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Role of Calcium Compounds and Ethylene Absorbents in Fruits crops

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Abstract—*India is the largest producer of fruits in the world but there is about 30% of post-harvest loss of produced fruits which reduces net per capita availability of fruits. Hence there is a need to reduce post-harvest loss to minimize cost of production.India incurs post-harvest fruits and vegetable losses worth over Rs 2 lakh crore each year largely owing to the absence of modern cold storage facilities and lack of proper food processing units. West Bengal stands 1st by incurring post harvest losses worth over 13,600 crores annually followed by Gujarat which is as high as 11,400 crores. Hence several methods are adopted to avoid that. Among them post harvest application of calcium compounds and ethylene absorbents are found to be the most effective, cheaply available and easily applicable methods for delaying fruit ripening & senescence and are also found to be effective in control of decay loss.*

Treatment of fruits with calcium compounds will offer a degree of resistance against certain pathogens by improving firmness. There are different of methods in reducing the undesirable effect of ethylene. Among all use of ethylene absorbents like potassium permanganate, activated charcoal based ethylene scavengers, zeolite films and japanese oya stone (films) will reduce the post-harvest loss triggered by ethylene gas.

1. INTRODUCTION:

India is the largest producer of fruits in the world but there is about 30% of post-harvest loss of produced fruits which reduces net per capita availability of fruits. Hence there is a need to reduce post-harvest loss to minimize cost of production.

Post-harvest loss:

Post-harvest loss can be defined as "that weight of wholesome edible product (exclusive of moisture content) that is normally consumed by human and that has been separated from the medium and sites of its immediate growth and production by deliberate human action with the intention of using it for human feeding but which for any reasons fails to be consumed by human" Sudheer and Indira (1).

Fruit	Production (000'MT)	Post-harvest loss
Banana	29780	20-30 %
Mango	15188	17-33 %
Citrus	7464	08-31 %
Papaya	4196	20-25 %
Guava	2462	03-15 %

Anonymous (2)

India incurs post-harvest fruits and vegetable losses worth over Rs two lakh crore each year largely owing to the absence of modern cold storage facilities and lack of proper food processing units. West Bengal is India's leading horticulture producing state with over 27,000 tonnes of fruits and vegetable produced across the state annually. Unfortunately, this is also the state which stands first by incurring post harvest losses worth over 13,600 crores annually. Gujarat ranks second in post harvest fruit and vegetable losses which is as high as 11,400 crores, followed by Bihar (Rs 10,700 crore), Uttar Pradesh (Rs 10,300 crore) and Maharashtra (Rs 10,100 crore) Anonymous (3).

Reduction in post-harvest loss of fruits is a complementary means for increasing production. It may not be necessary to step up production of fruits with growing demand if post-harvest loss is reduced to a great extent. Cost of preventing losses after harvest in general is less than the cost of producing a similar additional amount of fruits of same quality. Attention to the concept of post-harvest food loss reduction, as a significant means to increase food availability.

Post harvest loss occurs in terms of:

a. **Economical loss** which refers to reduction in monitory value as a result of physical loss.
b. **Quantitative loss** which includes reduction in weight by moisture loss and loss of dry matter by respiration.
c. **Incidental loss** in terms of quality of food.
d. **Qualitative loss** which refers to loss of consumer appeal.
e. **Nutritive loss** which includes loss in vitamins, minerals, sugars, etc.

Control of Post-Harvest Losses:

Magnitude of post-harvest loss can be minimised by proper cultural practices, harvesting and handling, storage, transportation and pre and post-harvesting treatments. Pre and post-harvesting treatments include chemical treatments like application of fungicides, calcium treatments, growth regulators treatment and ethylene absorbers usage in storage rooms and packages. Among them post harvest application of calcium compounds and ethylene absorbents are found to be the most effective, cheaply available and easily applicable methods for delaying fruit ripening & senescence and are also found to be effective in control of decay loss, Ravishankar *et al*., (4).

2. ROLE OF CALCIUM IN CONTROL OF POST-HARVEST LOSS OF FRUITS:

Calcium is involved in maintaining the textural quality of produce since calcium ions form cross links or bridges between free carboxyl groups of the pectin chains, resulting in strengthening of the cell wall Garcia *et al*., (5). Calcium complexes to cell wall and middle lamella polygalacturonic acid residues, improving structural integrity Van Buren (6). Calcium conserves the qualities of fruits, prevents physiological disorders, reduced the rate of respiration, lessens the solubilization of pectic substance, maintaining the firmness and slows down the ripening process Burns and Pressey (7). Since calcium is a constituent of cell wall and middle lamella, this association of calcium and the cell wall may explain the reason that increased calcium imparts a degree of resistance to decay by certain pathogens. The increased amount of calcium exogenously applied becoming localized in the cell wall, thus increasing the number of salt bridges, could account for the resistance of this tissue to maceration by fungal polygalacturonase and for resistance to pathogens like *Penicillium expansum* and *Botrytis cinerea* Conway *et al*.,(8).

Thus, storage potential of fruits is largely dependent on the level of calcium. Any other nutrients, which disturb the calcium content also adversely affects the shelf life of fruits.The higher levels of N, P, and Mg and low level of K and B leads to the calcium deficiency in fruits and reduce its storage life. Zn is known to act as a vehicle for carrying ion across the tissue and increases the calcium content of the fruit. Boron improves the mobility of Calcium. Calcium treatment delays ripening and senescence. Many physiological disorders of storage organs such as bitter pit in apple and cork rot in pear are related to low calcium content of the tissue. Exogenous application calcium was found to be incorporated into protopectin molecules in the middle membrane and retards hydrolysis during post harvest ripening, inhibits fruits softening and extends storability of fruits, Bantash and Arasimovich, (9).

Calcium sources to maintain the shelf life of fresh fruits:

Different calcium salts have been studied for decay prevention, sanitation and nutritional enrichment of fresh fruits and vegetables. Calcium carbonate and calcium citrate are the main calcium salts added to foods in order to enhance the nutritional value. Other forms of calcium used in the food industry are calcium lactate, calcium chloride, calcium phosphate, calcium propionate and calcium gluconate, which are used more when the objective is the preservation and/or the enhancement of the product firmness, Manganaris *et al.,* (10). The selection of the appropriate source depends on several factors: bioavailability and solubility are the most significant, followed by flavour change and the interaction with food ingredients.

Calcium chloride has been widely used as preservative and firming agent in the fruits and vegetables industry for whole and fresh-cut commodities. The use of calcium chloride is associated with bitterness and off-flavours, Ohlsson, (11), mainly due to the residual chlorine remaining on the surface of the product. Calcium lactate, calcium propionate and calcium gluconate have shown some of the benefits of the use of calcium chloride, such as product firmness improvement, and avoid some of the disadvantages, such as bitterness and residual flavour, Yang & Lawsless, (12). Also, the use of calcium salts other than calcium chloride could avoid the formation of carcinogenic compounds (chloramines and trihalomethanes) linked to the use of chlorine. Manganaris *et al.* (10) compared the effect of calcium lactate, calcium chloride and calcium propionate dipping in peaches. Calcium increased in tissues with no dependence on the source used. Calcium incorporation by impregnation with two calcium sources, calcium lactate and calcium gluconate, was studied in fresh-cut apple, Anino *et al.*, (13). Other authors, Suutarinen *et al.*, (14) used calcium chloride as firming agent for processed strawberries. Wills and Mahendra (15) examined the effect of calcium chloride on fresh-cut peaches from a quality point of view, meanwhile Conway and Sams (16) evaluated the safety of strawberries treated with calcium chloride.

Two main ways of application of the calcium in fresh fruits has been reported: dipping-washing (I) and impregnation (II) processes.

Gregory and Poovaiah (17) conducted an experiment to study role of calcium in delaying softening of apples and cherries and stated that calcium-treated fruits of Golden delicious apples remained firm after 7 months of storage, had a greater amount of cell to cell contact, and did not appear to have increased intercellular space. Whereas, untreated fruits that had been stored for 7 months became mealy, showed very little cell to cell contact, and appeared to have an increase in intercellular space. Extensive degradation of the cell wall, especially the middle lamella, was observed in the untreated fruits after 7 months of storage and resulted in cell wall separation. In contrast, the cell wall structure of the calcium-treated fruits showed very little breakdown.

3. ROLE OF ETHYLENE IN POST-HARVEST LOSS OF FRUITS:

Ethylene is a naturally produced colourless gas, simple two carbon gaseous plant growth regulator that has numerous effects on the growth, development and storage life of many fruits. This powerful plant hormone is effective at part-per-million (ppm, ml l^{-1}) to part-per-billion (ppb, nl l^{-1}) concentrations. Both the synthesis and action of C_2H_4 involve complicated metabolic processes, which require oxygen and are sensitive to elevated concentrations of carbon dioxide. Endogenous sensitivity to C_2H_4 changes during plant development, as does its rate of synthesis and loss by diffusion from the plant.

Source of ethylene in the environment:

Burning agricultural waste, diesel and propane, truck and auto exhaust, cigarette smoke etc., could be named as the main sources of ethylene in the environment. Growing plant produce a small quantity of ethylene which is not enough to alter the environment. Ambient atmosphere levels of ethylene are normally 0.001-0.005 ppm while in some urban areas up to 0.5 ppm has also been recorded. Plants produce C_2H_4, but only ripening climacteric fruit and diseased or wounded tissue produce it in sufficient amounts to affect adjacent tissue.

Mechanism of action of ethylene:

The favoured model is that ethylene binds to a protein, called a binding site, thus stimulating release of a so-called secondary message instructing the DNA to form mRNA molecule specific for the effect of ethylene. The molecules are translated into protein by polyribosomes and the proteins so formed are the enzyme that causes the actual ethylene response.

Measurement of ethylene:

Since available at minute concentrations (1ppm for fruit ripening) its measurement is an expensive process gas chromatography ($7000-20000), flame ionization detector, laser-acoustic device and gas sampling tubes are used to measure the available ethylene in the atmosphere.

Undesirable effect of ethylene:

Detrimental effects are often caused by unintentional exposure of the harvested commodity to C_2H_4. Exposure of plants in the field and orchard is rare since normal levels of C_2H_4 in the atmosphere are exceedingly low and C_2H_4 is rapidly destroyed by soil microorganisms and solar radiation. Atmospheric pollution with C_2H_4 and its analogs is much more common when plants are grown or stored in confined spaces such as greenhouses, cold storage rooms, and packages.

1. **Accelerates senescence:** In green tissues, ethylene commonly stimulates senescence, as indicated by loss of chlorophyll and susceptibility to decay.

2. **Accelerates ripening:** Presence of ethylene in storage area reduces storage life.

3. **Induction of leaf disorders:** Ethylene causes many disorders in leafy vegetables, such as russet spotting in lettuce.

4. **Isocoumarin formation:** In carrots, ethylene exposure causes the biosynthesis of isocoumarin which makes the carrot bitter.

5. **Sprouting:** Ethylene stimulates sprouting of potatoes which leads to increase water loss and early shrivelling.

6. **Abscission of leaves, flowers and fruits:** Abscission is most often a problem in ornamentals.

7. **Susceptibility to pathogen:** Ethylene accelerates senescence and enhances the opportunities for pathogen

Overcoming undesirable effect of Ethylene:

Among the different methods tried, the removal of ethylene from the atmosphere around the commodity is the cheapest and most effective method.

1. Elimination source of ethylene: Such as avoiding loading and unloading operations of vehicles and engines in enclosed space.

2. Ventilation: where the outside storage area is not polluted one air change per hour is sufficient and could be provided by installing an intake fan and a passive exhaust.

3. Chemical removal:

a. Potassium permanganate: It oxidizes ethylene to CO_2 and H_2O. Vermiculate, pumice and bricks are used to manufacture permanganate absorbers.

b. Brominated charcoal: It could absorb ethylene from the air; it is mostly used in laboratories, as potassium permanganate absorbers are cheap and widely available.

Inhibiting the effects of ethylene:

a. **Modifying atmosphere:** Low oxygen and high carbon dioxide reduces ethylene production.
b. **Use of anti ethylene compounds:** Anti-ethylene compounds such as silver thiosulfate (STS) and 1-methylecyclopropane (1-MCP, EthyIBloc) by blocking ethylene binding sites resulting in inhibiting ethylene action, Asrey *et al.*, (18).
c. **Use of ethylene synthesis inhibitors:** Ethylene synthesis inhibitors such as aminoethoxy vinyl glycine (AVG) and aminooxyacetic acid (AOA), these inhibitors do not prevent the action of ethylene. These will prevent the conversion of ACC to Ethylene step in ethylene biosynthesis.
d. **Molecular manipulation of ethylene response:** the identification of the genes that encodes ACC synthase (the key enzyme in the biosynthesis of ethylene) and ETR-1 (the ethylene binding sites) have provided biotechnologists with the tools to modify the biosynthesis of ethylene in plants. Flowers of petunia and carnation plants transformed with *etr-1*, a mutant form of the ethylene binding site, have extended life because they no longer respond to endogenous or exogenous ethylene.

4. COMMERCIAL APPLICATION IN PACKAGING:

Most substances designed to remove ethylene from packages are delivered either as sachets that to inside the package or are integrated to the packaging material, usually a plastic film or the ink used to print on the package.

1. Potassium permanganate based scavengers:

Potassium permanganate is not integrated into food contact packaging because of its toxicity. However sachets could be used inside produce packages and have been shown to effectively scavenge ethylene from the packages. Typically such sachets contain 4-6 % KMnO4 on and inert substrate such as perlite, vermiculite and silica gel, Sihag *et al.*, (19).

Purafil (Isolette Sorber Sachet), a purple granular material containing potassium permanganate which we know to be a very effective ethylene absorbent. Highly permeable, the sachet allows for quick ethylene uptake. Each sachet contains 10 grams of Purafil® Select media and offers twice the ethylene removal capacity of other sachets.

Bioconservacion pellet sachets are the best insurance you can get against poor arrivals, waste, and rejects. The main advantage of the sachets is that they offer continuous protection, from the packing line to the retail backroom, by removing ethylene gas all along the distribution chain. Sachets also remove spores from the air; thereby, reducing moulds and rots. They also offer protection against smells by neutralizing odours. Since the pellets are transformed naturally into an organic fertilizer (manganese dioxide), they are environmentally friendly.

Frisspack, A new product developed by Hungarian paper manufacturer, Dunpack for use in corrugated fibreboard cases to prolong the shelf life of fresh produce. A component of "Frisspack" package tries to bond with the ethylene generated during fruit and vegetable ripening in order to decrease the rate of respiration. To bond with ethylene, the most commonly used materials are silica gel, with potassium permanganate com-pounds to react with the ethylene. According to Dunapack, silica gel adsorbs ethylene while $KMnO_4$ oxidizes it. One of the disadvantages of bag-in-box active packaging systems offered by other companies is that the ethylene-bonding capacity of the materials used as adsorbents (silica gel, activated carbon) is usually low and therefore relatively large amounts of absorbents are required. In addition, adsorbent materials bond with moisture and the chemicals within the pouch may contaminate the food. Frisspack paper was developed to chemically bond with ethylene released during fresh and minimally processed produce respiration. This objective can achieved in "Frisspack" by dispersing a chemosorbent of small particle size (average particle size 1 m) with high absorption capacities among the fibres in the early phase of the paper production, when the fibres are still in approximately 1% water suspension. The chemosorbent can be uniformly blended among the fibres and have surface characteristic features such that the particles connect to the paper fibres by hydrogen bonding. By this means, the chemosorbent particles are embedded in the paper so firmly that they do not become separated from the paper due to mechanical action or chemical effects (e.g., juice leakage from fruits during storage).

2. Activated earth ethylene removers:

In recent years, a number of packaging products have appeared based on putative ability of certain finely dispersed minarals to adsorb ethylene. Typically, these materials are local kinds of clays (often zeolites) that are incorporated into polyethylene bags which are then used to package fresh produce. Many, though not all, of the bags are marketed by Japanese or Korean companies, though some are also sold in the United States and Australia.

Zagory, in his section on ethylene removal in the book *Active Food Packaging*, asserts that the evidence offered in support of claims about ethylene removal by activated earth or clay is generally based on shelf life experiments comparing common polyethylene film bags with clay-filled film pouches. Such evidence generally shows an extension of shelf life and/or a reduction of headspace ethylene.

The Cho Yang Heung San Co. Ltd. of Korea markets a film bag called Orega bag, based on US patent of Dr Mitsuo Matsui. Fine porous material derived from pumice, zeolite, active carbon, cristobalite or clinoptilolite is sintered together with a small amount of metal oxide before being dispersed in a plastic film. Neither plastic containing chloride such as polyvinyl chloride or polyvinylidene chloride, nor plasticizers, are apparently suitable for these applications. The inorganic materials have pores ranging from 2000-2800 Å and the resulting film is reported to have the capacity to absorb at least 0.005 ppm ethylene per hour per m^2. Adsorption of this small amount of ethylene may not be helpful for some situations, Choi, (20).

Japan's Nissho suggests a film that incorporates finely ground coral (primarily calcium carbonate), having pore sizes in the range of 10 to 50 m. After incorporation into a polyethylene film, the coral is claimed to absorb ethylene.

"BO Film," marketed by Japan's Odja Shoji, is a low-density polyethylene film extruded with finely divided crysburite ceramic which is claimed to confer ethylene-adsorbing capacity.

Although the finely divided clays may adsorb ethylene gas, they can also create pores within the plastic bag and alter the gas-transmission properties of the bag. Because ethylene diffuses more rapidly through open pore spaces within the plastic than through the plastic itself, ethylene would be expected to diffuse out of these pouches faster than through pristine polyethylene film bags. In addition, carbon dioxide within these pouches is transmitted more rapidly and oxygen enters more rapidly than with a comparable conventional polyethylene film pouch due to the gaps in the film. These effects can enhance shelf life and reduce headspace ethylene concentrations independently of any ethylene adsorption.

Japan's Evert-Fresh film, claimed to have preservative effects. The bags are, presumably, polythene with Ohya stone dispersed within the film matrix. The active ingredient of Evert-Fresh is not a reproducible compound, but rather a natural stone excavated from a cave in Japan and that includes redundant or inert ballast materials. Ohya stone is a zeolite with a claimed affinity for ethylene and carbon dioxide. Films containing Ohya stone have been extruded with polyethylene into pouches used to contain ethylene-generating fruit or vegetables, Anonymous (21).

3. Activated carbon based scavengers:

Metal catalysts on activated carbon remove ethylene from air passing over the bed of activated carbon. Activated charcoal impregnated with a palladium catalyst and placed in paper sachets effectively removes ethylene by oxidation from packages of minimally processed kiwi, banana, broccoli, and spinach.

Japan's Sekisui Jushi has developed a sachet containing activated carbon and a water absorbent that is capable of absorbing up to 500 to 1000 times its weight of water. The company provides data showing that the product, trade named Neupalon, absorbs 40 ml ethylene per square meter of package surface area.

Japan's Honshu Paper offers the Hatofresh Systems, which are based on activated carbon impregnated with bromine-type inorganic chemicals. The carbon-bromine substance is embedded within a paper bag or corrugated fibre board case used to hold fresh produce. They claim that the bag will scavenge 20 ml of ethylene per gram of adsorbent by the combination of ethylene with bromine.

Japan's Mitsubishi Chemical Company produces SendoMate, which employs a palladium catalyst on activated carbon that adsorbs ethylene and then catalytically breaks it down. The product comes in woven sachets that can be placed in packages of produce.

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