Ozone delivery on food materials incorporating some bio-based processes: A succinct synopsis

Charles Odilichukwu R. Okpala*

Educare and Skills Training Network, Middlesex HA8 8EJ, United Kingdom

*Corresponding author: E-mail: charlesokpala@gmail.com

Received: 26 October 2016, Revised: 13 November 2016 and Accepted: 09 April 2017

DOI: 10.5185/amp.2017/802
www.vbripress.com/amp

Abstract

This paper reviews succinctly ozone delivery on food materials incorporating some bio-based processes. Particularly, ozone treatment is among existent bio-based process technologies applicable to wide range of food materials. Since declared 'Generally Recognized As Safe (GRAS)', the global technological progress of ozone has had its discharge settings to-date range between laboratory/domestic and industrial scales. Based on medium properties and probably owed to its unstable nature, whilst the chemistry and physics of ozone substantiates not only its efficacy, but also the delivery processes, incorporating both direct/indirect oxidation and ozonolysis contributes to its diversity. Ozone is widely under investigation as sanitizing agent for the food industry. So when it is applied to food materials, key variables of interest can include amount/quantity of concentration and exposure time/periods. Now and on-going into the future, it remains imperative that makers of ozone equipment continually search for 'best' safe applications that would cater for both consumer and industrial needs. Copyright © 2017 VBRI Press.

Keywords: Ozone treatment, laboratory/domestic scale, industrial scale, delivery methods/process.

Introduction

The design of innovative materials is among driving measures for (food) industry as quest to enhance societal welfare continually increases **[1]**. Whilst the global demand by consumers for better/improved food products is on the rise, to quantify the quality of food material(s) is imperative prior to application of preservative treatments **[2-4]**. (Non-thermal) food process technologies as widely documented in scientific literature are continually evolving for the eventual benefit of food industry, which include the applications of high-intensity pulsed light, high hydrostatic pressure, pulse electric fields, magnetic fields, ozone treatment, ultrasonication, and ultraviolet-C (UV-C) irradiation on foods **[5-26]**. Importantly, the focus of abovementioned process approaches has been to maintain key properties of food materials **[6-25]**. (Fresh) food materials often harbour microbial contaminants/entities and therefore the continuous need to seek ways to ensure its safety and this is largely the reason why food process industries are in continuous search of safe use of sanitizers. Ozone represents one such alternative environmental friendly sanitizer that initiates positive changes in foods following treatment. In many cases, the uncomplicated set-up of ozone facility, the capacity of ozone to be generated at high concentrations and reactivity, as well as at relatively low costs, are among the benefits associated with ozone treatment. Indeed, ozone application to food materials is widely under investigation and many of such studies suggest that ozone treatment may have great potential application **[3-4, 6-7, 16, 18, 21, 24-32]**. The efficacy of ozone processing in terms of food preservation has been previously discussed, which has highlighted such topics as the effects on key microbial, quality and nutritional parameters. Ozone treatment is described as promising technology that meets up with the United States Food and Drug Administration (FDA) requirement to treat pertinent microorganisms that detriment the safety of food materials **[33]**. Guzel-Seydim *et al.* **[34]** equally reviewed the use of ozone in food industry wherein some characteristic properties of ozone and how the food industry has engaged with ozone were addressed such as food waste plant, food surface hygiene, reuse of waste water, as well as food equipment/plant sanitation. Other areas reported about ozone application for food materials include the fruit, vegetable, dairy **[29, 32, 34, 35, 36]**, fish as well as meat sectors **[30, 37]**. The object of this work was therefore to succinctly review ozone delivery on food materials incorporating some bio-based processes. Starting with the technological progress of ozone highlighting key discoveries, ozone's chemistry and physics is followed with respect to its reactivity, solubility and stability. Adding key settings of ozone treatments and its application on food materials, the properties that substantiate its efficacy via medium properties is herein summarized.

Technological progress of ozone

The technological progress of ozone over the century since its discovery is depicted in **Fig. 1**. In it, notable discoveries majority of which laid a strong foundation to advance its diversity of application are highlighted **[8, 11-15, 34, 38]**. Guzel-Seydim *et al.* **[34]** indicated that the European researcher C.F. Schönbein first discovered ozone in 1839. However, other reports indicate the first report of ozone is attributable to the Dutch philosopher 'van Marum' who first noted a peculiar odor, which emerged from his electrostatic machine. Cruickshank later observed similar phenomena in the electrolytic preparation of O_2 from dilute acids **[38]**. However, the name "ozone", a Greek word meaning: "I smell", as found in memoir of C. F. Schonbein to the *Academy of Munich* where he demonstrated an oxygen substance liberated during electrolysis of acidulated water. W. Odling in 1861, after investigating critically the consistencies in previous discoveries, assigned "O_3" as the simplest formula for ozone. It was later, around 1866-1868, that J. L. Soret demonstrated the constituents of ozone where he showed that the diminution in volume when ozone is absorbed from ozonized oxygen by means of oil of turpentine twice great the increase in volume as ozone reconverted into oxygen on heating, also confirmed by B.C Brodie from 1862-1872, via his communications, namely: '*An experimental enquiry on the action of electricity on gases*' as well as '*On the oxidation and dissociation effected by the alkaline peroxides*' **[39]**. Earlier authors described an apparatus for production of O_3 after electrolytic-purification of O_2 via modified discharge **[38]**, which probably opened the door for the industrial application of ozone. The first commercial use of ozone for municipal water supply treatment was reported in as early years of between 1907 (Nice, France) and 1910 (St. Petersburg, old USSR, now Russia) **[11, 34, 40]**.

As several years passed, depicted here in **Fig. 1**, ozone usage became diverse for example starting with its use in processing bottled water in 1982 at USA following its ratification as 'Generally Recognized As Safe (GRAS)'. In 1997, the expert panel of the Electric Power Research Institute (EPRI) convened and declared ozone as GRAS for food processing. The US Food and Drug Administration (FDA) filed a petition against EPRI's declaration of ozone that was followed soon after by an EPRI petition against the FDA's and this led to a more thorough examination of data and further presentation of evidence to the FDA by EPRI. A final ruling in June 2001 by the FDA approved the use of ozone as a safe antimicrobial agent for food treatment, storage and processing. This amended previous regulations and granted regulatory acceptance of ozone as a food additive **[11, 33-34, 40]**. The diversity of ozone usage includes areas such as preservation of food materials, microbiological reduction, purification and artificial aging of alcoholic beverages, brewery disinfection, odor control and medical therapy, sanitization of drinking water and pools, municipal and industrial waste water control as well as prevention of fouling of cooling towers **[11,17,41-44]**. Further, gaseous ozone has also been used to sanitize packaging materials such as films and trays **[14]**.

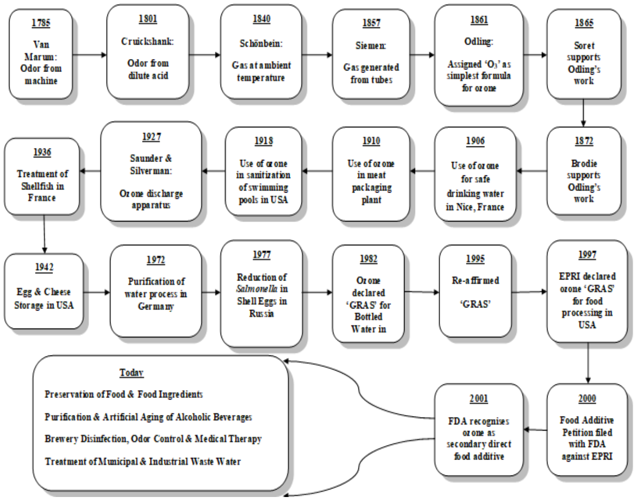

Fig. 1. Technological progress of ozone indicating key inventors, locations and contexts/situations (Adapted from Okpala [23]).

Chemistry and physics of ozone

To discuss the chemistry and physics of ozone, the latter's reactivity, solubility and stability should be considered as essential. Ozone, being formed in stratosphere by action of ultra-violet (*uv*) radiation (<240 nm), occupies 10% of troposphere but little concentration naturally occurring about the Earth's surface **[45]**. As a triatomic molecule, ozone has been classified as an allotrophic modification of oxygen. Typically, ozone remains in gaseous form between room and refrigeration temperatures even though it is in part soluble in water. In addition, ozone has oxidation-reduction potential of 2.07 v, which is probably the strongest oxidant that is of use in food applications compared with others, such as, hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), and chlorine (Cl_2). Density of ozone in gaseous state (2.14g/L, 0°C) is well above that of air (1.28g/L). Other physical attributes of ozone include: molecular weight = 48 g/mol; color = light blue; smell = photocopy machines; boiling point = –111.3°C; solubility in water = 0.64; and LO_3/LH_20 = 190 mg/L **[8, 45-47]**.

Specific to ozone's solubility, a physical parameter that directly determines how stable ozone turns out to be is 'water temperature'. Ozone solubility in liquid is directly proportional to the 'gas exerted' pressure above the liquid, following Henry's law **[8, 48]**. The concentration ratio of ozone solubility in water and gas phase include 0.26 and 1.13, respectively, all dependent on the water temperature **[49,50,51]**. The solubility ratio was measured of 0.16 for distilled water at ~ 22 °C, after which ozone was bubbled through water **[8, 14]**. Whilst different analytical methods to quantify ozone as well as gas flow rate obtained variations, ozone solubility also depends on pH, such that the latter increases in ozone solutions with molecular decomposition **[14]**. Whilst high pH interferes with ozone molecular solubility, ozone stability in water decreases with increase in pH of medium **[52-53]**. In addition, the rapid breakdown of ozone in aqueous solutions with increased pH may also depend on the catalytic activity of hydroxyl ion. However, the latter gets swallowed up during the initiated ozone breakdown process in water, pH value would decline **[8]**. Ozone is considered more stable in gas compared to aqueous phases **[14,54]**. Ozone concentration, presence of radical scavengers, application of turbulence, temperature and presence of organic matter and metal ions – all have the capacity to influence the stability of dissolved ozone (measured in half-life) **[49,55]**. At room temperature, the half-life of ozone in gaseous state equals near 12 h. However, in pure clean water, half-life of ozone can range between 20 to 30 min **[41]**, which can further increase in distilled-water (>85 min at 20°C) compared with the tap water (~ 20 min). Besides, in deionised and tap water of 25°C the half-life of ozone was 12 and 6 min, respectively **[7, 8]**. In addition, the presence of contaminants, such as metal ions together with amount of ozone-demand materials may also affect the stability of ozone in water **[8]**. Not only is the effectiveness of ozone dependent on its decomposition rate as it actively degrades, its half-life is well established to lengthen in gaseous compared with aqueous state(s) **[14, 24]**.

The chemical reactivity of ozone can be considered in three (3) facets, i.e., molecular ozone, reactions with inorganic compounds, and products of decomposition-free radical species **[8]**. The limited/selective nature of molecular ozone reactions can be connected with unsaturated aromatic and aliphatic compounds, with reference to specific functional groups. Typically, ozone undergoes three major reactions, i.e., dipolar, electrophilic and nucleophilic reactions. Dipolar reactions occur by way of cyclo-addition with unsaturated carbon-carbon bonds while electrophilic reaction is associated with aromatic compounds, amines, and sulphides, which have strong density. Nucleophilic reaction is associated with carbons, which carry electron-withdrawing groups **[8, 56]**. Because unstable ozone rapidly breaks down when it comes in contact with air **[19-21,23,47]**, the auto-decomposition of dissolved ozone is considered to follow a first order reaction at low concentrations, which is accompanied by the production of numerous free radical species such as hydroperoxyl (HO_2^-), hydroxyl (^-OH), and superoxide (O_2^-) radicals **[57-58]**. The oxidizing power of ozone has been associated with these free radicals, which is believed to bring about its high reactivity. The hydroxyl radical for example remains among vital transient species and chain propagating radical. With many substrates, the hydroxyl radical reactions occur very fast **[58]**. The chain reaction processes of ozone decomposition can include initiation, propagation and termination steps. Initiators, such as hydroxyl, and hydroperoxide ions, including some cations and organic compounds constitute some capacity to induce the formation of superoxide radicals (O_2^-). The regeneration of superoxide radical from hydroxyl radical takes place in the form of the promotion reaction. Examples of promoters include aryl groups, phosphate species, primary alcohols, and acids such as formic, glyoxylics, and humics. Also, antioxidants from food materials, e.g., ascorbic acid and tocopherol, possess the capacity to scavenge the free radicals and block (some of the chain) reactions **[8,59]**.

Some researchers have showed that halogens, hydroxyl ions, metals, and minerals by catalysing ozone decomposition are capable of increasing the demand of ozone **[57, 60-61]**. For example, both Fe^{3+} and Mn^{4+} can be precipitated out in (drinking) water and can be filtered, which makes such reactions vital for the removal of contaminant metals from drinking water. It should be noted the oxidation-reduction potential values of ozone, chloride, bromide and iodine is reported to be 2.07, 1.49, 1.33 and 0.99 (v), respectively. However, ozone oxidizes slowly with chlorine ions but moderate with bromides yet rapidly with iodide ions, which eventually results in elemental bromine and iodine, respectively **[14, 62]**.

Ozone reaction process

The reaction of ozone takes place via three major pathways, which include direct, indirect and ozonolysis. Specifically, direct oxidation reaction of ozone resulting from action of one atom of oxygen and typical first order high redox reaction. Indirect oxidation reactions involve ozone molecule that decompose to realize free radicals, which then react quickly to oxidize organic and inorganic compounds **[14]**. Ozonolysis – well known organic reaction that can achieve a peak owed to the presence of unsaturated bonds of alkenes, alkynes, etc. does so by fixing of complete molecules on double-linked atoms to produce two simple molecules to bring about different properties and molecular characteristics **[11]**. The major steps involved in oxygen splitting up to the formation of ozone can be seen in **Fig. 2**. Clearly, the generation of ozone requires that the di-atomic O_2 molecule must inevitably be split **[8,11, 14, 34, 63]**. Ventilation of electrical charges at high voltage in air or pure oxygen can also bring about the production of ozone. Specifically, the free oxygen molecules would collide with each other to yield ozone and high amount of energy is required to make this reaction possible. To achieve similar outcome(s), the use of ultraviolet (*uv*) radiation can allow for initiation reaction(s) and subsequently, free radical oxygen can then help to form the ozone **[11, 34]**. "*Ozonation*" is a term used when ozone is pumped into liquid/water medium (in a washing tank) at a specified flow rate (measured in g/min) and time period (measured in min) **[12]**. Ozone may also dissolve in deionised water with the help of an inverse mixer, which can be typical of a dissolution tank **[14]**. At the point of contact with food material(s)/substance(s) the physical properties of ozone play crucial role toward both constituent and structure interaction(s) **[11,34]**.

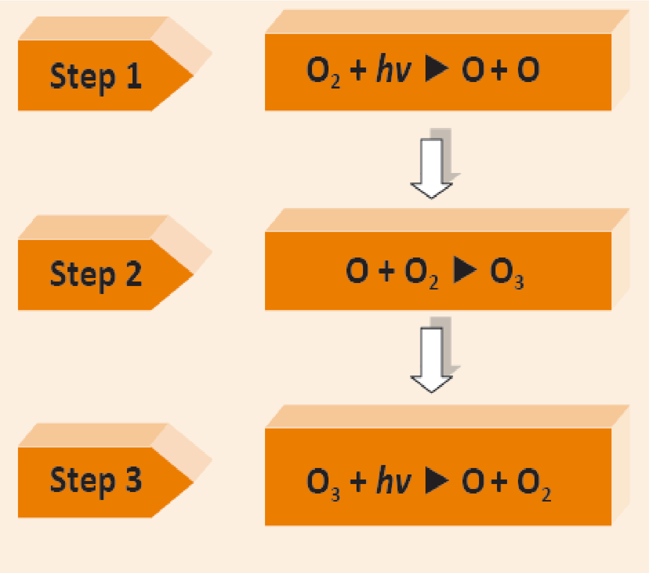

Fig. 2. O_2 split to form unstable ozone (Adapted from Okpala [63])

Ozone in its molecular form is unstable and degrades, interacts with products or microorganisms resulting to its destruction **[14, 23]**. Ozone combined with organic compounds yields rather/relatively slow but direct reaction **[64]**. Despite the combination of ozone with other technologies, improved oxidation processes and techniques has to be designed in such a way to promote the formation of hydroxyl free radicals, which can lead to improved sanitization outcome(s) above that of ozone alone **[8]**. Whereas the reaction with ozone has been proved to be quite slow, the presence of hydroperoxide ion can be accounting for its high chemical reactivity **[8, 65]**. It should be noted that combining ozone with H_2O_2 (aqueous solution) yields hydroxyl radicals, which is achievable by adding sufficient amount of H_2O_2 to the H_2O undergoing treatment, and thereafter, passing such solution(s) through the ozone-contacting instrument **[41]**.

Ozone discharge methods/settings

Ozone discharge operates by three major methods namely: a) corona; b) ultra-violet (*uv*) lamp; and c) electrochemical. For the corona discharge instrument, the method / activity is dependent on sufficient build-up of kinetic energy between low-/high-tension electrodes. For the ultra-violet lamp method, oxygen is converted to ozone by the ultra-violet lamp but produces ozone at much lower intensity when compared to corona discharge method. In the electrochemical method however, an electrical current is applied between anode and cathode located in an electrolytic solution, which contains a highly electronegative anion-based solution with water. Both oxygen and ozone gather at the anode end. Benefits of three major methods of ozone treatment delivery has been summarised in **Table 1**. These (above-mentioned) three methods have been used to discharge ozone on food materials/substances as well as other surfaces **[11,13,28,33]**.

Table 1. Summary of benefits of 3 main methods of ozone treatment delivery.

Corona discharge	Ultra-violet light	Electrochemical method
1. Longevity of equipment with minimal maintenance needs 2. Odour removal from organic material is rapid 3. Most recommended for water based applications 4. Releases ozone in high concentrations	1. Reduced by-products compared with corona discharge 2. Minimal humidity influence on output 3. Lower cost relative to corona discharge 4. Uncomplicated set-up	1. Ozone can be generated through water 2. Ozone can be generated at high concentrations 3. Equipment size is smaller relative to corona discharge and ultra-violet light 4. No need for feed gas preparation 5. Use of low DC current

Adapted from Blogoslawski & Stewart [**28**], Cullen *et al.* [**33**], Goncalves [**11**], O'Donnell *et al.* [**14**] and Mahapatra *et al.* [**13**]

Ozone generators can be of either laboratory or industrial settings. Alothman *et al.* [**6**] employed laboratory-scale ozone generator model SA – 100P (Ishimori – Seisakusho Co. Ltd., Kure, Japan) on fresh fruits (honey pineapple, banana and guava). Here, corona discharge applied reactor cells in, which diatomic oxygen is forced through a high-voltage electric field produced between conductive and dielectric surfaces, to generate the ozone. Rong *et al.* **[66]** employed laboratory scale ozone treatment Model OL80 (Ozone Services, Canada) with an electronic ozone destructor was used by other workers on orange juice. Similarly, Patil *et al.* **[67]** discharged ozone using a corona discharge generator. Rong, Qi, Yin *et al.* **[30]** also generated ozonated water by an electrochemical process using an ozone generator (GW-100, ChaoTuo, China). In this endeavour, the ozone concentration was measured using a modified iodometric method.

Scheme of laboratory scale set-up of semi-batch type ozone generator with corona discharge instrument is presented in **Fig. 3 [6, 11, 34]**. The generator is connected to an oxygen cylinder via a valve-controlled flow rate apparatus and a bubble-type flow meter. When power is turned on diatomic oxygen becomes forced through an electric field of high voltage produced between the conductive and dielectric surfaces. Food samples are placed typically in the rotating vessel with an operating speed up to 90 rpm. This rotating vessel is connected to the ozone generator. The valves remain open and excess ozone becomes trapped (in 4% potassium iodide [KI]) during the exposure period when the generator is switched off and the two valves closed, further exposure of food samples to the ozone gas occurs in the closed rotating vessel **[6]**. The rotating vessel functions to enable an even, homogenous interaction between food materials and discharged ozone. Thus, the rotation speed require effective control in order to (i) ensure a smooth turning around of intended food material(s); and (ii) prevent physical damage of food material(s) during the turning process **[6, 11-12, 23, 34, 40]**.

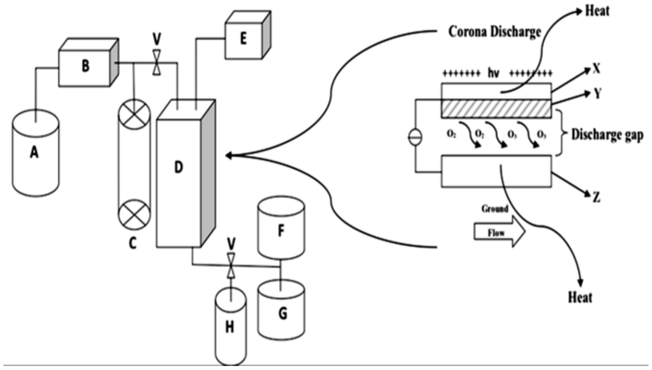

Fig. 3. Schematic diagram for set-up of ozone generator highlighting corona discharge instrument; Key: A= Oxygen Cylinder; B = Flow Rate Controller; C = Bubble Type Flow Meter; D = Ozone Generator; E = Transformer; F&G = Excess Ozone Traps (4% KI); H = Rotating Vessel (90 rpm); V = Valve; X = High Tension Electrode; Y = Dielectric; Z = Low Tension Electrode (Adapted from Okpala [**23**]).

Alothman *et al.* **[6]** employed laboratory scale semi-batch type ozone generator. In their report, following ozone treatment, there was a need to store excess ozone. This was carried out with help of 4% KI (potassium iodide) solution which ozone was passed through in combination with H_2SO_4 to prevent ozone gas from being released into the environment. The reaction between ozone and KI occurs as described in Eqn (1):

$$O_3 + 2KI + H_2O \rightarrow O_2 + I_2 + 2KOH \quad (1)$$

The amount of iodine (I_2) released was determined by standard titration using 0.2 M $Na_2S_2O_3$ solution and starch solution as indicated in Eqn (2):

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI \quad (2)$$

Thus, 1 mol $Na_2S_2O_3$ consumed equal 0.5 mol of ozone. A calibration curve was determined by plotting the amount of O_3 generated against the ozone generation time, which brought about a linear relationship defined by Eqn (3):

$$A\ (\text{mmol}) = 0.559\ t\ (\text{min}) + 0.297 \quad (3)$$

The amount of O_3 involved in the reaction was calculated by subtracting the non-reacted amount from amount generated. Determinations should be repeated to ensure experimental validity. Ozone treatment is best performed in a fume cupboard for purposes of safety. Food materials are then removed from reaction vessel for analysis **[6]**. Patil *et al.* **[10]** reported laboratory ozone generation apparatus using corona discharge mechanism as showed in **Fig. 4**, very different set-up compared to that of Alothman *et al.* **[6]**.

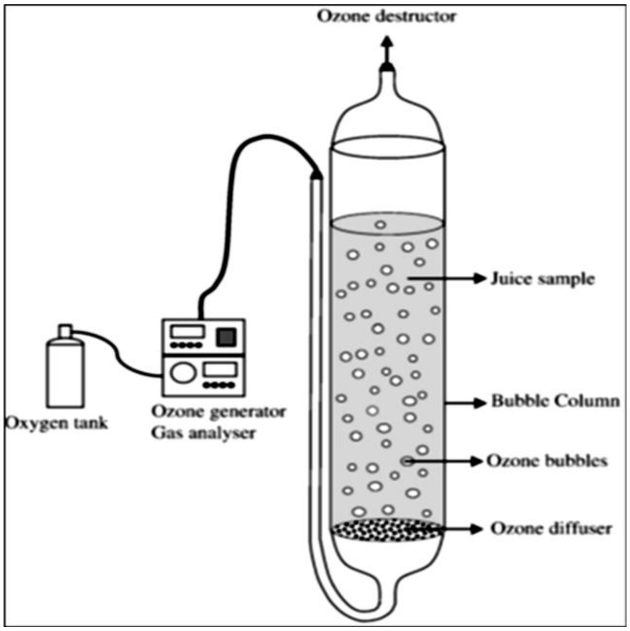

Fig. 4. Scheme of ozone treatment system with an electronic ozone destructor (Adapted from: Patil *et al.* [**10**]).

Here, ozone was generated and pumped into 100mL glass bubble column while the pure oxygen was supplied using oxygen cylinder (Air Products Ltd., Dublin, Ireland). The oxygen flow regulator would control flow rate optimum at 0.12 $Lmin^{-1}$ whereas concentration would range between 75 and 78µg mL^{-1}. Ozone analyzer (OL80A/DLS, ozone services, Burton, Canada) was used to do the readings of ozone concentration. Ozone destroyer unit was incorporated to cater for the excess ozone discharge that might perhaps take place. Also, as the excess foaming could be anticipated, a 20µL sterile antifoaming agent (Antifoam B emulsion, Sigma Aldrich, Ireland Ltd.) was adapted **[10]**. In this laboratory context, the author to best of knowledge seems to be the first to test a commercial available domestic facility (‘O_3 Fresh’ Model SXQ8-BA-W, Ovoproducts, Leicestershire, UK) that safely discharged ozone on food material. The domestic facility was built/manufactured with a fixed ozone concentration discharge of 100 mg/h into water, a wash and spin capacity of 4 L, three ozone exposure levels/wash cycles of 1, 3 and 5 min, and maximum loading capacity of 1.5 kg. In author’s published reports, the ozone exposure/wash cycle times were used to define the ozone treatments **[19-21, 24-26]**.

The corona discharge has evolved starting from domestic up to industrial scale/settings. Notably, the most common mechanism of ozone delivery is the corona discharge method, which has attained industrial scale **[14]**. Typically, of the two electrodes found in the corona discharge, one is the high-tension electrode while the other is the low tension or ground electrode. These electrodes are neatly demarcated by a ceramic dielectric medium followed by a narrow discharge gap. Electrons build-up with a sufficient kinetic energy (6 – 7 *ev*) to cause dissociation of the oxygen molecule and a specific fraction of these collide to form ozone **[11, 14]**. If air is passed through the generator as a feed gas, 1 – 4% ozone can be produced, while use of pure oxygen permits yield up to 6 – 14% ozone. Ozone concentration cannot be increased especially beyond the point where the rates of formation and destruction show equal. Ozone gas cannot be stored due to its spontaneous degradation into oxygen atoms **[11, 34]**. Hence, excess ozone is then captured using 4% KI (**Fig. 3**) **[23]**. In addition, many different materials and of various configurations have been used as dielectrics **[14]**.

Moreover, another commercial/industrial use of ozone was cooling tower treatment system purposed for water treatment, where ozone treatment dramatically reduced the continuous flow of steam and/or water under high differential pressure to make it environmental-friendly and cost-effective design methodology for cooling water systems **[27]**. Another ozone industrial setting can be found in water disinfection processes in which cooling tower is a key aspect. However, the cooling tower water needs a treatment that limits microbial deposits. The key reason is presence of microbial deposits cause decline in cooling efficiency of water heat transfer **[14]**. Water-cooling system possess heat rejection within a heat-exchanger network. The quality of cooling as well as make-up of water is considered for optimal operation conditions. Thus, introducing ozone treatment into such a scheme can disinfect water optimally. A scheme of ozone treatment of cooling tower water can be seen in **Fig. 5** **[27]**. The main components include computer system, ozone generator, contactor, cooling tower, make-up as well as blow-down valves for water tower the heat exchanger. Ambient air is harnessed and compressed, dried and ionized within the generator to eventually produce the ozone. The circulating water present in the tower receives the ozone. Specifically, ozone functions to inactivate any infectious bacteria, algae and viruses that may be present. Therefore, the integration of ozone treatment into the cooling tower possesses potential to elevate the latter’s concentration cycle. When the ‘blow down’ valve is reduced, the system function can be considered as environmental-friendly **[27]**.

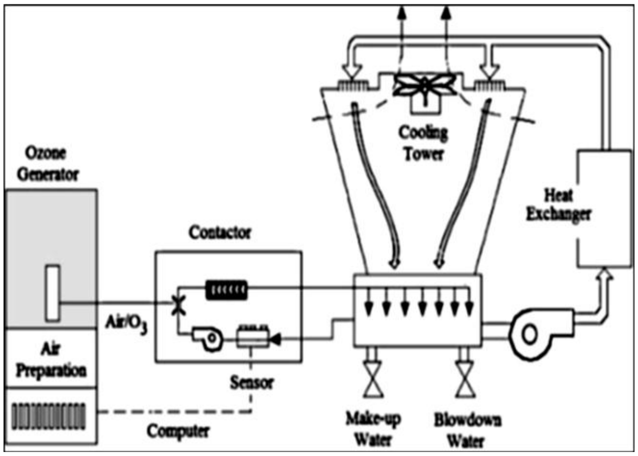

Fig. 5. Ozone treatment of cooling tower water (Adapted from: Ataei *et al.* [**27**])

To consider the manner/type of design of ozone reactor / contact vessel is essential if an effective ozonation process is to be attained. An example of reactor designs entail deep u-tube reactors, fine bubble diffusers, injectors, packed columns, static mixers, spray contact chambers and turbine contactors. In addition, there are some important factors that requires key attention/ consideration when choosing a reactor, which include (a) ozone transfer efficiency; (b) leak-free design and construction; and (c) construction with ozone resistant materials. Instead, the application of ozone can be continuous, either as series of (daily) treatments or as batch/single (daily) treatment **[40]**. Pascual *et al.* **[67]** had reported about the use of ozone in food industries to reduce the environmental impact for both cleaning and disinfection activities. These authors also identified with industries such as wineries where such ozone systems had successfully achieved sanitization of system installations including (well) water treatment, where it performed functions such as removal of microorganisms, organic matter and replacement of SO_2 in the barrel storage **[67]**. The efforts of ozone combined with other preservative substances have been aimed to achieve commercial scale. Examples include the combination of ozone and corresponding rates of water exchange in view to detect water quality (and rainbow trout performance) in recirculating aquaculture systems **[68]**. Another example includes the combination of ozone and ultrasound as an alternative processes in the treatment of fermented coffee **[69]**. Another example also includes the utilizing ozone and chlorination in vegetable washing system (FTNON equipment produced by Noord-Oost, The Netherlands) **[42]**. Greene, Vergano *et al.* **[70]** had previously applied ozone treatments of 0.5 ppm discharged on water for 36 h at 25 to 33°C under fluid food processing setting(s) specifically on seven gaskets (1.5 in or 36.1 mm diameter), which was made from seven different substances namely: Buna N, white Buna N, EPDM (ethylene propylene diene monomer), polyethylene, silicone rubber, PTFE (polytetrafluoroethylene or Teflon) and steam-resistant Viton.). It is from these activitied that the following observations were established: (a) Tensile strength has not been affected significantly in ozonated water; (b) Only PTFE gasket that had been treated with ozone showed significant differences ($p<0.05$); (c) Bleaching effect on black gaskets as affected by both treatments seemed very obvious; (d) Tensile strength of EPDM and Viton had declined during ozone application but not that significantly relative to chlorine treatment.

Ozone treatment of food materials

The applications of ozone on food material(s)/product(s) by purpose/ types are summarized in **Table 2**. Evidently, the nature of ozone on foods, i.e., gas and aqueous, obtain dominantly the decontamination/shelf-life extension of food and food packaging material(s)/product(s). To support abovementioned, the applications of ozone on food processing facilities are summarized in **Table 3**. Generally, apart from either the aqueous or gaseous form of application, combination of ozone with other chemicals has shown to effectively reduce the microbial load/numbers.

Hence, the application of ozone can increase the quality shelf of food materials **[6, 11,13,23, 28,34,63, 71,72, 73]**. Ozonated water has other useful role(s) in the food industry for example, the sanitation given its antimicrobial effect. Cumulatively, ozone's capacity to disinfect food materials and processing surfaces towards achieving high standards of food hygiene cannot be underestimated although in some cases, there have been minimum up to no statistical effects/responses **[16, 34]**. Guzel-Seydim *et al.* **[63]** studied the efficacy of ozone to reduce bacterial populations of food material(s)/product(s). Khadre, Yousef *et al.* **[74]** reviewed the microbiological aspects of ozone applications on foods and dealt with factors that alter its antimicrobial efficacy as well as reactivity, which include temperature, pH value, and ozone-consuming compounds. Essentially, treatment temperature was considered pertinent to differently influence both reactivity and solubility of ozone. Many researchers **[6,19-22,24-26,33-34,72,75]** have demonstrated ozone's capacity to induce specific characteristic effects on food material(s). Guzel-Seydim *et al.* **[34]** had reviewed the use of ozone for food industry and highlighted some treatment applications that would potentially lower both biological oxygen demand (BOD) and chemical oxygen demand (COD) in food waste plant. Also, the use of ozone to treat food material(s)/product(s) have resulted in a number of patents **[34].**

Table 2: Summary of ozone applications on food materials/products by purpose/type(s).

Food Material/Product	Type of Ozone Treatment	Purpose of Application	References
Grains, wheat flour (powder or whole)	Gas / Aqueous	Decontamination	[14]
Meat, beef/beef brisket fat, and fish	Aqueous	Decontamination Extension of shelf-life and quality improvement	[14, 23-26]
Poultry meat and carcasses	Aqueous	Decontamination	[14]
Eggs	Gas + vacuum + heat	Hyperpasteurization process, Decontamination	[47-48]
Apples, ingredients for fruit juices; blackberries; strawberries and grapes	Gas / Aqueous	Decontamination; Extension of shelf-life and quality improvement	[14, 47-48]
Lettuce, broccoli, florets, and cauliflower,	Gas / Aqueous	Decontamination; Extension of shelf-life and quality improvement	[14]
Various spices used to prepare *Kimchi*	Gas / Aqueous	Improving fermentation process	[7,8, 47-48]

Table 3. Summary of some food process facility/system and corresponding ozone application(s) with attained microbial reduction.

Food Process Facility/System	Ozone application / combination	Microbial reduction	References
Packaging films	Ozone + H_2O_2	N/A	[14]
Confectionary plant	Ozone + H_2O_2	Up to 99% microbial plate count reduction	[14]
Hatchery equipment	Ozone + H_2O_2	Up to 99% microbial plate count reduction	[14]
Barrel/Tank cleaning and sanitation, and general purpose; Clean-In-Place (CIP) Operation	Ozone (Gas/Aqueous)	Up to 95% microbial plate count reduction	[7-8]
Food processing equipment surfaces	Ozone (aqueous)	Up to 95% microbial plate count reduction	[14]
Reconditioning poultry chiller water	Ozone (Gas)	N/A	[7-8, 14]
Re-circulating aquaculture system Disinfection of water supplies and industrial effluents	Ozone (Aqueous)	N/A	[14]
Sanitizer for dairy and food plants	Ozone (Aqueous)	<5 log reduction	[14]
Domestic ozone facility	Ozone (Aqueous)	<3 log reduction	[19-24]
Selected food borne pathogens	Ozone + pulse electric fields (PEF)	< 4 log reduction	[14]

N/A = Not Available

Ozone efficacy based on medium properties

To keep food materials and decontaminate surfaces of food-related facilities/packaging materials are among areas where both gaseous and aqueous forms of ozone are applicable. The efficacy of ozone treatment for food materials is considerably affected by properties of treatment medium. Some properties of medium pertinent to ozone efficacy include temperature, relative humidity (RH), and ozone demand **[8]**. A consensus between treatment temperatures vis-à-vis ozone efficacy seems not yet completely arrived at. For example, ozone was more effective against microorganisms when applied at <10 °C. Inactivation kinetics of microorganisms has been more effective at temperatures starting from 5 down to 1 °C. The rate of microbial disinfection by ozone are likely not show strong effects when temperatures go up to 30 °C

[76-79]. Differences in temperatures associated with ozone properties have been such that any temperature increases are considered to support the reactivity of residual ozone, whereas temperature decreases in aqueous medium has been considered to increase both ozone solubility and stability. Experimental set-up may also bring about variation in the relative contribution of such factors as reactivity, solubility and stability **[8]**. However, for ozone gas to cause inactivation of microorganisms, a high relative humidity (RH) is obligatory. Hydrated microorganisms are more susceptible to ozone under humid conditions (RH range of 90-95%), making microbial inactivation by ozone potentially optimum. The decomposition of ozone is more rapid at high RH compared to low RH **[8, 48, 79]**. Application of 200ppm gaseous ozone would decrease microbial load in anti-caking agent with water activity (a_w) of ≤ 0.84. If anti-caking agent contain 0.96 (a_w) and subject to 150 ppm gaseous ozone, a decline in microbial load by over 2 log units can equally take place. The 300 ppm of gaseous ozone can contribute to decrease the microbial load to an undetectable level. Also, increasing water activity (a_w) of anti-caking agent(s) resembling bio/food materials that naturally contain high a_w from 0.85 to 0.95 can allow the application of ozone to potentially decrease microbial load **[8]**. Whilst the presence of organic materials can reduce the effectiveness of ozone, there is also the need to ascertain the fungicidal effect in relation to ozone coefficient of diffusion into processed materials **[14]**. On the other hand, residual ozone refers to detectable concentration in ozone treatment medium after it has been applied to target substance(s). The effectiveness of ozone against microorganisms depends on amount applied and more importantly, the residual ozone in medium **[8, 47]**. Under certain conditions, the instability of ozone as well as presence of ozone-consuming materials put together can influence the level of residual ozone available in the medium **[67]**. In a previous study about eviscerated carcass subject to ozonated chilled water at 1.7 and 4.4 °C, the ozone generator employed was able to produce up to 20 gL^{-1} to yield Oxidation Reduction Potential (ORP) of approximate 270 mV value. After ozonation, whilst higher antibacterial effect was found, ozone concentration would gradually decrease **[80]**. Bubbling ozone water has also been applied to contaminated food materials, which appeared with no apparent effects **[81]**. Low ozone concentration may well be ineffective to disinfect food material(s)/product(s) in the presence of extraneous organic matter **[8]**. There could also be some hindrances to the antibacterial effects of ozone such as the presence of impurities, such as formic and glyoxylic acids, humic substances as well as irritate ozone decomposition **[8,47,61]**. In addition, bactericidal efficacy of ozone could be reduced in some solution for e.g., Ringer solution, which could hinder its capacity to progress microbial inactivation **[14]**. Moreover, food material(s)/substance(s) can equally release antioxidants that subsequently, may generate some ozone demand by way of scavenging radicals, which are formed during ozone decomposition **[8, 14, 24-26, 82]**.

Conclusion

A succinct synopsis about ozone delivery on food materials incorporating bio-based processes has been performed. It started with how ozone evolved technologically with key discoveries over the years. It also examined ozone's chemistry and physics especially how it presents itself in various states adding the delivery mechanism and typical schemes. Nonetheless, there are issues like ozone toxicity that may still carry some concerns. Thus, monitoring of workers engaged in any activity where ozone is utilized must never be taken for granted. The quick decomposition rate of ozone structure resulting in no residue remains its strong advantage. Now and on-going into the future, it remains imperative that makers of ozone equipment continue to search for 'best' safe applications that would cater for both consumer and industrial needs.

Acknowledgements

Author acknowledges financial support from Educare and Skills Training Network, Middlesex, UK.

Conflict of Interest

Author declares no conflict of interest.

References

1. Tiwari, A. *Adv. Mater. Lett.* **2016**, *7*, 1.
   DOI: 10.5185/amlett.2016.1001
2. Okpala, C.O.R.; Choo, W-S.; Dykes, G.A. *LWT Food Sci Technol.* **2014**, *55*, 110.
   DOI: 10.1016/j.lwt.2013.07.020
3. Okpala, C.O.R. *Food Nutr Sci.* **2015**, 6(10), 906-922.
   DOI: 10.4236/fns.2015.610095
4. Okpala, C.O.R. *Nigerian Food J.* **2015**, 33(2), 74.
5. Alothman, M.; Bhat, R.; Karim, A. A. *Trends Food Sci Technol.* **2009**, *20*, 201.
   DOI: 10.1016/j.tifs.2009.02.003
6. Alothman, M.; Kaur, B.; Fazilah, A.; Bhat, R.; Karim, A. A. *Innov Food Sci Emerg Technol.* **2010**, *11*, 666.
   DOI: 10.1016/j.ifset.2010.08.008
7. Okpala, C.O.R. *Iranian J Fish Sci.* **2017**, 16(2), 625.
8. Kim, J. G.; Yousef, A. E.; Khadre, M. A. *Adv Food Nutr Res.* **2003**, *45*, 167.
   DOI: 10.1016/S1043-4526(03)45005-5
9. Okpala, C. O. R.; Piggott, J. R.; Schaschke, C. J. *Afr J Biotechnol.* **2009**, *8*, 7391.
   ISSN: 1684-5315
10. Patil, S.; Bourke, P.; Frias, J. M.; Tiwari, B. K.; Cullen, P. J. *Innov Food Sci Emerg Technol.* **2009**, *10*, 551.
    DOI: 10.1016/j.ifset.2009.05.011
11. Goncalves, A. A. *Brazilian Arch Biol Technol.* **2009**, *52*, 1527.
    DOI: 10.1590/S1516-89132009000600025
12. Jiang, S. T.; Ho, M. L.; Jiang, S. H.; Lo, L.; Chen, H. C. *J Food Sci.* **1998**, *63*, 652.
    DOI: 10.1111/j.1365-2621.1998.tb15805.x
13. Mahapatra, A. K.; Muthukumarappan, K.; Julson, J. L. *Crit Rev Food Sci Nutr.* **2005**, *45*, 447.
    DOI: 10.1080/10408390591034454

14. O'Donnell, C.; Tiwari, B.K.; Cullen, P.J.; Rice, R.G. (Eds.). *Ozone in food processing.* United Kingdom: Wiley-Blackwell, **2012**, pp. 312.
    ISBN: 978-1444334425
15. Okpala, C. O. R.; Piggott, J. R.; Schaschke, C. J. *Innov Food Sci Emerg Technol.* **2010**, *11*, 61.
    DOI: 10.1016/j.ifset.2009.10.003
16. Skog, L. J.; Chu, C. L. *Canadian J Plant Sci.* **2001**, *81*, 773.
    DOI: 10.4141/P00-110
17. Strittmatter, R. J.; Johnson, D. A. *ASHRAE* **1996**, *38*, 27.
18. Xu, L. J. *Food Technol.* **1999**, *53*, 58.
19. Okpala, C.O.R. *Curr Nutr Food Sci.* **2014**, *10*, 218.
    DOI: 10.2174/1573401310666140306003557
20. Okpala, C.O.R. *LWT Food Sci Technol* **2014**, *57*, 538.
    DOI: 10.1016/j.lwt.2014.02.007
21. Okpala, C.O.R. *J Verbraucerschutz und Lebensmittelsicherheit* **2015**, *10*, 49.
    DOI: 10.1007/s00003-014-0904-x
22. Okpala, C.O.R. *Lipid Technol.* (May/June) **2016**, *28*, 93.
    DOI: 10.1002/lite.201600026
23. Okpala, C.O.R. *Chem Eng Trans* **2017,** *57*, 1813.
    DOI: 10.3303/CET1757303
24. Okpala, C.O.R.; Bono, G.; Geraci, M.L.; Sardo, G.; Vitale, S.; Schaschke, C. J. *Food Biosci.* **2016**, *16*, 5.
    DOI: 10.1016/j.fbio.2016.07.005
25. Okpala, C.O.R.; Bono, G.; Falsone, F.; Cani, M.V.; Scannella, D.; DiMaio, F. *Procedia Food Sci.* **2016**, *7*, 47. **DOI**: 10.1016/j.profoo.2016.02.084
26. Okpala, C.O.R.; Bono, G.; Cannizzaro, L.; Jereb, P. *Eur J Lipid Sci Technol.* **2016**, 118(12), 1942
    DOI: 10.1002/ejlt.201500347
27. Ataei, A.; Gharaie, M.; Parand, R.; Panjeshahi, E. *Int J Energy Res.* **2010**, *34*, 494.
    DOI: 10.1002/er.1568
28. Blogoslawski, W.; Stewart, M. *Ozone: Sci Eng.* **2011**, *33*, 368.
    DOI: 10.1080/01919512.2011.602006
29. Patil, S.; Torres, B.; Tiwari, B. K.; Wijngaard, H. H.; Bourke, P.; Cullen, P. J.; O'Donnell, C. P.; Valdramidis, V. P. *J Food Sci.* **2010**, *75*, M437-M443
    DOI: 10.1111/j.1750-3841.2010.01750.x.
30. Rong, C.; Qi, L.; Yin, B. Z.; Zhu, L. L. *Innov Food Sci Emerg Technol.* **2010**, *11*, 108
    DOI: 10.1016/j.ifset.2009.08.006
31. Tiwari, B. K.; Brennan, C. S.; Curran, T.; Gallagher, E.; Cullen, P. J.; Donnell, C. P. *J Cereal Sci.* **2010**, *51*, 248.
    DOI: 10.1016/j.jcs.2010.01.007
32. Tiwari, B. K.; O'Donnell, C. P.; Muthukumarappan, K.; Cullen, P. J. *Innov Food Sci Emerg Technol.* **2009**, *10*, 70.
    DOI: 10.1016/j.ifset.2008.08.002
33. Cullen, P. J.; Valdramidis, V. P.; Tiwari, B. K.; Patil, S.; Bourke, P.; O'Donnell, C. P. *Ozone - Sci Eng.* **2010**, *32*, 166.
    DOI: 10.1080/01919511003785361
34. Guzel-Seydim, Z. B.; Greene, A. K.; Seydim, A. C. *Lebensmittel-Wissenschaft Und-Technologie-Food Sci Technol.* **2004**, *37*, 453.
    DOI: 10.1016/j.lwt.2003.10.014
35. McLoughlin, G. *Water Technol.* **2000**, *23*, 53.
36. An, J. S.; Zhang, M.; Lu, Q. R. *J Food Eng.* **2007**, *78*, 340.
    DOI: 10.1016/j.jfoodeng.2005.10.001
37. Coll Cardenas, F.; Andres, S.; Giannuzzi, L.; Zaritzky, N. *Food Cont.* **2011,** *22*, 1442.
    DOI: 10.1016/j.foodcont.2011.03.006
38. Saunders, P. C.; Silverman, A. *Ind Eng Chem.* **1927**, *19*, 1316.
    DOI: 10.1021/ie50216a008
39. Burns, D. T. *Fresenius' J Anal Chem.* **1997**, 357, 178.
    DOI: 10.1007/s002160050133
40. Goncalves, A. A.; Gagnon, G. A. *Ozone-Sci Eng* **2011**, 33(5), 345-367.
    DOI: 10.1080/01919512.2011.604595.
41. Graham, D. M. *Food Technol.* **1997**, 51, 72-75.
42. Sopher, C. D.; Battles, G. T.; Johnson, D. *Ozone-Sci Eng.* **2009,** 31(4), 309-315.
    DOI: 10.1080/01919510903042105.
43. Sugita, H.; Asai, T.; Hayashi, K.; Mitsuya, T.; Amanuma, K.; Maruyama, C.; Deguchi, Y. *Applied Environ Microbiol* **1992**, *58*, 4072.
44. Videla, H. A.; Viera, M. R.; Guiamet, P. S.; Alais, J. C. S. *Materials Performance* **1995**, *34*, 40.
45. Wojtowicz, J. A. Ozone. In R. E. Kirk & D. E. Othmer (Eds.), *Encyclopedia of Chemical Technology* **1996** (4th ed., Vol. 17, pp. 953-994). New York: Wiley-Interscience.
46. Brady, J. E.; Humiston, G. E. *General Chemistry Principles and Structure* **1978** (2nd ed.). New York: John Wiley & Sons.
47. Kim, J. G.; Yousef, A. E.; Dave, S. *J Food Prot.* **1999**, *62*, 1071.
48. Kim, J. G.; Yousef, A. E. *J Food Sci* **2000**, 65, 521.
    DOI: 10.1111/j.1365-2621.2000.tb16040.x
49. Horvath, M.; Bilitzky, L.; Huttner, J. *Ozone.* **1985,** New York: Elsevier.
50. Meddows-Taylor, J. *J Inst Water Eng* **1947**, *1*, 187.
51. Watson, G. *Refrigeration Eng* **1943**, *46*, 103.
52. Ouederni, A.; Mora, J. C.; Bes, R. S. *Ozone: Sci Eng* **1987**, *9*, 1.
    DOI: 10.1080/01919518708552384
53. Roth, J. A.; Sullivan, D. E. *Ind Eng Chem Fundamentals* **1981**, *20*, 137.
    DOI: 10.1021/i100002a004
54. Tomiyasu, H.; Fukutomi, H.; Gordon, G. *Inorganic Chemistry* **1985**, *24*, 2962.
    DOI: 10.1021/ic00213a018.
55. Shechter, H. *Water Research* **1973**, *7*, 729.
    DOI: 10.1016/0043-1354(73)90089-4
56. Bailey, P. S. *Ozonation in Organic Chemistry*, **1978**, New York: Academic Press Inc.
57. Adler, M. G.; Hill, G. R. *J Am Chem Soc.* **1950**, *72*, 1884.
    DOI: 10.1021/ja01161a007.
58. Hoigne, J.; Bader, H. *Science* **1975**, *190*, 782.
    DOI: 10.1126/science.190.4216.782
59. Hoigne, J.; Bader, H. *Water Res.* **1985**, *19*, 993.
    DOI: 10.1016/0043-1354(85)90368-9
60. Hewes, C. G.; Davison, R. R. *Am Inst Chem Eng Symp Series* **1973**, *69*, 71.
61. Hoigne, J.; Bader, H. *Water Res.* **1976**, *10*, 377.
    DOI: 10.1016/0043-1354(76)90055-5.
62. Haag, W. R.; Hoigne, J. *Environ Sci Technol.* **1983**, *17*, 261. **DOI**: 10.1021/es00111a004
63. Okpala, C.O.R. *Inform* **2017**, *28(2)*, 28.
    DOI: 10.21748/inform.02.2017.28
64. Hoigne, J.; Bader, H. *Ozone: Sci Eng.* **1979**, *1*, 73.
    DOI: 10.1080/01919517908550834
65. Taube, H.; Bray, W. C. *J Am Chem Soc.* **1940**, *62*, 3357.
    DOI: 10.1021/ja01869a027
66. Chawla, A.; Bell, J.W.; Janes, M.E. *J Aquat Food Product Technol.* **2007**, *16*, 41.
    DOI: 10.1300/J030v16n02_05

67. Pascual, A.; Llorca, I.; Canut, A. *Trends Food Sci Technol*. **2007**, *18*, S29-S35.
    DOI: 10.1016/j.tifs.2006.10.006
68. Davidson, J.; Good, C.; Welsh, C.; Summerfelt, S. *Aquat Eng*. **2011**, 44(3), 80.
    DOI: 10.1016/j.aquaeng.2011.04.001
69. do Nascimento, L. C.; Lima, L. C. D.; Picolli, R. H.; *et al*. *Ciencia E Tecnologia De Alimentos* **2008**, *28*, 282.
    DOI: 10.1590/S0101-20612008000200004.
70. Greene, A. K.; Vergano, P. J.; Few, B. K.; Serafini, J. C. *J Food Eng*. **1994**, 21(4), 439.
    DOI: 10.1016/0260-8774(94)90065-5
71. Crowe, K. M.; Bushway, A.; Davis-Dentici, K. *LWT - Food Sci Technol*. **2012**, *47*, 213.
    DOI: 10.1016/j.lwt.2011.12.026
72. Beltran, D.; Selma, M. V.; Marin, A.; Gil, M. I. *J Agri Food Chem*. **2005**, *53*, 5654.
    DOI: 10.1021/jf050359c
73. Restaino, L.; Frampton, E. W.; Hemphill, J. B.; Palnikar, P. *Appl Environ Microbiol*. **1995**, *61*, 3471.
74. Khadre, M. A.; Yousef, A. E.; Kim, J. G. *J Food Sci*. **2001**, *66*, 1242.
    DOI: 10.1111/j.1365-2621.2001.tb15196.x
75. Beuchat, L. R. *J Food Protect*. **1995**, *59*, 204.
76. Herbold, K.; Flehmig, B.; Botzenhart, K. *Appl Environ Microbiol*. **1989**, *55*, 2949.
77. Katzenelson, E.; Kletter, B.; Shuval, H. I. *J Am Water Works Assoc*. **1974**, *66*, 725.
    DOI: www.jstor.org/stable/41267651
78. Kinman, R. N. *Crit Rev Environ Cont*. **1975**, *5*, 141.
    DOI: 10.1080/10643387509381625
79. Kuprianoff, J. *Z. Kalentechnik* **1953**, *10*, 1.
80. Izat, A. L.; Adams, M.; Colberg, M.; Reiber, M. *Arkansas Farm Research* **1990**, *39*, 9.
81. Achen, M.; Yousef, A. E. *J Food Sci*. **2001**, *66*, 1380.
    DOI: 10.1111/j.1365-2621.2001.tb15218.x
82. Yang, P. P. W.; Chen, T. C. *J Food Sci*. **1979**, *44*, 501.
    DOI: 10.1111/j.1365-2621.1979.tb03821.x