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Shivani Mottan
Sher-e-kashmir University of agriculture sciences and Technology, Jammu, India

Neeraj Gupta
Sher-e-kashmir University of agriculture sciences and Technology, Jammu, India

Monika Sood
Sher-e-kashmir University of agriculture sciences and Technology, Jammu, India

Julie D Bandral
Sher-e-kashmir University of agriculture sciences and Technology, Jammu, India

Jagmohan Singh
Sher-e-kashmir University of agriculture sciences and Technology, Jammu, India

Anju Bhat
Sher-e-kashmir University of agriculture sciences and Technology, Jammu, India

Corresponding Author
Shivani Mottan
Sher-e-kashmir University of agriculture sciences and Technology, Jammu, India

A review on ozone technology in food industry

Shivani Mottan, Neeraj Gupta, Monika Sood, Julie D Bandral, Jagmohan Singh and Anju Bhat

Abstract
In the last few years, there has been a growing concern on Nutritional security as consumer need high quality food that are clean, safe and healthy altogether. This can be accomplished by employing more innovative technology like ozone treatment that ensures quality and safety of products. It can be successfully applied in purification of water, Sanitization of food handling machinery, disinfection of fruits and vegetables, elimination of smell from storage units, seafood preservation, killing or inactivation of bacteria, Yeasts, molds, parasites, and viruses, destruction of mycotoxins and biodegradation of pesticides. Ozone automatically break down to form Oxygen and a nascent oxygen on heating. Thus, ozone act as one of the most effective oxidising agent, leaving no residual effect on food. Ozone technology is an eco-friendly technology, which prolong the shelf life and retain the quality of food items without Generating unsafe by-products that have negative impact on the environment.

Keywords: Ozone, disinfection, sanitization, preservation, biodegradation, oxidising agent, mycotoxins, eco-friendly

Introduction
Food industry is one of the impressionable sectors which need adoption of and adaptation to modern technologies to bring forth high quality products by keeping their nutritive and sensory quality to meet the demand of consumers for safe and nutritious food.

Food industries use different technologies like pulse electric field, frozen foods technology, Nanotechnology, sensors, high pressure processing, ultrasonic and cold plasma technology, vacumm drying, high intensity pulsed light, biotechnology etc. but many studies has revealed that, the ultra processed foods are posing health threats. These foods have been linked to increase the risk of coronary heart diseases, cardiovascular diseases, cancer, cholesterol etc. therefore advanced technology are needed to be used in food industries for producing such food products which have least health hazards safeguarding the health of the consumers. Extensive research have been made in the recent years to find realizable processing alternatives with the ability to produce fresh products with good qualities safety and storage stability of food.

In recent times there has been growing interest in ozone and its application in the food industry for use as a sanitizer (Lelieveld *et al*., 2016) [19] because reducing pathogen and spoilage micro-organisms in fruits, vegetables dairy food products etc are a principle food safety concern. Favorable results have been unveiled in solving the problems of food industry like pesticide residue microbial attack, pests infestation, mycotoxins, enzymatic activity and non enzymatic activity etc by ozonation.

Ozone or triatomic oxygen (O_3) is an unstable allotrope of oxygen. It is powerful substitute to chlorine compounds in the food industry (Ziyaina and Alzogne, 2010) [34]. it is the most dominant disinfecting agent. Its reduction potential is 2.07V, that certify it as one of the potent known oxidizers. Discovery of ozone was done by schoinbein in 1839 and its initial commercial application was only in disinfection of drinking water in france. ozone decomposes voluntarily without forming harmful residues in the treatment medium making its use safe in food application.

Ozone has bacterial properties that makes it as an efficient practical antimicrobial agent that can kill different micro-organisms such as bacteria fungi, viruses and protozoa. Which are the potential sources of food borne illness and food spoilage (Guzel-Seydim *et al*., 2004; Oztekin *et al*., 2006) [15, 23].

What is ozone?
Ozone or triatomic oxygen (O_3) is an allotropic type of oxygen (O_2), i.e., it is comprised of same atoms but they are joined in various forms.

The distinction is the presence of three oxygen atoms, whereas "common oxygen" has just two oxygen atoms.

Ozone properties

ozone is a pale blue gas with a strong smell. It is highly reactive and unsteady triatomic oxygen molecule (O3) having high oxidation capability of 2.07V that makes it a potent antimicrobial compound owing to its expansive range antimicrobial properties. It is generated when free oxygen radicals combine with O2 molecules to form O3.
If ozone is utilized in low concentration it is certifiably not a very poisonous gas but at high levels it can result in serious negative impacts on well being and can even be deadly. A few federal agencies have set up health guidelines or proposals to restrict exposure of humans to ozone. These exposure limits are summed up in Table 1.

Table 1: Recommendation levels for exposure of ozone.

Institution	Accepted levels
Food and Drug Administration (FDA)	Requires application limit exposure of 0.05 ppm during 8h
Occupational Safety and Health Administration (OSHA)	Requires fixation limit openness of 0 to 10 ppm during 8h
National Institution of Occupational Safety and Health (NIOSH)	Suggests a maximum constraint of 0.10 ppm, not to be greater than this at any time
Environmental Protection Agency (EAP)	Requires a focus limit openness of 0.08 ppm during 8h

Table 2: Physical properties of ozone (Rice *et al*., 1981; Kim *et al*., 1999; Khadre *et al*., 2001; Guzel- sey-dim *et al*., 2004) [26, 17, 16, 15]

Parameter	value
Molecular weight	48
Thickness (kg/m3)	2.14
Boiling point (oC)	-111.9
Melting point (oC)	-192.6
Critical temperature (oC)	-12.1
Critical pressure (atm)	54.6
Oxidation potential (V)	-2.07
Solvency in water at 0oC (L/L)	0.640
Solvency in water at 15oC (L/L)	0.451
Solvency in water at 40oC (L/L)	0.112
Solvency in water at 60oC (L/L)	0.000

Table 3: Relative oxidation potentials (Khadre *et al*., 2001) [16]

Species	Oxidation Potential, eV
Fluorine	3.06
Hydroxyl radical	2.80
Nascent oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Perhydroxyl radical	1.70
Hypochlorous acid	1.49
Chlorine	1.36

Methods of ozone generation

Due to commercial demand of ozone for treatment and various applications, there have been many years of research and improvement put into strategies for production of ozone industrially. Today there are four perceived techniques (Smith, 2002) [31].

1. Electrochemical method
2. Ultraviolet Radiation method
3. Corona discharge method
4. Radiochemical method

Electrochemical method

The electrochemical strategy generally employs an electrical current between an anode and cathode in an electrolytic arrangement water and a suspension of extremely electronegative anions. This outcomes in the creation of a combination of oxygen and ozone at the anode. The ozone generated through this method has many benefits including: low voltage activity of the possibility of producing high centralization of ozone in the gas and liquid phase with high current productivity, no requirement for gas feeds of any depiction and powerful and basic framework plan (Christensen *et al*., 2009) [8].
The electrolysis of water is usually assumed to generate ozone through 9 6 – electron process (Da silva *et al*., 2003) [10]:

$$3H2O \rightarrow O3 + 6H+ + 6e- \quad EO = +1.51V \qquad (1)$$

The oxidation potential for the oxidation of water to oxygen is to few degree decreased, +1.23V.

$$2H2O \rightarrow O2 + 4H+ + 4e\text{-}EO = +1.23V \qquad (2)$$

Oxygen is continuously generated along with ozone.

Photochemical generation with UV light

Photochemically, ozone is delivered through the effect of high energy, short wave UV light from the separation of oxygen particles. The energy for the disintegration of oxygen molecule into its atoms is provided by photons at frequencies under 193nm. If longer frequencies (>200nm) are utilized, separation responses occur, which lead to wasting of ozone. Generally air is transmitted over UV lamps that give a frequency of 185nm and the delivered ozone gas is then splitted up in water. By the utilization of vacumm UV ozone generators, for instance in pools, development of nitrogenous mixtures can be inhibited during the ozone creation. This method is appropriate just for the generation of small quantities of ozone with high current utilization, likewise. (Silva *et al*., 2003; Smith, 2010; Briner, 1959) [10, 5].

Corona discharge method

There are two anodes in corona discharge, one of which is the high pressure terminal and the other is low pressure terminal (ground cathode). There are isolated by an earthenware dielectric medium and then release hole is given (Goncalves, 2009) [13]. At the point when a high voltage rotating current is applied across a release hole when oxygen is present, it energizes oxygen electrons and in this way prompts parting of oxygen particles. Atoms obtained after breaking of oxygen molecules join with other oxygen atom to make ozone. Ozone generation changes relying upon voltage, constancy of current, dielectric material property and thickness, releases hole and outright tension inside the release hole (Khadre *et al*., 2001) [16]. In case air is passed through the generator as a feed gas, a 1 to 4 percent of ozone can be delivered. Though, utilizing pure oxygen let oxygen production to reach 6 to 14 percent.

Ozone gas cannot be reserved because ozone converts back into oxygen (Guzel-seyelim *et al*., 2004; Goncalves, 2009) [15, 13]. Dried gas is utilized to limit the errosion of metal surface because of accumulation of nitric acid delivered from wet gas inside the generator (Khadre *et al*., 2001) [16].

Benefits of corona discharge method

- High ozone fixations
- Best for water applications
- machinery can keep going for quite long time without service.

Radiochemical method

In radiochemical ozone creation the separation step is started by high energy products resulting from reactions of radiochemical decay. The response is free of the encompassing pressure and temperature. Generally isotopes, for example, 137C5, 60Co or 90Sr are utilized for energizing of flowing air in a water-cooled shut framework. The thermodynamic qualities of this type of ozone creation are entirely ideal, since around 35% of the accessible energy is utilized for decay of oxygen atoms.

Usage of extreme electronegative gas (for instance SF6) can evidently further increment the production of ozone. Be that as it may, this method is hardly utilized practically because the application is complication and there is a risk of radioactive contamination. (Smith, 2010; Elsayad *et al*., 1986; Steinberg *et al*., 1973) [11, 32].

How ozone works?

Fresh fruits and vegetables are ozonated by showering and washing to decrease the quantity of micro-organisms that come into contact with the surface of material. Ozone can kill organisms that adhere to the surface by striking the cell walls, resulting in changes in the cell penetrability. Cells lose cytoplasm and cannot reactivate. Its penetrability change cause lysis of bacterial cell.

Especially, by trying to strike glycoprotiens and glycolipids in cell layers causing bursting of cell, ozone eradicate microbes. Also some enzymes sulfhydryl group limits cell enzymatic movement and capability.

Ozone further strike purine bases and nucleic acids that harm DNA. ozone\'s antimicrobial power includes bacteria as well as molds, viruses and protozoa. Ozone likewise oxidize metal particles like Fe(II), Mn(II), or As(III), which produce insoluble strong oxides. Subsequently, sedimentation can efficiently separate it from water.

Improving the efficiency of ozone

Utilization of ozone as a decontaminat in treatment of water began long back, and its utilization in food industry began in 2001 after the FDA gave the ranking of "generally recognized as safe"

(GRAS) to the ozone that can be used as an immediate additive in food. Ozone is being utilized for quite some time purpose for example, for up keeping the quality of meat, poultry (Sheldon and Broun, 1986) [29] shrimp (chen *et al*., 1992) [7] and fruits and vegetables (Badianiet *et al*., 1996; Achen and Yousef, 1999) [2], and moreover to oxidize harmful natural compounds, to minimize the smell, surface cleaning in food ventures, and to minimize BOD in the climate. The utilization of ozone limits inorganic waste on the grounds that the molecules breakdown automatically to oxygen (Adler and Hill, 1950) [1].

Food items are generally treated with gaseous and aqueous forms of ozone. The type of ozone treatment is decided by the sorts of food items being handled (Cutten *et al*., 2010) [9]. Different analyst have recommended utilization of water containing ozone for higher productiveness (Kim *et al*., 1999; Qiang *et al*., 2005; Zorlugene *et al*., 2008) [17, 25, 35] but one more association of scientist announced that gaseous ozone is more productive prompting higher log deduction in microbial (Singh *et al*., 2002) [30]. These unsteady outcomes might be a direct result of contrast in products and treatment condition utilized by scientist.

Ozone application at the post harvest stage of products is for the inactivation of pathogens and food spoiling microorganism and minimizing residues of pesticides and chemicals. Many fruits like apple, blackberries, blueberries, melons, peaches, oranges, and so on were examined for the activity of ozone against various microorganism in recent years. Apple (Meloughlin, 2000) [22] and sliced salad mixes (Strickland *et al*., 2010) [33] are being analysed industrially with water containing ozone to extend their shelf life. Gaseous ozone has further effectivally applied for decreasing the microbial burden in different vegetables like tomatoes, broccoli, cucumber, green beans and lettuce. Rice (2005) [27] stated that the ozone treatment suppressed the diseases caused by fungi in potatoes and onion. Ozone has further utilized for surface discoloration of broccoli florets (Lewis *et al*., 1996) [20], spinach leaves (Sakaki and Kondo, 1981), and peaches (Bacliani *et al*., 1996) [2], Liew and Prange (1994) [21] likewise revealed that ozone treated carrots were lighter in shade in comparison to non treated carrots. Though, it lead to destruction of Chlorophyll in fresh romaine lettuce (Bermudez and Barbosa, 2013) [3].

Utilization of ozone as a food additive to the fruit juice for conservative was the subject of interest for many scientist all over the world as ozone processing can possibly become one of the most affordable conservation method among non-thermal processing.

Effect of ozone on fruits and vegetables

Now a days there has been a developing interest in the ozone application during the handling and preservation of fruits and vegetables. Microbial contamination of food can occur at any stage right from the development in the field to the post harvest handling, processing and marketing, therefore there is need of employing such technology that can help in dealing these problems. (Beuchat, 1991) [4] demonstrated that treatment with ozone appears to have a helpful impact in measuring the life of fresh non-cut items like broccoli, cucumber, apples, grapes, oranges, pears, raspberries and strawberries by lessening the microbial load and through ethylene oxidation.

Table 4: Overview of the impact of ozone treatments on quality and safety characteristics of fruit and vegetables.

Food Type	Treatment (Type, Concentration, Time)	Targeted microorganisms	Inference	Reference
Apple	Aqueous ozone (23–30 mg/L, 3 min)	*Escherichia coli* O157:H7	Up to 3.7 log reduction on surface, 1 log reduction in stem-calyx	Perry *et al.* (2008) [24]
Blueberry	Gaseous ozone (5%, wt/wt, 64 min)	*E. coli O157:H7* *Salmonella enterica*	2.2 log reduction 1.0 log reduction	Bialka and Demirci (2007, 2008)
Spinach	In-package gaseous ozone (1.6 mg/L for air 4.3 mg/L for oxygen gas, 5 min) and with 5% (wt/wt) gaseous ozone	*E. coli O157:H7*	Up to 5 log reduction	Bialka and Demirci (2007) and Bialka *et al.* (2008)
Red pepper flake	Gaseous ozone (9 ppm, 360 min)	*Bacillus cereus* spores	1.5 log reduction	Akbas and Ozdemir (2008) and Asill *et al.* 2013)
Fabricated beef surfaces	Aqueous ozone (5 ppm) followed by heating (55 °C)	*Clostridium perfringens* spores	2.09 log reduction for vegetative cells 0.87 log reduction for spores	Novak and Yuan (2004) and Pohlman (2012)
Alfalfa seeds	Aqueous ozone (21.8 ppm, 10–20 min) followed by heating (60 °C, 3 h)	*Listeria monocytogenes*	1.48 log10 CFU/g	Wade *et al.* (2003)
Table grapes Dried figs Corn kernels	Gaseous ozone (5000 µL/L, up to 60 min) Gaseous ozone (13.8 mg/L, 180 min) Gaseous ozone (10–12%, wt/wt, 96 h)	*Botrytis cinerea* (gray mold) Aflatoxin B1 Aflatoxin	50–60% reduction 95% reduction 92% reduction	Ozkan *et al.* (2011) Oner and Demirci (2016) Oner and Demirci (2016)
Potato strips	Heating (60 °C for 10 min, 100 °C for 5 min) followed by in-package gaseous ozone (5%, wt/wt, 15–30 min)	Mesophilic Psychrotrophic Mold-yeast	No growth up to 4 weeks at 4 °C	Oner *et al.* (2011)
Raspberries	Upto 5µl/L for upto 4min, 17 °C, 52 %	*Murine norovirus*-1 *hepatitis* A virus (HAV)	Upto 33 log(3µl/L, 1min) reduction little effect on HAV even for the highest dose(5µl/L,3min)	Brie *et al.* (2018)
strawberries	36, 202µl/L, 6% (wt/wt) (ca. 80 g/m3), 30 min, 22 °C, 60%-70% RH	*Salmonella E. faecium Murine nonovirus*-1 (MNV-1)	Upto 2.1 log reduction Upto1.5 log reduction Upto1.8 log reduction	Zohu *et al.* (2018)
Cantaloupe	Exposure to 4.3 ppm for 5 min & thin storage at room temp for 24h.	*Salmonella poona*	brought about about 4.29 log CFU/g reduction	Trinetta *et al.* (2003)

Source: Lelieveld *et al.* (2016) [19].

Application of ozone in raw poultry and meats

Many cases of foodborn illness have been reported in humans are caused by raw poultry and meat products contaminated with contagious bacteria such as *L. monocytogenes*, *campylobacter* Spp., *salmonella* Spp. and other enteric bacteria. If meat and poultry products are contaminated it diminish their shelf life. Ozone is a powerful agent for disinfection of beef. (Kim *et al*., 2003) [18] Summarized that application of gaseous ozone has been proved effective against growth of various micro-organisms on meat surface. Ozone has also demonstrated the efficacy and safety of disinfectants for cleaning poultry remnants (Kim *et al*., 2003) [18].

Moreover, ozone can be used to control salmonella enterica in shelled eggs by employing low temperature and mild pressure for pasteurization. Yousef and Rodriguez-Romo (2008) found that treatment of salmonella in eggs with ozone gas at 22-25 °C and 15 psi inch for 10 min resulted in a reduction population growth of at least 5 log units (Perry *et al*., 2008) [24].

Application as a potential sanitizer and in wastewater treatment

Fresh produce industry is subjected to losses that are due to the spoilage by micro-organisms between the time of harvest and consumption and these losses are estimated to be as high as 30% (Beuchat, 1991) [4]. Chlorine is the most commonly used sanitizer in the Food/Fish industry to retain the quality of produce by reducing microbial load. Many Environmental and health agencies are coming forth with concerns associated with these traditional sanitizer agents in regard to the formation of harmful by-products, such as tri-halomethanes (THMs) and other chemical residues formed in the wastewater returned to the environment (Anonymous, 1998; Cena, 1998; EPRI, 1997; Graham, 1997) [2, 12, 14].

Now-a-days the pesticide application in the fields to safeguard the produce against pest has been on the increasing trend and this is the potential reason why people are suffering due to many diseases as these pesticides residue on the surface of fruits and vegetables are not being completely destroyed by current technologies and react with other chemical residues and form chemical by products. These by products ultimately is consumed by customers and affect health of the people in both direct and indirect ways. Ozone has emerged as one of the safe sanitizer, disinfectant, bleaching agent in the food processing industry.

Produce industry also generates billions of gallons of wastewater annually, with very high concentrations of biochemical oxygen demand (BOD) and chemical residues every year. These wastewater have been reported to cause many serious problems such as cancer, fish death, water pollution, psychological and physiological diseases and damage to the ecosystem. Ozone is now being employed to treat or recycle food processing wastewater to overcome this problem.

Ozone use for surface sanitation in food processing units

In food processing plants pathogen free environment is very much important to keep the quality of food products and reducing the potential for cross-contamination of many pathogenic micro- organisms. Therefore surface sanitation is the foremost factor in these food processing units.

Many processing plants use aqueous ozone or ozone in water for sterilization of the surface of food products, equipments etc. The source of cross-contamination on food processing equipments is build-up of bio-film. Biofilms are layers of micro-organisms adhered to a surface. Microbes can attach themselves to a surface and continue to grow layer upon layer of new microbes. These layers become very much resistant to sanitizers over a period of time and sanitization process become more difficult if it is not done on a regular basis.

Aqueous ozone can be used for sanitization process. During sanitization with ozone, first surfaces are cleaned and removal of bio-films are done with a hot-water and then aqueous ozone is used for surface sanitization destroying all bacteria viruses, fungi and spores and it is one such powerful sanitizer that leaves no residual on the surface of equipment or materials.

Aqueous ozone can be sprayed within the plant safely. All the equipments, walls, floors, drains, tanks, tubes, racks, knives and tables can be sanitized with aqueous ozone.

Effectiveness of ozone with different materials

Surface material	Percent reduction in plate count
Stainless steel Kettle	89.7-98.2
Stainless steel tabletop	98.9-99.7
Plastic shipping containers	96.9-97.2
High traffic floor	67.0-95.6

By Brian Hampson, PhD, Food Science and Nutrition Dept california polytechnic state university, San Luis Obispo, CA

Application in Fruit Juice Preservation

There are wide range of heat-resistant bacteria and fungi that are not get killed during pasteurization of juice and pose a serious problems to citrus processors. Ozone is potentially useful in activating heat-resistant spores in juice components. Therefore, the effectiveness of ozone against spores of *Alicyclobacillus acidocaldarius*, *Neosartorya fischeri* and *Zygo saccharomyces bailii*, which are the source of spoilage in juices, was examined in selected juice ingredients.

Orange juice concentrate (OJC), high fructose corn syrup (HFCS), fruit Juice components and pineapple juice concentrate (PJC), containing these spores (c,107mL-1), were treated with gaseous ozone. The susceptibility of spores to ozone different depending on the type of spores require 0.31, 0.28 and 0.41 mg ozone per ml of spore suspension in HFCS, OJC and PJC respectively. The dose of ozone needed for inactivation of 5 log units of *N. fischeri* spores was 0.12-0.51 mg/mL-1 for achieving reduction of 5 log units of *Z. bailii* spores, 0.04-0.24 mg/mL-1 was required, depending on the juice component.

Other applications of ozone

1. Disinfection of aquaculture farms.
2. Sterilization of food packaging material.
3. It can be successfully used as a germicide agent in processing of seafood and extension of their shelf life and quality.
4. It can be used for disinfection of drinking water and bottled water production.
5. It can be used to purify the atmosphere contaminated with micro-organisms.
6. It can be used in cold storage against molds and bacteria and extend the shelf life of product.

Advantages

1. ozone is 1.5 times more powerful than chlorine and 3000 times faster acting. It has no residual effect in water, or on food.
2. It is cost effective as it requires only oxygen or air for its production.
3. No need of storage, as it can be produced onsite.
4. It can be applied in both forms aqueous or gaseous.
5. It is safer alternative for treating water and for sanitization process as it is non-chemical.
6. It efficiently degrades pesticides, herbicides and contaminants present on food or water.
7. Ozone safely reverts back to normal oxygen so eco-friendly method.

Disadvantages

1. It is unstable, it cannot be stored for a longer period of time.
2. Its maintenance and operation is highly complicated.
3. Highly toxic if used beyond permissible limits.

Potential Risk and Health Concern

Studies have shown that sensory attributes of food may experience alteration, depending on constitution of food and use of diversified ozone dose and exposure conditions, it can have considerable effect on the nutritional content of the food, therefore it is to be used carefully as it's utilisation beyond permissible limits can be harmful for the quality of food as well as for the well being of humans as it is a poisonous gas. Good ventilation, inactivation systems are needed when using ozone because gas is given off during the most ozonation processes. ozone's threshold limit value is 0.1 parts per million (ppm). If it is used above this level it can become toxic and can cause discomfort to vulnerable people amd symptoms like headaches, throat dryness, coughing, nose and eyes irritability can be commonly observed after exposure to higher levels of ozone.

Ozone can be easily smelled by workers at concentrations as low as 0.01 to 0.05 ppm. Now a days many advanced wall-mounted or hand-held devices are available which can be used for monitoring the levels of ozone in air and safeguard the workers against health hazards.

Conclusion

Increased demand of new alternative technologies for novel industrial application has made ozone technology as a promising technology. Its current uses in food industry are extension of shelf life of fruits and vegetables fruits juices, surface sanitization and sterilization of equipments for keeping the food processing units free of microbial environment. It is highly desirable technology in the food industry due to its phenomenal ability to preserve the quality of food by protecting it against wide range of pathogenic micro-organisms. It is recognized as a green technology for the food industry because it do not produce any harmful by products after treatment of products.

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