal and small-scale entrepreneurs. With regard to chemical treatment, it is unsafe due to the formation of toxic intermediates or sometimes produces more toxic products than the initial pesticides. Therefore, there is a need to develop an alternative, safe approach which is chemical-free and eco-friendly which reduces or diminishes the



Flow diagram of processing practices, sample preparation and residue analysis in apple

toxic effect of pesticide on human well-being. Hot water treatment (HWT) is one such approach which has been both protective as well as curative.

Mechanism of Hot Water treatment (HWT) for the dissipation of pesticide residues

Hot water treatment activates the phytoalexins, which stimulates the self-defense mechanism in the treated fruits. Moreover, hot water treatment also cleans the surface of the fruit. In addition to this, it breaks down the chain of chemical bonds of pesticides and thus reduces pesticide residue concentrations from the treated fruit by the process of volatilization, hydrolysis and decomposition of pesticides at elevated temperatures. Hot water technique is a cost-effective and chemical-free approach and does not compromise on the quality attributes of treated apples.

The effect of hot water treatment on citrus fruit to prevent the decay through thermal inhibition of pathogen growth by the accumulation of phytoalexins (scoparone and scopoletin) has also been reported in research works. Preservative heat treatments are used to kill most pathogens found in the first few layers under the skin of fruits and vegetables, so pre-storage heat treatments are used to inhibit the growth of pathogens. Water is the best medium because it is a more efficient heat transfer medium than air. Heat is applied to commodities in various ways as physical treatment, which includes hot water dips, vapor heat, hot dry air, and hot water rinsing as well as brushing (HWRB). Vapor heat treatment was specifically used for insect control, while hot dry air has been used for both fungal and insect control. In this study, after the hot water treatment, pesticide residues were extracted and cleaned up using a simple, time and cost-effective QuEChERS method and the extracted residues were quantified by Liquid Chromatography-Tandem Mass Spectroscopy (LC-MS/MS).

Dipping of pesticide treated fruits in the hot water bath

Pesticide residue extraction methods

QuEChERS method: Residue analysts are continuously challenged to develop methods that are faster, greener, more precise and more accurate in ensuring the quality, authenticity, safety, and traceability of target pesticide residues in a wide range of fresh produce. Hence, to solve this issue, the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method is one of the most promising user-friendly and high-throughput extraction procedure which helps to quantify residues in less time as well as reduces the sample amounts, organic solvents, and laboratory glassware in accordance with green chemistry principles. The QuEChERS method was first presented by Michelangelo Anastassiades at the European Pesticides Residue Workshop (EPRW) in Rome in 2002 and later, it was validated by Lehotay and his co-workers (2010).

Liquid Chromatography-Tandem Mass Spectroscopy (LC-MS/MS): For the detection and quantification of different pesticide residues, Liquid Chromatography-Tandem Mass Spectrometry with Electrospray Ionization (ESI) technique is used. LC-MS/MS is mostly used because of its high sensitivity and selectivity toward the detection of varied classes of target pesticides from complex matrices in a single run.

SUMMARY

Apple is important in the human diet as it has high nutraceutical value, primarily because it is a rich source of antioxidant and fiber content. With increasing biotic and abiotic stress, pesticide usage is indiscriminate. Although management strategies provide satisfactory control of pests, diseases, and/or disorders, they are expensive and unfriendly to the environment and also the pesticide residues persisting in fruits are a matter of concern among consumers. Hence, considering the beneficial effect of hot water treatment along with its effectiveness and low cost, it could be an alternative, eco-friendly and safe approach for the degradation of pesticide residues in quality produce.

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