

REVIEW PAPER

Effect of Gamma Irradiation on Degradation of Pesticide Residues in Fruits and Vegetables

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ABSTRACT

Fruits and Vegetables have nutritional characteristics, which are supportive in growth of human body. To prevent them from infestation by insects and pests, various pesticides are used. These include herbicides, insecticides and fungicides. But these pesticides induce harmful effects on human body upon consumption. These effects can be hypothyroidism, breast cancer, Alzheimer's disease, etc. The gamma radiation is effective tool to degrade such harmful pesticides and also kill the microbes present in the fruits and vegetables. This review also provides information on the possibility of application of irradiation for improving shelf-life and quality of fruits and vegetables through various storage conditions.

Keywords *Gamma irradiation, pesticides residues, shelf-life*

Vegetables enclose priceless nutritional characteristics, which are supportive in repairing and appropriate growth of human body. Conversely, they can also be a source of toxic contaminants that are formulated to control pests in crops known as pesticides [1]. Contamination of crops and environment is directly associated to agro-chemical applications, industrial and domestic discharges [2].

Pesticides can be herbicides, insecticides and fungicides depending on the target pests. Based on the composition and mode of action, insecticides are further classified into organophosphate, organochlorine, carbamates, pyrethroids, and neonicotinoids. Among various pesticide classes, organophosphorus pesticide (OPPs) group is the most widely used class of agricultural pesticides to increase world food production [3, 4].

Pesticide residues in food and crops are a direct result of the application of pesticides to crops growing in the field, and to a lesser extent from pesticide residues remaining in the soil [5].

Persistent chemicals can be magnified through the food chain and have been detected in products ranging from meat, poultry, and fish, to vegetable oils, nuts, and various fruits and vegetables [6].

The application of pesticide is widely used for grains before harvest and after harvest to protect the grains from damage or loss. Cultivation and storage of grains often require an intensive use of pesticides, which may then be found in grains and in foods prepared from them [7]. Cereal grains are treated with pesticides, including organophosphates, carbamate, synthetic pyrethroids and

insect growth regulators, both in storages and prior to shipment in order to prevent insect infestation [8].

The most consumed pesticides for vegetables, fruits and food grains in India include endosulfan, mancozeb, phorate, methyl parathion, monocrotophos, cypermethrin, isoproturon, chlorpyrifos, malathion, carbendazim, butachlor, quinalphos, copper oxychloride, and dichlorvos (Source: <http://indiaforsafefood.in>).

In India, Food Safety and Standards Authority of India sets the maximum residue limits for pesticides in crops, foods, vegetables and fruits [9].

A study in Nigeria on organochlorine pesticide residues in cereal grains showed the presence of aldrin, dichloran, dieldrin, endrin, endosulfan, heptachlor epoxide, dichloro-diphenyl trichloroethane lindane, methoxychlor, and mirex [10]. A study in Pakistan on pesticide residue of cereals showed that wheat contained the highest concentration of tested pesticides than maize and rice and maize contained a much higher concentration of pesticides than rice [11]. The insecticide residues reported in market samples of grapes were acephate, methamidophos, chlorpyrifos, monocrotophos and quinalphos [12].

Gamma irradiation becomes an important technology in food industry, including preservation of a variety of fruits and vegetables (Cast, 1996) [13].

The effects of gamma radiation on fruits and vegetables

Radiation process is one of the most powerful AOPs (advanced oxidation processes), where irradiation with a beam of accelerated electrons or gamma radiation is employed for the decomposition of various pollutants like pesticide residues. The food irradiation was investigated by many scientists, but limited studies focused on the effect of gamma irradiation on degradation of pesticide residues below MRLs (maximum residue limits) (Cin and Kroger, 1982) [14].

Gamma radiation is used for pesticide degradation from different types of vegetables. Many of the samples contained pesticides, and 6-7% samples had residual levels above the maximum residue levels determined by the World Health Organization. Three carbamates (carbaryl, carbofuran, and pirimicarb) and six organophosphates (phenthoate, diazinon, parathion, dimethoate, phosphamidon, and pirimiphos-methyl) were detected in eggplant samples; the highest carbofuran level detected was 1.86 mg/kg, while phenthoate was detected at 0.311 mg/kg. Gamma radiation decreased pesticide levels proportionately with increasing radiation doses. Diazinon, chlorpyrifos, and phosphamidon were reduced by 40–48%, 35–43%, and 30–45%, respectively, when a radiation

strength of 0.5 kGy was utilized. However, when the radiation dose was increased to 1.0 kGy, the levels of the pesticides were reduced to 85–90%, 80–91% and 90–95%, respectively. This study revealed that pesticide residues are present at high amounts in vegetable samples and that gamma radiation at 1.0 kGy can remove 80–95% of some pesticides (chowdhary, 2014) [15].

Susheela *et al.*, (1997) [16] found no significant loss of sugar and ascorbic acid contents in three-quarter ripe and fully ripe pineapple fruit (*Ananas comosus*) irradiated at 0.15 kGy. The latter after having been irradiated at 0.05, 0.1, and 0.15 kGy and stored at 25–29°C with 90–97% relative humidity was shown to maintain their texture better than the controls. The maximum tolerable dose was approximately 0.25 kGy.

Wang and Chao (2003) [17] investigated the irradiation effects on dehydration characteristics and quality of apples (Fuji apple). They found that the vitamin C content of apples, the dehydration rate, and the rehydration ratio were greatly affected by irradiation dose (1.5, 4.5, 5, and 6 kGy). It was shown that the greater the dose, the higher the dehydration rate, the less the vitamin C content, and the lower the rehydration ratio.

Rubio *et al.*, (2001) [18] studied the effects of irradiation (0.50, 0.75, and 1.00 kGy) on the vitamin C content of lettuce (*Lactuca sativa*), cabbage (*Brassica oleracea*), and celery (*Apium graveolens*). There was a marked difference in the natural total ascorbic acid content of the vegetables studied with cabbage showing the highest. Irradiation did not decrease these initial concentrations, and in the case of cabbage, it actually increased them.

For lettuce, cabbage, and celery the initial ascorbic acid content was 2.357, 3.085, and 0.549 mg/100 g, respectively and after irradiation was 2.036, 5.018, and 0.616 mg/100 g, respectively irradiated with 1.00 kGy.

Drake *et al.*, (1999) [19] found that titratable acidity (TA) of “Gala” apples was reduced at irradiation doses of 0.60 kGy and above. On the other hand, no loss of TA due to the irradiation dose was evident, for “Fuji” or “Granny Smith” apples.

Thomas *et al.*, (1971) [20] found that in varieties Fill Basket bananas and Red bananas irradiated in the pre climacteric stage with 0.25 and 0.40 kGy doses, the contents of reducing sugars on ripening showed close agreement with that of non-irradiated fruits. However, in Gaint Cavendish variety, irradiated (0.35 kGy) fruits recorded lower sugar than in control. When analyzed at yellow skin color stage indicating that hydrolysis of starch to sugar had not progressed.

Mitchell *et al.*, (1990) [21] found that in red capsicums Cv.Five Star irradiated at 75 and 300 Gy. Carotene levels decreased with increasing irradiation dose, but the change was not statistically significant. No significant effect was found in the carotene levels in mangoes Cv. Kensington Pride irradiated at 75, 300 and 600Gy. It is concluded that mangoes and capsicums can be irradiated at doses optimal for disinfestation without significant loss of carotene.

Prakash *et al.*, (2000 a) [22] compared the effects of 0.5 and 1.0 kGy gamma irradiation on microbial and sensory

characteristics of diced celery to conventional treatments such as acidification, blanching and chlorination. Control samples surpassed aerobic microbial counts of 10 cfu/g and irradiated celery did not exceed 10 cfu/g in contrast in 22, 19, 12 and 8 days of storage. Sensory shelf life of the 1.0 kGy treated celery was 29 days compared to 22 days for control, chlorinated and 0.5 kGy and 15 days for the acidified and blanched celery.

Prakash *et al.*, (2000, b) [23] found that in cut romaine lettuce irradiation at 0.35 kGy decreased aerobic plate counts by 1.5 logs and yeast and mould counts by 1 log; these differences were maintained throughout the 22 day storage. Irradiation at 0.15 kGy caused smaller reduction in microbial counts. Ten percent loss in firmness was observed at 0.35 kGy, while other sensory attributes such as color, generation of off-flavor and appearance of visual defects were not affected.

De Figueiredo *et al.*, (2014) [24] investigated that the effect of gamma irradiation on functional constituents on papaya fruits cv. Golden. Fruits were harvested into maturation 1 degree (stage) and irradiated with 0.8 kGy (Cobalt 60 source-MSD Nordion irradiator), and then stored at 24 ± 2°C. Total carotenoids and vitamin C contents were evaluated in the pulp fruits, in the 5, 7 e 9th days post-harvest by a reversed-phase and ion exclusion column by a high performance liquid chromatography. Results demonstrated that the irradiation induced alterations in the total carotenoids and vitamin C levels. In conclusion, the present data provide evidence that the irradiated papaya, did not impair reduce these nutritional characteristics.

Majeed *et al.*, (2014) [25] evaluated that the gamma irradiation doses 0.5, 1.0 and 1.5 kGy for their effect on shelf life and chemical attributes of Strawberry (*Fragaria xananassa*) cv. Corona stored for nine days at room temperature. Berries irradiated with 1.0 and 1.5 kGy showed significantly prolonged storage life (5.75 and 7.75, days respectively) when compared to non-irradiated control fruits (3.25 days). Non-irradiated fruit samples showed maximum decay (94.5 %) and weight loss (58 %) at 9th day of storage; however, irradiation significantly reduced these two quality parameters especially at higher doses which corresponded to lower weight loss and fruit decay. Neither radiation treatment nor storage period had significant effect on total soluble solids, titratable acidity and pH of fruits. Results indicated that radiation doses 1.0 and 1.5 kGy might be used as consumers’ acceptable doses for shelf life extension, minimum weight loss and decay, without affecting the chemical quality of strawberry.

The effects of gamma irradiation on the Microbiological quality

Pesticide fate in the environment is affected by microbial activity. Some pesticides are readily degraded by micro-organisms, others have proven to be recalcitrant. A diverse group of bacteria, including members of the genera *Alcaligenes*, *Flavobacterium*, *Pseudomonas* and *Rhodococcus*, metabolize pesticides. Microbial degradation depends not only on the presence of microbes with the appropriate degradative enzymes, but also on a wide range of environmental parameters (Aislabie, 1995) [26].

Wang *et al.*, (2006) [27] measured and analyzed the enzyme activity in Golden Empress cantaloupe juice after 60Co irradiation. Enzyme activity determination revealed that lipoxygenase was the easiest one to be inactivated by irradiation, followed by polyphenoloxidase and peroxidase. However, all three enzymes remained active even at 5 kGy.

Afify *et al.*, (2013) [28] studied the possibility of stimulating *Trichoderma* spp with low dose gamma radiation for biodegradation of Oxamyl pesticides. Fungi strains capable for biodegradation of oxamyl are identified as *Trichoderma* spp., including *T. harzianum*, *T. viride*, *Aspergillus niger*, *Fusarium oxysporum* and *Penicillium cyclopium*. The results indicated that *Trichoderma* spp. used Oxamyl as source of carbon and nitrogen and possesses enzyme(s), which acts on amide and ester bond in Oxamyl structure. Degradation of oxamyl was 72.5% within 10 days of incubation by *T. harzianum* strain.

Song *et al.*, (2006) [29] studied that the radiation sterilization of fresh vegetable juice, and the effectiveness of g irradiation for inactivating *Salmonella typhimurium* and *Escherichia coli* in the carrot and kale juice was investigated. D10 values of *S. typhimurium* in the carrot and kale juice were 0.4457 ± 0.004 and 0.4417 ± 0.006 kGy, while those of *E. coli* were 0.3017 ± 0.005 and 0.2997 ± 0.006 kGy. The test organisms (inoculated at 107 cfu/ml) were eliminated by irradiation at 3 kGy.

Al-Suhaibani and Al-Kuraieef (2016) [30] studied that the effect of gamma radiation on the assessment of microbial quality of Spinach. Spinach was treated by using three doses of gamma radiation, 0.5, 1.0, 1.5 and 2.0 kGy. The results of microbial quality revealed that radioactive transactions have led to a significant reduction (indicate level of significant $p < 0.05$) in *E. coli*, total number of Bacteria, yeasts and fungi.

Zhang *et al.*, (2006) [31] studied that the effects of irradiation on microorganisms and physiological quality of fresh-cut lettuce were evaluated during storage at 4°C. The total bacterial counts on fresh-cut lettuce irradiated with 1.0 kGy were reduced by the order of 2.35 Log CFU/g, and the total coliform group were lowered to less than 30 MPN (most probably number)/100 g. The polyphenol oxidase activity of fresh-cut lettuce was significantly inhibited by irradiation. In addition, the loss of vitamin C of fresh-cut lettuce irradiated with 1.0 kGy was significantly ($\alpha = 0.05$) lower than that of non-irradiated. The best treatment of maintaining quality of fresh-cut lettuce appeared to be 1.0 kGy irradiation.

The effects of storage conditions

Srinu *et al.*, (2015) [33] reported in their experiment that, Irradiation of sapota fruits with 0.2 kGy gamma radiations and stored at 15°C for 20 days increased the post-harvest life 100% of sapota fruits by 26 days over control 5 days, lower doses of gamma radiation without affecting fruit quality. Higher doses of irradiation 0.8 kGy exhibited brownish spots after 3 days of storage on surface of the fruits.

Salunkhe and Desai, (1984) [34] stated that exposure of sapotas fruit to gamma irradiation at 0.1 KGY extended storage life by 3–5 days at 26.7 C and 15 days at 10°C

temperatures without any effect on ascorbate content.

Khalil *et al.*, (2009) [35] reported that for citrus fruits with doses of 0.25 and 0.5 kGy stored at room temperature for 42 days, their acidity and ascorbic acid values were higher for the oranges irradiated at 0.5 kGy. Their weight loss decreased and total soluble solid (TSS) increased during storage period.

Verde *et al.*, (2013) [36] studied that the evaluate effects of gamma radiation on raspberries in order to assess consequences of irradiation. Freshly packed raspberries (*Rubus idaeus L.*) were irradiated in a (60) Co source at several doses (0.5, 1, or 1.5 kGy). Bioburden, total phenolic content, antioxidant activity, physicochemical properties such as texture, color, pH, soluble solids content, and acidity, and sensorial parameters were assessed before and after irradiation and during storage time up to 14 d at 4°C.

Zhang *et al.*, (2014) [37] studied that was the effects of Co-60 gamma irradiation on the nutrient composition of citrus (Shatang mandarin); selected fruits were divided into different groups and each group was irradiated at 0.0, 0.2, 0.3, 0.4, 0.5, and 0.6, respectively. And then the treated fruits were stored at 4±%C and the nutrient composition was studied in the following days. The results showed that the shelf-life could be extended when fruits were irradiated in the dose range of 0.2– 0.4 kGy, while most un-irradiated citrus decayed by 15 days. It also turned out that the citrus irradiated at 0.5 and 0.6 kGy were fully decayed within 45 days of refrigerated storage.

Yadav and Patel (2014) [38] reported that the experiment was arranged from the 2008 and 2010 with 16 treatment combinations of irradiation dose (that is, 0.00, 0.20, 0.40, and 0.60 kGy) and stored at different storage temperatures viz., ambient at $27 \pm 2^\circ\text{C}$ and 60 to 70% RH, 9°C and 90% RH, 12°C and 90% RH, and Control atmospheric storage (12°C, O₂ 2%, CO₂ 3% and RH 90%). The fruits were exposed to gamma radiation from the source of 60Co. The two years collective data indicated that, the significantly minimum percent reduction in physiological loss in weight, reduced ripening percent, increased marketability of fruits, maximum total soluble solids, total and reducing sugars, and ascorbic acid content and minimum acidity were noted in 0.40 kGy gamma rays irradiated fruits stored at 12°C as compared to the other irradiated or un-irradiated fruits stored at ambient condition and other storage environment.

Harmful Effects of Pesticides in Fruits and Vegetables

There are many health issues linked to pesticide exposure. Generally, insecticides and fungicides are more toxic to humans than herbicides (2,4 D and Atrazine are huge exceptions to this). Many insecticides are neurotoxins and act on insects and humans in much the same way. Because they're toxic to your nervous system, exposure to them is linked to Parkinson's and Alzheimer's.

Fungicides are often applied near harvest time to prevent mold during transport. They are classified as endocrine disruptors and carcinogens. Exposure to fungicides has also been linked to hypothyroidism and breast cancer. Some herbicides, such as atrazine, may cause cancer, reproductive or developmental effects, and endocrine system effects.

Chlorpyrifos, used on corn, cranberries, brussels sprouts, and broccoli, can have harmful neurodevelopmental effects on fetuses and on young children. Research also ties the chemical to attention deficit problems, tremors, and autism.

2,4-D is an endocrine disrupter that interferes with thyroid hormones. It's also linked to risk factors for acute myocardial infarction and type-2 diabetes and poor semen quality. Cancer risks include non-Hodgkin lymphoma in people.

Glyphosate exposure can affect your health in a bunch of different ways. It is also an endocrine disruptor, it damages DNA, causes cell death and kills the beneficial bacteria in your gut.

And here's something to ponder - Neither the FDA nor the USDA has tested food for glyphosate (the active ingredient in Roundup). Even though it's the world's most widely used herbicide, and testing by academics, consumer groups and other countries has shown residues of this weed killer in food.

As commercial farming slowly gained popularity over organic farming, the natural methods were replaced with the ones using chemicals for fertilizers, pesticides and weed killers. The promise of higher yield in a shorter period of time is the selling point of these chemicals. But heavy reliance on chemicals is starting to take its toll on the vast farmlands and on the people's health. Fruits and vegetables are highly nutritious and form as key food commodity in the human consumption. They are highly perishable due to their low shelf life. These food commodities are reported to be contaminated with toxic and health hazardous chemicals.

But now a days, this process is widely used by the Indian farmers or the fruit vendors for ripening of many fruits like mango, banana, papaya, plums, sapota, apples, avocados, melons, peaches, pears, and tomatoes, pineapples, dates, etc. and vegetables that are heavily-laden with pesticides include lettuce, spinach, peppers, celery, potatoes, carrots, cucumbers, green beans, cauliflower, tomatoes, sweet potatoes, eggplant, broccoli and mushrooms. Among all of these, celery and lettuce contain the most pesticides while broccoli and eggplants contain the least amounts ^[39].

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