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Review Article

Ozone (O_3): An Emerging Technology in the Food Industry

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Abstract

Ozone is a powerful oxidant which is effectiveagainst various kinds of microorganisms on fruits, vegetables, meat, grains and their products. The multifunctionof ozone makes it a promising foodprocessing. It breaks down quickly to deliver oxygen and hence takes off no buildups in nourishments from its deterioration. It is used in water treatment, sanitizing, washing anddisinfection of equipment, odour removal, fruit andvegetable, meat and seafood processing, etc. It assures the maximum retention of sensory, nutritional and physicochemical characteristics offood. Ozone become a superior disinfecting agent compared to chlorine which have wide spread applications to assure safety and quality in the food industry. In later a long time Ozone has extended in reaction to buyer requests for greener nourishment added substances, administrative endorsement and the expanding acknowledgement that's a naturally neighborly innovation. In this manner, the nourishment industry in look of applications that are: viable in inactivation of common and developing pathogens, and evacuating poisonous contaminants; driving to less misfortune in item quality and guarantee freshness; adaptable to food processes, economically feasible and environmental friendly.

Keywords: Disinfectant; Food industry; Ozone; Pesticide residues; Replacement produce

Introduction

Food industry is one of the sensitive sectors which need the innovation technology to produce high quality products with high retention of nutrients and sensory quality to meet consumers demand. The different technologies have been used in food industry like High Pressure Processing (HPP), pulsed electric field, ultrasonic, high intensity pulsed light etc. Research findings revealed that, the processing of food by food industry increasing receiving negative press [1-3]. Coining and use of terminologies such as "Ultra processing food" [4] and linking this to detrimental health effects causing an increase in non-communicable diseases such as cancer, cardiovascular disease, cholesterol etc. According to this reason, novel technologies required to be used in food processing with minimal health hazards to consumers safe and quality food products. Ozone deteriorates to shape oxygen; in this manner, food items treated with ozone are liberated from substance buildup [5]. In this way, as indicated by the United States Department of Agriculture, food can be treated with ozone can in any case be delegated "100% natural" or "natural", contingent upon the O_3 use [6]. Therefore; ozone is an emerging technology in food industry which produces novel products with minimal health risk to consumers. Ozone has expanded in recent years in response to consumer demands for 'greener' food additives, regulatory approval and the increasing acceptance that ozone is an environmentally friendly technology.

What is ozone and how it is produced

Ozone (O_3) is the natural gas in the atmosphere and one of the most potent sanitizers against a wide spectrum of microorganisms. It is generated by the passage of air or oxygen gas through a high voltage electrical discharge or by ultraviolet light irradiation and is used for sterilization, virus inactivation, deodorization, bleaching (decoloration), decomposition of organic matter, mycotoxin degradation and others [7]. As ozone changes to oxygen by autolysis, it has been generally recognized as safe for food contact applications. It can be formed through ultraviolet and corona discharge. In ultraviolet, Ozone is formed throughout the atmosphere in multistep chemical processes that require sunlight. In the stratosphere, the process begins with an oxygen molecule (O_2) being broken apart by ultraviolet radiation from the Sun. In the lower atmosphere (troposphere), ozone is formed by a different set of chemical reactions which undergo two steps. In the first step, solar ultraviolet radiation breaks apart one oxygen molecule (O_2) to produce two oxygen atoms (2O). In the second step, each of these highly reactive atoms combines with an oxygen molecule to produce an ozone molecule (O_3). These reactions occur continually whenever solar ultraviolet radiation is present in the stratosphere. As a result, the largest ozone production occurs in the tropical stratosphere.

The corona discharge is the most commercial-industrial processes; ozone is generated by corona discharge reactor cells. A corona discharge is a diffuse and continuous luminous electrical discharge that occurs when a high-voltage electric field is produced between conductive and dielectric surfaces. A dielectric is a substance that is a poor conductor of electricity (an insulator) but an efficient supporter of an electric field. In a corona discharge ozone reactor cell, the dielectric facilitates the formation of a broad and continuous corona across its surface to maximize the effective area of the corona in the reactor cell. Corona discharge can produce moderate to high concentrations of ozone (typically 1 to 3% by weight from clean, dry air and up to 15% weight from concentrated oxygen) over broad ranges of output.

Working principle

The unstable third oxygen atom of ozone can combine with organic and inorganic molecules to destroy them through oxidation**.** Finally, ozone reverts back to oxygen after it is used. This makes it a very environmentally friendly oxidant.

History of Ozone in food processing

Ozone Discovered by Christian Friedrich Schonbein in German in 1840 and was first used commercially to treat portable water in France. After sixty-nine years later (1909) it was used firstly as food preservative for cold storage of meat and after 30 years (1939) used to inactivate the growth of yeast and mould during the storage of fruits. In forty-three years later (1982), it declares to be Generally Recognized as Safe (GRAS) for treatment of bottled water. In 1997 it was approved by industrial expert panel as safe in food processing for human consumption while in 2000 it was approved and granted to be food additive by FDA and USDA. In recent years, it was recognized as novel emerging non-thermal technology for degradation of pesticide residues from fresh produce in food processing industries. It is also considered as a green technology because unlike other conventional methods ozone treatment leaves little residual trace in foods.

Different application of ozone in food industries

Dissipation of pesticide residue in foods

Pesticides include all the particular synthetic compounds utilized in agribusiness, planned to murder bothers, control the contagious development and bugs, in this way balancing out the yield creation [8]. The utilization of pesticides is unavoidable for its commitment towards better return and great quality horticultural produce. The Maximum Residue Limits (MRL) of pesticides are crucial for residue level enforcements and dietary intake assessment [9]. A major concern encountered with the use of pesticides is its detrimental effect on the environment, wildlife populations, and human health. Blends of pesticides when applied to the harvests leave buildups in food, in the wellsprings of drinking water, and furthermore influencing the amphibian condition. Presently, different degrees of pesticide buildups are found in rural produce around the world [10-14], which makes a bottleneck in the universal exchange of food items.

The pesticide exposure on fresh fruits and vegetables, which account for 30 per cent of an individual's diet as they are consumed raw or processed, is high [15]. As the requirement for utilization of foods grown from the ground is expanding, the reaped rural produce is legitimately carried to advertise weighed down with a huge quantum of pesticides [16]. Conventional techniques such as washing with various agents, salting, peeling, cooking, drying and chemical oxidants were employed to remove pesticides in agricultural produces. Various factors such as the location of residue, its polarity, time, temperature and the type of washing [17] influence the efficiency of washing. Washing in tap water has little effect on pesticide removal since most of the pesticides are hydrophobic in nature [7]. Washing with chlorine has its limitations, particularly at a higher pH or against spore-forming bacteria; it produces harmful by-products including haloacetic and trihalomethanes acids which are considered to be harmful to human health and environment [18].

In recent years' scientists have been focusing on the development of non-thermal and non-conventional thermal techniques to eliminate the undesirable effects of pesticides in the food matrix. As the demand for pesticide-free, organic and quality food products is gaining momentum, green techniques such as ozone (O_3) have gained attention, owing to its significant disinfectant and antimicrobial activity [19]. Ozone is an allotrope form of oxygen that oxidizes many organic compounds [20]. In 2001, the utility of ozone in the food industry to arrest the growth of microorganisms has been Generally Recognized as Safe (GRAS) by the U.S. FDA [21]. Also, the US Environmental Protection Agency (U.S.EPA) considers the use of ozone in waste water treatment as a disinfection process [22]. Furthermore, rinsing of food contact surfaces or food with aqueous ozone is considered as sanitization measures [23].

Pesticide degradation in fruits and vegetables

Fruits

The removal of pesticide residues on the surfaces of fruits and vegetables using ozonated water revealed that 56-97 per cent reduction of mancozeb on apple surface treated with an ozone concentration of 1-10 mg kg^{-1} [24,25]. Another study found that removal percentages of pesticides from the different varieties of dates fruits in the presence of ozonated water (2mg.L^{-1}) were found to be significantly higher than plunging the organic products in refined water [26]. Further, the expulsion rates of pesticides upon ozone treatment fluctuated relying upon the assortment and the treating time. Antos P, et al. [27] considered the impact of ozone treatment on the debasement of fungicide buildups, for example, trifloxystrobin, captan, and boscalid in apples during cold stockpiling. The capacity test was led for 84 days and the ozone portion of 1 ppm was regulated for 1 min in each 12 h.

Chlorpyrifos ethyl, Malathion, tetradifon, imazalil, difenoconazole, and chlorothalonil are some of the more frequently used pesticides to improve the quality and yield of citrus fruits. Along these lines, most extreme buildup limits (MRLs) in citrus natural products are under the cautious perception of government specialists. Whangchai K, et al. [28] proposed that ozone in vaporous structure was more powerful than fluid ozone in the chlorpyrifos corruption. Metzger C, et al. [29] revealed that the buildup levels of Malathion, imazalil, and chlorpyrifos on citrus natural product put away in ozone-improved semi-business conditions decay to least levels following 35 days of capacity. The ozone treatment diminished the difenoconazole buildup in strawberries from 5 to 0.5 mg kg^{-1} [30]. In an investigation led utilizing 3 frameworks of lemon, orange and grapefruit, adsorption of chlorpyrifos ethyl, tetradifon and chlorothalonil were found to shift contingent upon the ware [31]. The creators found that ozonation for 5 min brought about the total expulsion of chlorothalonil buildups from the orange lattice. The most noteworthy adsorption and dissemination were accounted for tetradifon in the lemon lattice. Be that as it may, a connection between the basic properties of the frameworks and the evacuation of pesticides was not be set up however ozone is found to powerful in expelling each of the three pesticide deposits in both stripped and unpeeled networks.

Vegetables

Impacts of ozonated water on parathion, diazinon, cypermethrin, and methyl parathion in vegetables under watery conditions were researched in two distinct techniques: in a first strategy, 1 ml of 10 mg L^{-1} pesticide arrangement was blended in with an over the top portion of ozone (99 ml of 1.4 mg L^{-1} ozonated water) while in the second technique pesticide spiked vegetables were dealt with ozonated water for different conditions. Excluding methyl-parathion, over 75% of all the pesticides were degraded upon ozone treatment for 10 min [32]. Ikeura H, et al. [33] accentuated that the lower corruption pace of fenitrothion deposits in cherry tomatoes contrasted with strawberries was expected with the lower surface zone of the previous contrasted with the last mentioned. The low surface zone successfully decreases the contact with the ozone, henceforth, prompting wasteful expulsion of fenitrothion from the sarcocarp tissue of cherry tomatoes. It was further corroborated by the studies of [34], who documented that the pesticide residues deposited in spinach were easier to remove than cucumber and kumquat because of its high surface area. Kırış S, et al. [35] reported that wash time did not have significant effect in the quantum of pesticide reduction when using the tap water for pesticide removal. Interestingly, to eliminate the shaking effects of the ozone, the authors have applied the same quantum (600mL. min^{-1}) of nitrogen gas during washing with tap water. From the aforementioned studies, it is clear that the efficiency of ozone treatment for pesticide degradation depends on the concentration of ozone applied, physical properties of the food matrix, and the availability of residual ozone in the medium.

Wu Y, et al. [34] compared six different pesticide-washing strategies tap water, ozone water, alkaline electrolyzed water, micron calcium solution sodium bicarbonate, and active oxygen) for removal of 10 pesticide residues from spinach, kumquat, and cucumber. Fresh vegetables (cucumber and kumquat) were steeped for 15 min in 10 pesticide mixed solution (volume 5L), whereas, the spinach was immersed for 15 min in 10L mixed solution. The contaminated vegetables were air-dried for 24h. The pesticide residues were determined using chromatography-tandem mass spectrometry (GC-MS/MS, LC-MS/MS). It was accounted for that the dynamic oxygen arrangement was more powerful than other washing techniques to expel the 10 pesticide buildups in three vegetables in view of its oxidizability and alkalinity. Washing the vegetables with ozone water (0.4 mg. L^{-1}) led to 20-40% more removal of the pesticide residues than tap water. The authors justified that active oxygen and ozone possess a strong oxidation potential, which can degrade the unsaturated bonds in the pesticides and oxidize the functional groups to destroy most of the organic compounds. The authors concluded that the pesticide removal depends on the time of treatment, the pH of the washing solutions and the intrinsic characteristics of pesticides such as mode of action, octanol-water partition coefficient and the stability of hydrolysis and photolysis.

Pesticide degradation in water

The pesticides are regularly utilized in rural grounds and their overflows represent the tainting of drinking water [36]. Pesticide buildups in water bodies hurt the oceanic condition. The essential utility of ozone is in the treatment of drinking water to expel off-flavor, shading, diminishing the development of cleansing results, for sterilization itself and for the corruption of natural exacerbates that are damaging to the earth and human wellbeing. Norms have been defined in a few nations and tough guidelines are executed to follow the degree of pesticides in both regular water and drinking waters [37-39]. Atrazine is seen as the most well-known pesticide recognized in surface and drinking waters [40]. The metabolites of atrazine-Desethyl Atrazine (DEA) and De-Isopropyl Atrazine (DIA) shaped by the consequence of concoction oxidation are seen as the most moving mixes to debase. The study by [41] revealed the effect of ozonation on drinking water and its impact on the degradation of pesticides (atrazine and its metabolites - DEA and DIA) and other compounds like endocrine disruptors and pharmaceuticals. In this way, promising outcomes uncover that ozone could be utilized for the expulsion of follow contaminants in this manner decreasing the pesticide sullying by and large (65% decrease).

The treatment of drinking water for disinfection with chlorine resulted in harmful substances that are listed as carcinogens like Haloacetic Acids (HAAs) and Trihalomethanes (THMs) [42]. The application of ozone in combination with Biologically Activated Carbon (BAC) technology along with different phosphate doses at a concentration of 0.3 or 0.6mg. L^{-1} was found to produce lower DBPs and inactivation of the opportunistic pathogens [43]. Among the chlorinated organophosphorus pesticides being used, dichlorvos (2, 2-dihclorovinyl dimethyl phosphate, DDVP) is a likely cancer-causing agent and is recorded among the most unsafe pesticide by the World Health Organization (WHO) [44]. Despite the antagonistic impacts of pesticides, their utilization in agribusiness and food preparing enterprises is monstrous and furthermore utilized as a disinfectant in household creatures and domesticated animals [45,46]. Because of its wide utilization dichlorvos (DDVP) has been distinguished in surface waters additionally however the regular water medicines were seen as inadequate in scattering the dichlorvos determined buildups.

Wastewater treatments

The exhaustive use of natural water resources has to lead to water scarcity and a need for re-circulating the waste after its use in various industries. But sufficient care has to be taken to detoxify the water and make it safe for further use. The traditional methods of treating wastewater are time-consuming and are not efficient. Hence, a modern advanced oxidation technology like ozonation which is more efficient in the removal of micropollutants and disinfects the water without any possible DBPs is adopted. The municipal wastewater is subjected to ozonation treatment to remove the toxic substances and to make it suitable for reuse [47]. These refractory natural contaminations in water can be debased by cutting edge oxidation procedures with the joined utilization of the plasma-ozonation framework. Above 90% mineralization effectiveness was accomplished at a response consistent of 0.195 min^{-1} for corruption of 2, 4-D [48]. Acetamiprid having a place with neonicotinoids gathering of bug sprays that are progressively being applied in development of the cotton, natural products, and vegetable because of their capacity to supplant organophosphate mixes. The application of ozone to improve the water quality is suggested and confirmed by [49]. A reduction of organic compounds in the range of 53-70% was achieved and no toxic byproducts or fish mortality was observed during the application of ozone treatment. The effluent wastes from the oil mills are characterized by many potential organic toxic compounds with high BOD and COD. It creates a serious threat to the environment [50]. The wastewaters were subjected to ozonation at a dose of 765 mg L^{-1} O_3 that resulted in 20% removal of COD and in combination with biological step a 36% increase in COD removal was observed. The ozonation step resulted in oxygen enrichment in the wastewater making it more biodegradable [51]. Ozonation was applied with the aid of ceramic membranes on the surface waters contaminated by organic compounds and micropollutants such as Benzotriazole (BZT), Carbamazepine (CBZ), Atrazine (ATZ), and p-Chlorobenzoic Acid (pCBA). Greater than 90% removal rate was observed with a reduction in transformation levels [52].

Dairy Industries

Dairy industries are one of the sensitive sector which need lots of hygiene so as to produce good quality products free from physical, chemical and microbial hazards. Milk is among the perishable product which is very susceptible to microorganisms. The equipment and utensils which used during processing of milk should be sterilized. The pipelines, which convey the milk from individual draining stations to the mass tank, must be cleaned after each draining. High temperature water with synthetic concoctions is commonly utilized in the cleaning and sanitization forms devouring a lot of vitality and synthetic compounds. The use of ozone can considerably lower chemical costs and completely eliminate hot water costs on dairy farms. Heacox D, et al. [53] filed a patent for an ozone delivery method, system and apparatus whereby ozonated water, containing ozone at a preferable level of 0.04-1.2 ppm, is used to clean and disinfect dairy animals, milking equipment and various surfaces in dairy settings. If the hind legs, udder and teats of cows are thoroughly washed off with ozonated water prior to milking, many hygienic problems may easily be prevented [54].

The removal of milk residues and biofilm-forming bacteria from stainless steel surfaces by pre-rinse with warm water is normally the first step in cleaning dairy processing equipment in order to remove the bulk of milk residues. Guzel-Seydim ZB, et al. [55] quantified and visualized the effectiveness of warm water (40 ^{o}C) for removing dairy soil from stainless steel plates. Scanning electron micrographs indicated that the metal surfaces were cleaned more proficiently by ozonation than by the 40 °C warm water treatment. As indicated by the aftereffects of Compound Oxygen Request (COD) estimations, ozonated water expelled 84% of milk buildups from plates, though the non-ozonated warm water treatment evacuated just 51% of dairy soil materials. Also, [56,57] considered the reasonableness of ozone for expulsion of warmth denatured whey proteins from hardened steel surfaces. Both fluid and vaporous ozonation encouraged whey protein desorption.

Milk pasteurization is one of the unit operations done in milk to inactivate enzyme (alkaline phosphatase) and microorganisms. Thermal processing is among the conventional techniques used in milk pasteurization of which it imparts bunt flavour and loss of heat sensitive nutrients which is negative attitude to consumer acceptability to the product. For this reason, [58] patented a method for the mild ozone treatment of liquids, including milk and fluid dairy foods, thereby minimizing their possible quality deterioration. Jorek U, et al. [59] utilized pressurized ozone (5-35 mg/L for 5-25 min) to safeguard skim milk by diminishing its microbial populaces. The treatment was appeared to decrease the quantity of Psychrotrophs by over 99 per cent. Sheelamary M, et al. [60] totally wiped out *Listeria monocytogenes* from both crude and marked milk tests through ozonation. In an ongoing report, the viability of microbial inactivation in crude milk by ozone treatment was assessed [61]. Ozone gas rising at 1.5 mg/L for 15 min was found to decrease bacterial and contagious checks by up to 1 log10 cycle.

In powdered milk research has been revealed the presence of *Cronobacter sakazakii* ATCC cells [62]. The authors' uncovered entire and skim milk powder tests to vaporous ozone at convergences of 2.8 mg/L or 5.3 mg/L for 0.5-2 h. Both ozone levels decreased Cronobacter includes in skim milk powder by roughly 3 log10 orders following 120 min of presentation. The adequacy of ozone treatment was, be that as it may, unfavorably influenced by the nearness of fat in the item, in light of the fact that a decrease of just under 2 log10 units was seen in the suitability of C. sakazakii in entire milk powder after 2 h of vaporous ozonation

Drinking water treatment

Water is very important ingredient in human being. More than 70% of human body consists of water. Strictly no water no life. Ozone has been applied for a long time to the treatment of drinking water, anyway because of absence of exploration about its results; it was not utilized in numerous nations for water treatment. After discovery of trihalomethanes in chlorinated water, uses of ozone in drinking water by and by began picking up ubiquity. Drinking water treated with ozone slaughters or inactivates any pathogenic microorganisms including infections, microscopic organisms, and parasites. It removes inorganic trace contaminants found in water systems due to pollution. The chlorine and chloramines cannot be used to deactivate protozoa like *Cryptosporidium.*

Ozone treatment likewise diminishes normally happening natural mixes, for example, humic corrosive and algal metabolites. Pre-ozonation can dispense with taste, shading, scent and different mineral mixes. It can likewise be used for regular natural issue debasement and smaller scale life form inactivation. The component of bacterial inactivation by ozone is thought to happen by broad inactivation of the entire cell. In this manner, ozone makes harm the cell film, to the nucleic acids, and to specific compounds. It is especially compelling against infections, where its utilization can accomplish the best expectations [63]. The system of viral inactivation includes coagulation of the protein and oxidation of the nucleobases shaping the nucleic corrosive. It is additionally used to evacuate inorganic species utilizing pre-oxidation [64].

Ozone is a powerful oxidizer of shading because of disintegrated natural mixes and dissimilar to chlorine won't make chlorinated natural mixes. For fulvic and humic substances ozone dosages of 1-3 mg ozone/mg of carbon can influence almost finish expulsion of shading [65,66]. Likewise, contemplates have indicated that 1 mg ozone/liter can expel 10 shading units, [67]. Tosik has demonstrated that around 1 mg ozone/mg color is required to accomplish 95% shading expulsion, despite the fact that this proportion fluctuates by color type. The proportion increments to about 1.5 for 100% evacuation. It has been used to remove colour, odor and taste forming compounds present in raw water which formed during water treatment. These compounds derived from the decomposition of plant matter, but they are result of the activity of living organisms present in the water. Utilizing hypochlorite as a wet substance in scouring frameworks can cause emanation of chlorinated mixes and particulate from the scrubber fumes stack, just as a potential for discharge of a sanitizer scent if synthetic feed isn't appropriately controlled. The utilization of ozone as the oxidant can limit these issues. Wet concoction scouring utilizing ozone are a decent answer for scent control in circumstances where there is high power smell, high air volumes, or restricted space to site a scent control framework. Ozone is more successful for the oxidation of unsaturated mixes.

Disinfection of microorganisms

The rot of ozone in water, structure free radicals hydrogen peroxy (HO_2) and hydroxyl (OH) that are encircled have mind blowing oxidizing restrain and accept a working activity in the purifying technique. It is generally acknowledged that the minute life forms are destroyed considering protoplasmic oxidation realizing cell divider separating (cell lysis). The ampleness of decontamination depends upon the lack of protection of the target living creatures, the contact time, and the union of the ozone. *Giardia muris* and enteric diseases can inactivated by ozone as the fundamental disinfectant with 5 minutes contact time and ozone residuals of 0.5 to 0.6 mg/L to 3-log and 4-log clearings, independently. Gomella and partners watched all out demolition of poliovirus tests in refined water at an extra of 0.3 mg/L at the completion of 3 minutes of presentation. They by then viewed a comparable sufficiency when the contaminations were suspended in Seine conduit water and proposed the use of 0.4 mg/L following a contact of 4 minutes.

Factors affecting the pesticide removal rate

Ozone is considered to be used as an oxidant for pesticide removal. The rate of pesticide removal using ozone depends not only on the chemical reaction of the pesticides but also on the ozone properties. Ozonation may occur through the direct reaction of ozone to target pesticide compound or radical products produced from them ozone decomposition process. It is obvious that particular conditions are required for the viability of the ozonation procedure. In this manner, the evacuation pace of pesticide buildup is constrained by the states of use (pH, temperature and dampness), type of utilization (fluid and vaporous), natural issue content, ozone focus production rate, and its geometry-size [68,19]. Therefore, important process parameters governing the efficacy of liquid-phase as well as gas-phase ozone treatments are presented.

Phase of ozone

The ozone treatments for pesticide degradations are mainly applied in two phases: (1) continuous application of gaseous ozone in an atmosphere of stored agro-produce or (2) the produce is dipped or washed in water containing ozone (Corona discharge is an industrial method for ozone generation. In this method, high purity oxygen (>90%) is used as feed gas to achieve a higher yield of ozone. Once gaseous ozone is produced, it can be injected directly in the atmosphere or passed into a suitable medium (water) to produce aqueous ozone suited for washing the F &V and other applications. Ozone is highly unstable in aqueous phase compared to the gaseous phase. The half-life of ozone is 20 min in an aqueous medium at 20^{o}C, whereas it is 3 days in a gaseous state [69] (Goncalves, 2009). Ozone rapidly degrades to oxygen in the water.

Water temperature and pH

The temperature of the water and the levels of dissolved ozone in water are the major factors that determine the rate of degradation of pesticides [70]. It was likewise recorded that ozone shows a water dissolvability of 12.07 mg. L^{-1} at 20 ˚C [16]. Henry's law states that the solubility of ozone decreases with an increase in water temperature however, the rate of reaction of ozone is high in increased water temperature [71]. Heleno FF, et al. [30] archived that difenoconazole buildups in strawberries got decreased enormously with the expansion in measurement of ozone broke down in water. The difenoconazole residue showed a 95% reduction compared to the untreated samples after a one-hour exposure to ozone at a dose of 0.800 mg. L^{-1}. Rice RG, et al. [72] studied the relationship between water temperature and the solubility of ozone. The solubility of ozone in the water at 0 ^{o}C is 0.64, whereas it is 0.112 at 40 ^{o}C. This investigation brings up that water temperature is conversely corresponding to the solvency of ozone. Likewise, the solvency of ozone increments with an expansion in virtue of water, in light of the fact that the nearness of natural issue and minerals catalyze the disintegration of ozone in water [70]. Wu J, et al. [32] treated vegetables with low centralization of ozonated water to evacuate the buildups of diazinon, parathion, and methyl-parathion and cypermethrin. Despite the fact that the capacity to evacuate pesticides relies to a great extent upon ozone fixation, the high temperature conditions likewise improve its viability. Ikeura H, et al. [73] additionally saw that fenitrothion corruption expanded with an expansion in temperature from 15 to 30 ˚C. However, there is an optimum temperature for each pesticide (15-20 ˚C for diazinon removal). Ikeura H, et al. [33] found that the treatment temperature of 30 ˚C was more compelling on the fenitrothion buildup corruption by ozone in cherry tomatoes and lettuce. The productivity of ozone treatment in debasing pesticides additionally relies upon the pH of the framework being dealt with. Lin L, et al. [74] revealed that ozone with soluble conditions is appropriate for dichlorvos and malathion corruption, though acidic conditions are reasonable for debasement of cypermethrin.

Usharani K, et al. [75] contemplated the impact of pH on the debasement of methyl parathion in wastewater utilizing ozonated water. It was seen that ozonated water with pH more noteworthy than 7 had the most noteworthy impact on methyl parathion decrease contrasted with water with a pH of 7 and 3. Then again, Heleno FF, et al. [76] found that there was no huge distinction in chlorothalonil evacuations in potatoes in the wake of washing with ozonated water at various pH conditions (4, 7, 9 and without pH modification).

Humidity in the gas phase

Humidity plays a greater role in the rate of ozone generation and the rate of recombination of gaseous ozone [77]. Savi GD, et al. [78] applied the ozone gas at 60μmol.mol^{-1} during the storage of wheat grains in different humidity conditions. The authors found that the residues of organophosphate and pyrethroid in higher humidity (20% moisture with a_w 0.9) were destroyed with high efficiency than a lower humidity system (12% moisture with a_w 0.6). This could be probably due to the higher half-life of ozone at higher humidity.

Ozone concentration and production rate

de Souza LP, et al. [79] (2018b) reported that ozone treatments, both gaseous and liquid phase, were effective in the removal of linuron and difenoconazole from carrots. The removal percentage increased with increased ozone concentration and treatment period attaining the highest removal percentage at 5 and 10 mg. L^{-1} in gas and water phase; respectively for 120 min. Al-Dabbas MM, et al. [80] noted that the ozone treatment on the degradation of cypermethrin and chlorpyrifos residues in tomato is time-dependent. Hence, exposure time is directly proportional to the degradation rate of pesticide residues. Although there are no limits of ozone concentration used in food application, Heleno FF, et al. [81] found that the table grape qualities changed at high ozone concentration. The nature of grapes is kept up when it is submerged in water rose with ozone (centralization of 2 mg L^{-1}), anyway at higher focuses the nature of organic product is weakened. When ozone was applied at different production rate, the pesticide removal efficiencies were found to increase with the increasing rate, thus the pesticide residual in foods met the standards. Chen JY, et al. [82] developed a washing machine for removing of pesticide in vegetables; the residuals were compared in three different conditions of ozone production rate (without ozone generated as control, 250 mg.h^{-1} and 500 mg.h^{-1}). The higher rate of ozone generated (500 mg.h^{-1}) increased removal ability of 10% and 24%, respectively over lower rate (250 mg.h^{-1}) and control condition.

Produce geometry and the bubble size generated

The level of debasement of pesticides with ozone washing relies upon the geometry of the item being dealt with. Ikeura H, et al. [33] reveal that lettuce is more amenable for ozone microbubble treatment to degrade fenitrothion compared to the cherry tomatoes. It was suggested that the thick pericarp of cherry tomatoes mess up's ozone entrance on the tissues. Bubble size is an important factor to remove the pesticides in an aqueous system. The ozone bubbles size determines the kinetics of the reactions in the reactor. Millibubbles are large in diameter (2-3mm) compared to microbubble (<50μm). In terms of their technical applications, millibubbles or larger than that in diameter (normal macrobubbles) quickly rise up and burst at the surface showing low solubility in water. In contrast to typical air pockets, microbubbles are steady for a more extended time under surface (exceptionally solvent in water) and empower total disintegration of gas in water which is conceivably valuable for ozone application in natural compound breaking down [83,74]. Lin L, et al. [74] considered the buildups of fenitrothion pesticides in foods grown from the ground (lettuce, cherry tomato, and strawberry) subsequent to drenching in ozonated arrangement with three distinctive air pocket conditions (ozone/microbubbles, ozone/millibubbles and dechlorinated water as control). It was clear that ozone/microbubbles were the most effective in fenitrothion removal among other conditions due to a combination of ozone oxidative power and free radical generated from the collapse of microbubbles. The microbubbles enhance the mass transfer rates of ozone, which reflects in their efficacy compared to millibubbles.

Impact of ozonation on quality of agro-products

Although ozonation ensures microbial safety and pesticide degradation in agro produces with an extensive shelf life, the physicochemical, nutritional, and sensorial quality of the final product must be ensured. In spite of the fact that high ozone measurement and treatment time are viable in expelling pesticide buildups, these conditions can contrarily influence the nature of foods grown from the ground. Many researchers have estimated the impacts of ozone (in aqueous and gaseous form) on the nutritional profile of oranges, lemons, apples, strawberries, figs, peaches, and blackberry [84-86,72]. Adjustments in morphology, decay, staining, weight reduction, and bothersome smells can happen [87]. Further, a higher convergence of ozone on the outside of organic product or vegetable is found to adversely influence nutrient C content. In a study using fresh-cut honey pineapple, guava, and 'Pisang mas' bananas ozone treatment was found to significantly decrease the vitamin C content of all three fruits [88] In contrast, the vitamin C content was retained in the ozone-treated fruit about 3 times than the control at the end of the cold storage period [89]. The difference in vitamin C content could be due to the degree of ozone treatment and the nature of the food matrix. The quality changes observed on exposure to ozonation gives an important perspective of ozone and its impact on fresh fruits and vegetables.

Sensorial characteristics

Sensorial characteristics are mostly perceived as a quality attribute. Consumers generally purchase the agro produce based on its fresh appearance. Color, smell, surface, taste, and appearance are imperative sensorial characteristics that eventually characterize the inclination of the customer. The discoveries of [90,91] did not uncover any noteworthy contrasts between ozonated and control (non-ozonated) lettuce and tomatoes. Sintuya P, et al. [92] concluded that ozone treated coriander clears out appeared engaging quality maintenance compared to the coriander that experienced treatment with corrosive electrolyzed water. The coriander takes off have protected their new and green appearance, and no follow of off-odor was watched amid capacity. Ozone treatment was found to be exceptionally successful for verdant vegetables compared to other vegetables and natural products. This can be due to the tall surface zone of verdant vegetables that increments the viability of ozonation.

Color

Color is the key parameter of agro produce that influences consumer preference. Changes in color are mainly due to changes in the content of the natural pigments like anthocyanins, chlorophylls, and carotenoids resulting from enzymatic (polyphenol oxidase and peroxidase) and non-enzymatic reactions. However, no change in the color of fruits and vegetables is observed following ozone treatments. In a recent study, Surintraporn C, et al. [93] reported that gaseous ozone treatment (5.5 g.h^{-1} for 30 min) did not affect the color of dried chilies. Selma MV, et al. [94] had already documented that the color of fresh chilies was not significantly affected by ozone treatment. Forney CF, et al. [95] also noted that a high degree of color changes in fresh-cut cantaloupe treated with higher concentrations of gaseous ozone. Contrarily, Aday MS, et al. [96] observed that low ozone doses slightly reduced the yellowing of broccoli. The higher doses of ozone greatly reduced the rate of yellowing of broccoli due to the stimulation of chlorophyll antioxidants and/or chlorophyll degrading enzymes inhibition. In general, ozonation has a bleaching effect (increasing lightness) on fresh agro-produces that contain a high water activity [97]. Hence, the authors reported that ozone treatment did not affect the quality of low moisture foods [93]. Impact of ozone on fruit juices color degradation has been reported for orange [98], tomato [99], blackberry [100], grape [5], strawberry [101,102], and apple [103].

Aroma

The aroma of the fresh produce is severely reduced following the ozone treatment [104,97]). For instance, ozone-enriched cold storage of strawberries caused a reversible loss of aroma [86]. The authors concluded that the oxidation of volatiles released by the strawberries resulted in the loss of aroma. Baur S, et al. [89] noted a 40% reduction in the volatile esters emission in ozone-treated strawberries. Once alterations in the enzymes such as alcohol acyltransferase, hydroperoxide lyase, and lipoxygenase which are related to aroma biosynthesis were not detected, the volatile emission reduction can be correlated to the physical alteration of the surface of fruit [71].

Acidity, pH, TSS, and total sugars

Significant changes in pH and titratable acidity of fruit juices, fruits, and vegetables treated with ozone are uncommon. Non-significant changes of total acidity and pH were observed in apples during the storage in a modified atmosphere enriched with ozone [105]. The ozone-enriched atmosphere did not cause any negative effect on pH, Brix, and total acidity values of grapes [106]. Similarly, Tiwari BK, et al. [99] showed that when the orange juices were treated with ozone at a concentration of 0.6-100% w/w with a flow rate of 0-25 $L.min^{-1}$ for 0-10 min, no significant changes in pH, Brix, acidity, cloud value and browning levels were observed. The cantaloupe melon juice when subjected to ozonation at a concentration of 2.4 g L^{-1} for 30 and 60 minutes showed no significant changes in the soluble solids, pH and acidity levels [107]. Contrarily, a significant lowering of pH of tomato stored under an ozonated atmosphere was reported [108]. Therefore, it is suffice to state that the rate of change of pH and acidity depends on ozone dose, treatment time and storage period. The significant differences in total soluble solids and total sugar content of ozone treated fruits and vegetables were not observed. Ozone, when use

On the other hand, Minas IS, et al. [109] detected a significant decrease in Total Soluble Solids (TSS) in shredded carrots when treated with aqueous ozone. The process of leaching could have accelerated because of ozone treatment. Zhang L, et al. [110] also noted a significant decrease in TSS content in kiwifruits but a higher degree of reduction was observed in control samples compared to gaseous ozone treatment. Total Sugar Content (TSC) of fresh-cut celery and tomato decreased by the ozone treatments [110] or when mild dose-short term gaseous ozone treatment [112]. Similarly, TSC fluctuations are documented when the agro-produces are stored in an ozone-enriched atmosphere. Baur S, et al. [89] recorded a decrease in the glucose, sucrose, and fructose contents of strawberries stored under the ozone-enriched atmosphere. It was elucidated that ozone may cause oxidative stress leading to the activation of other sucrose degradation pathways. However, Wang H, et al. [91] reported that higher glucose and fructose contents in sliced tomatoes stored under the ozone-enriched atmosphere. Tiwari BK, et al. [97] also observed that glucose and fructose concentrations increased during the storage of carrots treated with ozone. This could be a result of the conversion of sucrose into glucose and fructose.

Firmness

Ozone has been found to be very effective in preserving the firmness of apples [27], carrots [109,113], kiwifruit, strawberries and tomatoes. Nevertheless, ozonation has a non-significant impact on firmness decays over storage time. Carrots, when subjected to gaseous ozone treatment at rate 0-5 $mg.L^{-1}$ and dissolved in water at a concentration of 0-10 $mg.L^{-1}$ exhibited no significant changes in the textural profile [108]. Some adverse impact on the firmness could be due to the tissue injury [92] or reduction in cell turgor owing to water loss [114]. The quality evaluation of fresh-cut asparagus exposed to ozone treatment before packaging revealed that enzyme activities were inhibited and changes in cell wall components such as lignin, cellulose, and hemicelluloses were also observed [115]. It was also suggested that ozone could effectively induce oxidation of phenolic cross-linkages or feruloylated cross-linkages among the structural proteins or cell wall pectin [116]. This oxidation process causes damage to the cross-linking which ultimately affects the firmness of products. Rico D, et al. [117] concluded that ozone treatment decreased the activity of Pectin Methylesterase (PME) in fresh-cut lettuce, and correlated it to the low crispiness. Antos P, et al. [27] reported that ozone had a positive impact on the preservation of the mechanical proprieties of apple. It could be due to the effect of ozone in slowing down the conversion of saccharides during the storage. The authors concluded that ozone treatment inhibits the process of ripening in apples which could be ascribed to the ozone-mediated degradation of phytohormone and ethylene. Taken as a whole, it can be concluded the optimum ozone processing parameters (ozone concentration, exposure time) must prevent as far as possible the excessive losses of quality characteristics.

Challenges

The greatest setback with the use of ozone in the removal of pesticides is that ozone has to contact the pesticide hence challenges are immense when the vegetables of fruit surfaces have rough or hairy structures. The provision of the agitation mechanism during treatment may improve the ozone penetration for effective disinfection. However, certain intensities of pesticide residual removal could not be achieved through ozone treatment. Ozonation adequacy to corrupt the pesticides depends on the sort of nourishment, pH of water/aqueous arrangement, strategy of ozone presentation, ozone concentration, treatment time, mode of application (gas/water), dampness content of food, atmospheric condition (temperature/relative humidity), and dimension and shape of treatment chamber [19,20]. Ozone can cause some negative alterations on food components such as changes in sensory characteristics, oxidation of lipids, loss of ascorbic acid and carotenoids, degradation of some vitamins and phenolic compounds, loss of anthocyanin, changes in color, and other adverse effects [68,102,104,118]. Also, it was documented that apple lenticels are damaged when the concentration of ozone exceeds 3.25 ppm [106]. Smilanick JL (2003) [21] reported that ozone concentration of 200 ppm was harmful to the agro-produces including un-waxed fruits. However, with the development of optimized process conditions for each fruit and vegetable, these negative effects could be greatly reduced. Also, the available literature states that the ozone treatment yields some degradation products of pesticide residues that were found to be more toxic than the parent compounds [119,32].

Advantages of ozone for food processing

- ✓ It only requires oxygen or air for its production.
- ✓ It is faster and better at killing microbes than chlorine.
- ✓ It is a non-thermal way to control pathogens and microbes in food processing.
- ✓ It is a non-chemical alternative for treating water and sanitizing food contact surfaces.
- ✓ It saves money because water does not have to be heated.
- ✓ It is compatible with organic food processing.
- ✓ It can be generated onsite, so no storage is required.
- ✓ It leaves no residues in food or water.
- ✓ It can be applied in an aqueous or gaseous state.

Disadvantages of ozone for food processing

- ✓ It could damage rubber and other polymers used for gaskets and o-rings.
- ✓ Its active life in water is less than 30 minutes, so it cannot be stored or moved.
- ✓ Like chlorine ozone is not selective.
- ✓ It will oxidize all organic material present.
- ✓ Depending on the soil load, its ability to kill micro-organisms may be restricted. So, when disinfecting water, the water should be pre-filtered before ozonation.

Health and safety

As with other powerful oxidizing agents, precautions are needed when using ozone. Good ventilation, extraction or inactivation systems are needed when using ozone because gas is given off during most ozonation processes. Ozone's Threshold Limit Value (TLV) is 0.1 Parts Per Million (ppm). Anything above the threshold has potential health risks. When inhaled, ozone causes dry mouth, coughing and nose, throat and chest irritation. Ozone may also cause difficulty breathing, headaches or fatigue. The odour of ozone is easily smelled at concentrations as low as 0.01 to 0.05 ppm - which means workers are likely to smell it before it reaches a dangerous level. Monitoring ozone levels in air can be done with commercially available test strips. A color change on the strips is matched to a standard scale. More sophisticated wall-mounted or hand-held devices are available and can measure such factors as ultra violet absorption that is specific to ozone.

Future prospective regarding ozonation should focus on

- ▪ Comparison of the efficacy of different forms ozone (gaseous/aqueous phase) to degrade the different classes of pesticides on the surface of the foods.
- ▪ Development of advanced devices for efficient conversion of oxygen to ozone and generation of higher purity gaseous ozone to be employed for the production of aqueous ozone.
- ▪ Investigation of the production of aqueous ozone without prior generation of gaseous ozone.
- ▪ The degradation rate of ozone depends on the purity of water; hence, the kinetics of ozone at a different purity level of water needs to be studied.
- ▪ In-depth studies are required to document the efficacy of ozone on a large number of pesticides present on the surface of foods of target effects of ozone treatment on the quality of food must be studied to define the limits of this technology.
- ▪ High ozone concentrations may result in faster degradation of pesticides in shorter processing time, but the probable negative effects of high concentrations of ozone by oxidation of health-promoting compounds needs to be investigated.
- The ozone processing parameters cannot be generalized; specific studies are needed for of its application in highly perishable agro-produces.
- Effect of ozonation combined with other non-thermal technology (integrated system) including ultrasound, ultraviolet and cold plasma or with sanitizers/preservatives such as chlorine, dimethyl bicarbonate, acids, hydrogen peroxide, etc., for the degradation of organophosphorous pesticides residues in fruits and vegetables needs to be explored.
- Ozone energy consumption and economic feasibility studies need to be carried out to fully exploit this technique in a more realistic and commercially viable manner.

Conclusion and future directions

The current uses of ozone in the food industry include extending the shelf life of vegetables, fruits and fruit juices; sterilization of equipment and eliminating the undesirable additives and microbes during storage and transportation. Ozone is potentially a superior solution for the removal of pesticides and to protect the consumers from the ill effects of pesticide residues on the surface of foods. US Department of Agriculture and other regulatory agencies have not imposed restrictions on using ozone as a sanitizing agent, making it very promising venture in the food industry. The high oxidative nature of ozone or the radicals generated during the process of ozonation cause molecular degradation of pesticide residues. Recent evidences have suggested that ozone has exceptional ability to improve the safety and quality of food thereby attracting the interests of the food industry. Overall, ozone is recognized as a green technology for the food industry because its application causes no toxic traces on the food.

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