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Nano-ozone bubbles for drinking water treatment

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Safe drinking water is a key necessity, and ozonation is one of the common processes in drinking water preparation. The main drawbacks of using conventional ozone methods are the high-buoyancy-related low retention time and rapid decomposition of ozone eradicating residual ozone in water, which do not support prevention of regrowth of microorganisms in treated water. When ozone is delivered as nanobubbles, it increases the retention time due to the low-rising-velocity-related low buoyancy and increased higher specific area of nanobubbles compared to those of ordinary bubbles. The diffusion and concentration of ozone in the water are very important in the treatment process. Experimental results and theoretical calculations show that using nanobubbles leads to lower diffusion and higher ozone concentration compared to using ordinary bubbles. Decomposition of ozone in water generates oxygen where higher oxygen concentrations are obtained using nanobubbles. The oxygen formed during decomposition of ozone generates radicals that can oxidise pollutants. This paper summarises the methods of generating nanobubbles for drinking water treatment at the commercial scale and proposes a method of using ceramic diffusers in a treatment plant with increased efficiency. Moreover, the cost–benefit analysis presented highlights the benefits of using ozone as nanobubbles.

Notation

C'	concentration of ozone (O_3) in the gas–liquid interface
C_0	initial concentration
C_G	concentration in gas bulk
C_{ig}	concentration in the interface of gas bulk
C_{il}	solute concentration in the liquid bulk
C_L	molar concentration of ozone in the liquid phase
C_L^*	equilibrium molar concentration of ozone in the liquid phase
C_L^m	ozone decomposition in the liquid
$C_{O_3(\text{end})}$	ozone concentration at the end
$C_{O_3(\text{start})}$	ozone concentration at the beginning
C_w	molar concentration of water
D	diffusivity
d	vertical travel distance of a bubble
dC_L/dt	gas consumption rate
$d[O_3]/dt$	decomposition rate of ozone in the liquid
H	Henry's constant
K_G	gas-side mass transfer coefficient
K_L	liquid-side mass transfer coefficient
k_d	kinetic constant of ozone self-decomposition
k_La	volumetric mass transfer coefficient in the liquid phase
$[O_3]$	change in ozone concentration
P	average inside pressure of a bubble
r	radius of a gas bubble
S	surface area of a gas bubble
T	time of liquid exposure
v	rising velocity of a bubble
ΣV	total volume

Introduction

Obtaining safe drinking water is one of the key requirements to ensure the well-being of the general population. According to the World Economic Forum (WEF, 2015), water scarcity has been identified as the largest global risk in terms of potential impact over the next decade. Therefore, finding more effective, sustainable and environmentally friendly solutions for water treatment is a timely need. Using ozone (O_3) to disinfect drinking water during water treatment is commonly done around the world.

According to Loeb *et al.* (2012), the worldwide ozone capacity for drinking water treatment can be summarised as follows: in the USA, by the end of 2010, the installed ozone capacity for treating drinking water exceeds 525 000 pounds/d ($2{\cdot}38 \times 10^5$ kg), and since 2000, the growth rate of new ozone facilities has been about 8%. Starting in 2000–2002, the growth rate of installed ozone capacity has averaged about 25%. Japan has more than 17 000 drinking water treatment plants producing more than 16 billion m^3 of treated water, and the percentage of plants using ozonation is about 2%, with about 11% of the total water being treated by ozone. In Germany, in 2012, 100 water utilisation plants used ozone for municipal water supply, and in the Netherlands eight groundwater treatment plants have been installed. In France, by 1990, over 700 ozonation plants were in operation. As of 1999, in Canada, a total drinking of 68 water treatment plants have been using ozone in their systems.

The high effectiveness of chemical oxidation of a wide range of harmful pollutants has been demonstrated by many within the past two decades (Hoigné *et al.*, 1998; Ikehata *et al.*, 2006). Many industries have already incorporated ozone into their systems and have switched from using chlorine. There are many advantages to this. There is no lasting odour or taste from ozone like there is from chlorine. Using ozone is more environmentally friendly because the treated water is chemical-free. Radicals are formed during the decomposition of ozone, which is highly unstable with a very short lifespan. Due to their high instability, radicals possess strong oxidation capabilities. The decomposition of aqueous ozone is generally due to a chain reaction involving ·OH radicals. Many organic solutes (impurities) react with ·OH to yield $\cdot O_2^-$ upon addition of ozone (Staehelin and Hoigne, 1985). One advantage of the application of ozone is that there are no chemical residuals, where upon release of its oxidising potential, ozone reverts back to oxygen (O_2). However, the effectiveness of disinfection depends on the susceptibility of target organisms, the contact time and the concentration of ozone (EPA, 1999).

Nanobubbles have recently been a research topic of interest due to their multitude of applications. For the past few decades, nanobubble technology has been researched and applied to several fields, including biomedical engineering, agriculture, nanomaterials and many industrial sectors, due to its advantages which make nanobubbles so useful in so many fields of science (Takahashi, 2009). The most obvious advantage is their size; because nanobubbles are so small, they can be used in less invasive surgical procedures (Mondal *et al*., 2012). In general, nanobubbles can be classified according to size as nanobubbles, those with a diameter less than 1 μm; microbubbles, those with a diameter between 1 and 100 μm; and macrobubbles, those with a diameter bigger than 100 μm (Chaplin, 2007). Nanobubbles can increase the dissolved gas concentration in water. Nanobubbles can also change the density of water, which can be used to separate oil from waste water. Nanobubbles can also clean surfaces that cannot be scrubbed or have very small cracks or pores. Nanobubbles can be used to deliver increased oxygen in liquids. This is beneficial for seed germination and in the medical field to help patients who are suffocating. The small size and stability of nanobubbles are reasons for the wide popularity of this technology.

When ozone is delivered by using a regular diffuser as bubbles, the generated macrobubbles rise to the surface quickly due to their buoyancy (Baz-Rodríguez *et al*., 2012), causing low reaction rates and low removal efficiencies. Hence, they reduce the contact time of ozone with water for the gas to dissolve in water or to react with a contaminant. Nano-ozone bubbles are nanosize bubbles in aqueous solutions that have a longer lifespan than macrobubbles, and hence they provide ample time to react efficiently with pathogens and contaminants, thus indicating tremendous potential for drinking water treatment.

Ozone

Ozone is a very strong disinfectant and oxidiser. Use of ozone to disinfect drinking water is a technology that is practiced in many areas of the world. Among all chemicals used in water treatment, ozone is the strongest disinfectant and is second only to elemental fluorine with respect to oxidising power. Also, compared to chlorine, ozone is a more than 50% stronger oxidiser and acts over 3000 times faster (Eagleton, 1999). Many companies have already incorporated ozone into their systems and have switched from using chlorine. There are many advantages to this. There is no lasting odour or taste from ozone like there is from chlorine. Ozone is more environmentally friendly because the treated water is chemical-free. Ozone prevents residual build-up, which often occurs when using chemicals, and it removes the potential for bleaching. It has been shown that using chlorine can cause the formation of disinfection by-products. Luminescent bacteria and *Daphnia magna* acute toxicity, anti-estrogenic activity and cytotoxicity all increase after chlorination due to disinfection by-products. These by-products affect toxicity (Du *et al*., 2017). Ozone can also save money since it is produced on-site and eliminates demands on transportation and storage. Ozone readily reacts with organic and inorganic substances. It is a highly reactive and powerful oxidant that has been used in the chemical industry as an oxidising agent and is also used extensively in the treatment of drinking water (Camel and Bermond, 1998; Rositano *et al*., 2001). Radicals are formed during the decomposition of ozone, which is highly unstable with a very short lifespan. Due to the high instability of radicals, they possess strong oxidation potential. As stated before, the decomposition of aqueous ozone is generally due to a chain reaction involving the ·OH radical. Many organic solutes (impurities) can react with ·OH to yield $\cdot O_2^-$ upon addition of oxygen (Staehelin and Hoigne, 1985). One advantage of the application of ozone is that it does not leave a chemical residue. Upon release of its oxidising potential, ozone reverts back to oxygen, from which it was generated. The economics of ozonation processes is greatly affected by the characteristics of the ozone bubbles formed. The size, concentration and sustainability of the bubbles in the aqueous phase control the mass transfer and reaction kinetics of ozonation processes in various applications ranging from microbial disinfection to micropollutant destruction. The City of San Diego's Public Utilities Department is currently using ozone in their water treatment process (City of San Diego, 2017). Their process includes membrane filtration followed by reverse osmosis, which is then followed by an advanced oxidation process using ozone. They show a substantial cost saving by having a finer-size ozone diffuser. Ozone has been used for many treatment processes, including drinking water treatment, waste water treatment and water reclamation and reuses, due to its high efficiency in decomposition of refractory organic matters as well as disinfection of polluted water.

Nano-ozone

As stated before, the regular method of ozone delivery is through ordinary bubbles that travel to the water surface due to their high buoyancy, causing low removal efficiencies. Nano-ozone bubbles are nanoscopic bubbles in aqueous solutions that have longer lifespans as well as high specific areas compared to the macrobubbles and hence can destroy pathogens efficiently, thus indicating tremendous potential for drinking water treatment. Moreover, if higher amounts of ozone are in contact with contaminants, ozone can react at a faster rate. The faster diffusion can take place, the more efficient the ozone transfer from gas to the solution, which makes the disinfection efficient. For the same volume of macrobubble and nanobubble solution, nanobubbles show a high specific area, and this increased surface area allows a faster reaction capability. As an example, take a volume of 1000 bubbles with 5 mm diameter (total volume = $6{\cdot}54 \times 10^{-5}\,\mathrm{m}^3$) and total surface area = $0{\cdot}0785\,\mathrm{m}^2$. Now consider the same volume of gas with 100 nm diameter bubbles (volume/bubble = $5{\cdot}24 \times 10^{-22}\,\mathrm{m}^3$); the number of bubbles would be equal to $1{\cdot}25 \times 10^{17}$, which gives a total surface area of $3925\,\mathrm{m}^2$. Based on this calculation, when macrobubbles diffuse to smaller bubbles, the total surface area increases, which implies more contact time between water and ozone. This allows for a faster and more efficient reaction to occur.

According to the US Environmental Protection Agency, drinking water disinfection is considered in two ways (EPA, 1998). The first one is primary disinfection, which achieves the desired level of destruction of microorganisms or makes them inactive, while secondary disinfection is required to maintain a disinfectant residual in the treated water that prevents the regrowth of microorganisms during distribution until the point of consumption. One of the key drawbacks of the use of ozone in drinking water treatment is that it does not provide any disinfectant residual into distribution when ozone is used as ordinary bubbles. However, when ozone is delivered as nanobubbles, it has a substantial potential of remaining in water for a considerable time, and, therefore, it can be used not only for pretreatment, but also for final disinfection. However, the amount of ozone residual at the point of usage should have to be standardised as other concerns related to public health and safety might arise. Still, ozone in drinking water is controversial, as there are no proven scientific benefits, although some believe that ozone has significant healing properties.

However, the design objective would not be to provide additional ozone to drinking water as a residual, but to increase the ozone reaction time and to reduce the required amount of ozone to reduce the production cost of water. The amount of ozone required depends on two factors. First is the cumulative need, which is the number of milligrams of ozone necessary to oxidise specific milligrams of contaminant present. Second is the disinfection calculations, which involve concentration and time, needed for inactivating living organisms (Eagleton, 1999). However, in general, nanobubbles are considered to be in solution for an extended period of time. Literature shows that the lifespan of nanobubbles is likely to be from days to weeks and sometimes months. However, these data are relevant for bubbles formed in clean water. When the water is with the highly reactive ozone gas and has contaminants and bacteria, the lifespan of nanobubbles is reduced. However, that is advantageous in water treatment; there are faster reaction rates to generate clean water. The benefit of the long lifespan of ozone nanobubbles allows them to be used as a final disinfectant. Thus, this will prevent the regrowth of microorganisms during distribution. Moreover, Hu and Xia's (2018) experimental results showed that significant contribution of ozone nanobubbles on the remediation of trichloroethylene-contaminated groundwater possibly signifies an innovative technology for in situ remediation of organic-contaminated groundwater. Also, ozone has a strong antimicrobial activity against bacteria, fungi, protozoa and viruses (Kim *et al*., 1999).

Diffusivity of ozone nanobubbles

The diffusion of ozone is important in treating drinking water. The most important step in successful ozone water treatment is that ozone gas must be converted from its natural gas state into a dissolved state in order to oxidise dissolved contaminants in water. Figure 1 shows the gas–liquid interface. The gas–liquid interface is where the reaction between ozone and the contaminants in the water takes place. The gas inside the bubble diffuses through the gas–water interface into the liquid.

The diffusion of gas into water depends on several factors such as gas solubility, temperature, gas concentration, solution pressure, bubble size and internal gas pressure. Ozone is a very soluble gas in the water. At 25°C, ozone solubility is 109 mg/l. The solubility of oxygen is 8 mg/l. Ozone is 13 times more soluble than oxygen. However, when ozone is supplied as bubbles, due to high buoyancy, the bubbles rapidly leave the solution, without having sufficient time for ozone to dissolve in water. Thus, when using nanobubbles, due to their reduced buoyancy, they stay in the solution for a comparably longer time, and since the smaller bubbles' inside pressure is higher, and they increase the diffusion rates, allowing the water to be supersaturated with gas.

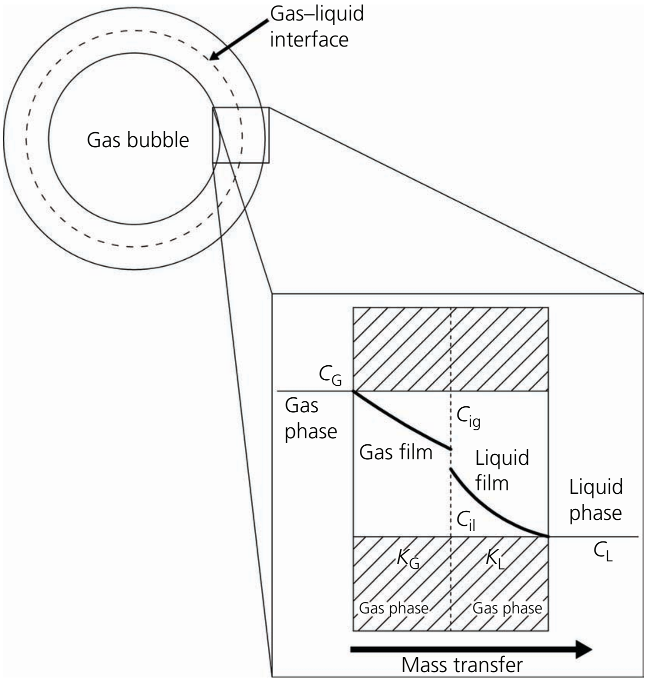

Figure 1. Gas–liquid interface. Redrawn based on International Union of Pure and Applied Chemistry's *Solubility Data Series: Volume 7: Oxygen and Ozone* (Battino, 1981)

In order to calculate the diffusion of ozone in water, the following equation can be used (Johnson and Davis, 1996)

$$r = 2S\left(C' - C_0\right)\sqrt{\frac{DT}{\pi}} \tag{1}$$

where S is the surface area of the gas bubble or $S = 4\pi r^2$. C' is the concentration of ozone in the gas–liquid interface or $C' = PC_w/H$. P is the pressure and is assumed to be 1·5 atm, which is the average pressure inside the bubble. C_w is the molar concentration of water. H is Henry's constant and is assumed to be $3{\cdot}90 \times 10^3$ atm for ozone (Kavanaugh and Trussell, 1980). C_0 is the initial concentration and is assumed to be zero. D is diffusivity and is given as $1{\cdot}76 \times 10^{-9}$ m^2/s (Johnson and Davis, 1996). T is the time of liquid exposure and can be solved by using $T = d/v$, where d is the distance and v is velocity. The velocity is based on the terminal velocities. The distance is assumed to be 10 m. It is assumed that the saturation of the liquid is zero. As the water is saturated, the diffusion rate decreases; these calculations do not account for saturation.

The calculations are based on the same total volume of macrobubbles and nanobubbles ($\Sigma V_{\text{macro}} = \Sigma V_{\text{nano}}$). The previous calculation shows the diffusivity of nano- and macro-bubbles as $4{\cdot}42 \times 10^{-8}$ and $4{\cdot}42 \times 10^{-16}$ m^2/s, respectively. This proves that the diffusion of nanobubbles is much greater than that of macrobubbles.

Ozone concentration

It is also important to note that with ozone nanobubbles, there is an increased ozone concentration in water. Figure 2 shows the variation in ozone concentration with time for both ozone nanobubbles and bubbles generated using a sandstone diffuser (a sandstone diffuser generates macrobubbles). In both situations, bubbles were generated in the chamber filled with up to 20 litres of water, and ozone gas was supplied for 3 min at the same flow rate. Results indicate that with ozone nanobubbles the initial ozone concentration in the solution was 52·79 mg/l, which is higher than that for ordinary bubbles (48·28 mg/l). Also, results show that with ozone nanobubbles a significant amount of ozone was present after a long period of time.

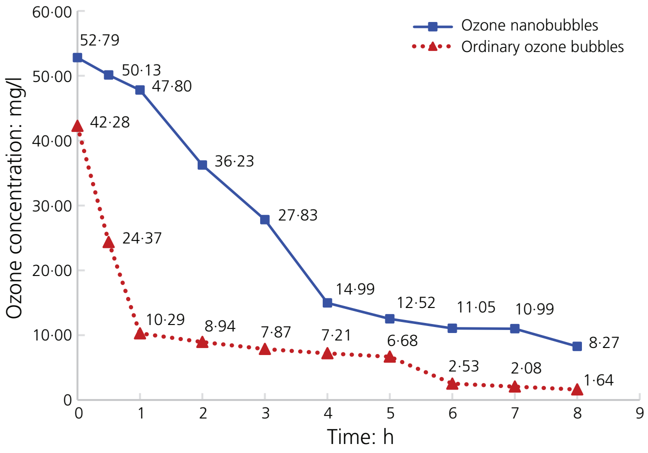

Figure 2. Concentration of macro- and nano-ozone in water with time (at 20°C)

There are many advantages of a longer residence time of ozone in water. The water continues to be disinfected over a longer period of time. Another advantage of the remaining ozone in the water would be to help clean filters. Some companies use ozone in the first step of their treatment and then filter the water. The filters are cleaned because of the ozone in the water. This helps keep filters clean for a longer time.

Ozone decomposition and release of dissolved ozone to the overhead space are two major reasons for the decrease in dissolved ozone concentrations over time. The stability and half-life of dissolved ozone depends on ozone concentration, temperature, pH level, availability of hydroxyl radicals, fluid dynamic conditions in the liquid and availability of organic and inorganic material. Aside from the mentioned parameters, there are other factors that can influence stability. Bin (2004) suggested the use of a constant-gas-consumption model from the gas phase to the liquid phase (Equation 2), neglecting the changes in ozone concentration during ozonation of the liquid.

$$\frac{\mathrm{d}C_{\mathrm{L}}}{\mathrm{d}t} = k_{\mathrm{L}}a(C_{\mathrm{L}}^{*} - C_{\mathrm{L}}) - k_{\mathrm{d}}C_{\mathrm{L}}^{\mathrm{m}} \tag{2}$$

C_{L} is the molar concentration of ozone in the liquid phase (mol/m^3), C_{L}^{*} is the equilibrium molar concentration of ozone in the liquid phase (mol/m^3), $k_{\mathrm{L}}a$ is the volumetric mass transfer coefficient in the liquid phase (s^{-1}), k_{d} is the kinetic constant of ozone self-decomposition (s^{-1}) and $C_{\mathrm{L}}^{\mathrm{m}}$ is ozone decomposition in the liquid (m; can be either 1 or 2 for first-order or second-order formation). The solubility of the gas phase and decomposition can lead to a much-complicated model which requires additional data. A mechanistic approach to decomposition requires defining multiple conditions and observations. Hence, to simplify the approach for the decomposition of ozone in the liquid, a generic formula (Equation 3) can be derived from Equation 2.

$$-\frac{\mathrm{d}[\mathrm{O}_3]}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{O}_3] \tag{3}$$

Keeping the temperature and pH constant, Gardoni *et al.* (2012) developed an empirical kinetic decomposition chart for the k_{d} constant. The imperial values were calculated based on the first-order kinetic studies performed by Czapski *et al.* (1968), Rizzuti *et al.* (1976), Teramoto *et al.* (1981), Sotelo *et al.* (1987), Huang and Chen (1993) and Ku *et al.* (1996). The upper boundaries and lower boundaries based on the studies are shown in Figure 3.

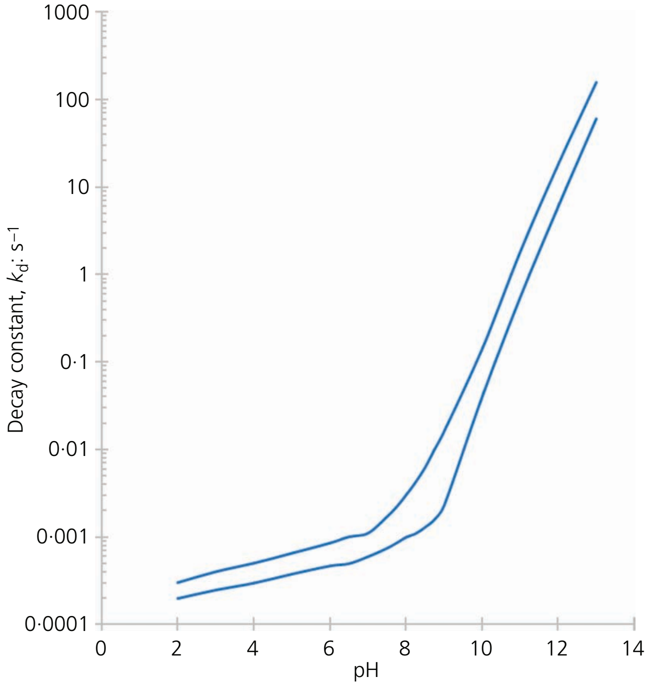

Figure 3. Ozone decomposition rate based on variation in pH (at 20°C). The constant is defined inside the two lines, which represent the lower and upper limits of the data of Czapski *et al*. (1968), Rizzuti *et al*. (1976), Teramoto *et al*. (1981), Sotelo *et al*. (1987), Huang and Chen (1993) and Ku *et al*. (1996). Source: adopted from Gardoni *et al*. (2012)

The pH level of the water used in the study was 7. Hence, from Figure 3, the decay constant $k_{\mathrm{d}} = 0{\cdot}0006\ \mathrm{s}^{-1}$. The ozone concentrations in water at the start and at the end of the experiment were used to calculate the ozone reduction rate. The ozone concentrations in the water were measured throughout the study using American Public Health Association standard method 4500-O_3 B – 1997 (Rice *et al*., 2017) due to the unavailability of ozone censors detecting dissolved concentrations above 20 mg/l. The ozone reduction rate was obtained for each observed hour throughout the study by using the equation

$$4.\quad \text{reduction rate} = \frac{\mathrm{d}[\mathrm{O_3}]}{\mathrm{d}t} = \frac{\left[C_{\mathrm{O_3}(\mathrm{start})} - C_{\mathrm{O_3}(\mathrm{end})}\right]}{3600\ \mathrm{s}}$$

The ozone reduction rates based on the empirical equation (Equation 3) and experimental data (Equation 4) are shown in Figure 4.

The reduction rate obtained from the theoretical formula is much higher than that based on experimental data. Using an ozone sensor (A-21ZX ozone sensor, manufactured by EcoSensors), the overhead concentration was monitored, and the ozone sensor failed to detect any ozone. Hence, it can be concluded that ozone nanobubbles improved ozone retention in water and prevented release of ozone from water. Ozone nanobubbles slowed the decomposition of ozone in the liquid, increasing the retention time of ozone in water.

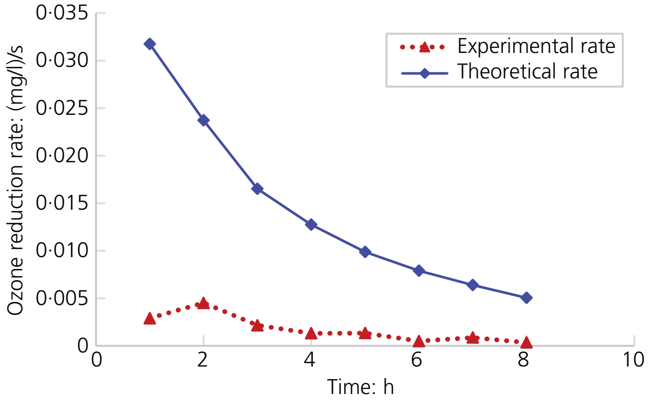

Figure 4. Calculated ozone reduction rates using empirical and experimental data

Figure 4 shows a convincing difference between the theoretical and experimental data. When gas diffuses from a bubble, the immediate vicinity of the bubble surface is saturated with the diffused gas. The ozone-saturated water surrounding nanobubbles slows down gas diffusion into the liquid.

The decomposition of ozone in water generates oxygen. With ozone, the dissolved oxygen concentration in water is increased. The decomposition of ozone is catalysed by the $\mathrm{OH^-}$ in water (Bader, 1982; Sehested *et al*., 1984) where $\mathrm{OH^-}$ promotes the formation of radicals that further react with water and form oxygen. This research investigated the concentration of oxygen generated during ozonation using a diffuser and nanobubbles. The oxygen levels were observed for 8 h starting from 30 min after introduction of ozone to water. Figure 5 shows the observed oxygen concentrations at 20°C.

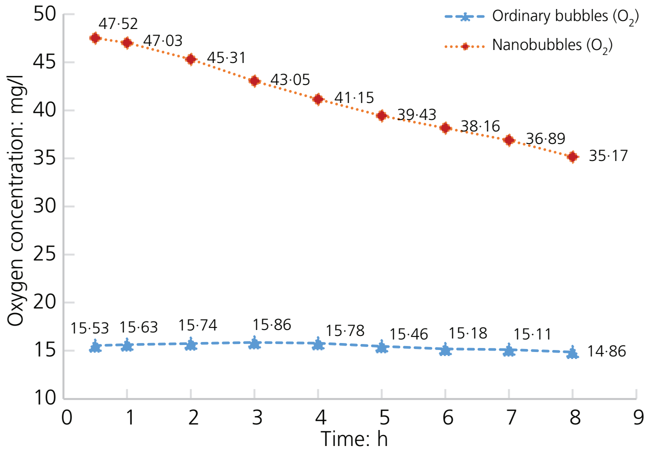

Figure 5. Oxygen concentration in water over time at 20°C

The highest oxygen levels observed in water were obtained when using a nanobubble generator to dissolve ozone in water. At 30 min, the oxygen concentration reached 37·28 mg/l and then the oxygen level slowly decreased over time. However, compared to rate of depletion of ozone, the rate of decline of oxygen was much slower due to the generation of oxygen during decomposition of ozone. A similar variation was observed when using a diffuser where the highest oxygen concentration observed in water was 20·60 mg/l. Having high oxygen concentrations in water further helps the decomposition of ozone, which generates radicals that can oxidise pollutants.

Methods of generating nanobubbles for drinking water treatment at commercial scale

Different methods are used in nanobubble generation; nanobubbles are frequently generated in solutions by creating cavities. Cavity generation mechanisms can be classified into five different types

- hydrodynamic – variation in the pressure of liquid flux due to system geometry
- acoustic – acoustic cavitation produced by applying ultrasound to liquids
- particle – passing high-intensity light photons in liquids
- temperature – sudden increase in temperature of gas-saturated liquids
- electrolysis – application of electrical current to fluid.

Some of these methods are not applicable or practical for producing nano-ozone for water treatment. Hydrodynamic cavitation is one of the most frequently used methods in water treatment practices. Flowing liquids can cause localized pressure reduction in the liquid, which can cause the pressure to drop below vapor pressure creating localized cavities. Figure 6 shows a sketch of the water phase diagram to show that gas cavitation occurs when the pressure inside the liquid becomes lower.

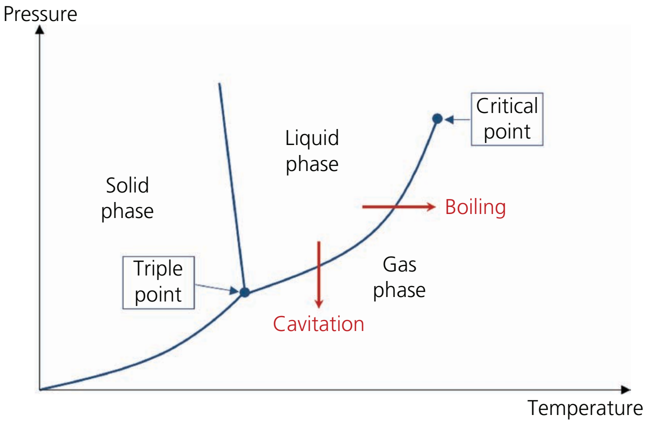

Figure 6. Reproduced sketch of the water phase diagram. Boiling is the phase change from liquid to gas by temperature increase, whereas cavitation is the phase change by pressure decrease (Tinguely, 2013)

Ozone bubbles are usually hydrodynamically generated using the following methods in water treatment practices

- injection of low-pressure gases into liquids to break the gas into bubbles by focusing, fluid oscillation or mechanical vibration
- full- or side-stream flow using a venturi
- dissolving gases in liquids by compressing gas flows in liquids and then releasing those mixtures through nano-sized pores (diffusers) to create nanobubbles.

The first method, with focusing, fluid oscillation or mechanical vibration, is a simple and easy method of generating smaller bubbles. However, it has a few disadvantages, including the generated bubble sample containing an unknown concentration of differently sized bubbles from micro to nano sizes.

In side-stream injection, a portion of the main flow is split off to a side stream. In the side stream, ozone is injected and then this side stream is connected back to the main flow. Here the injection of ozone needs a booster pump as a low volume flow rate has to be maintained. The side-stream flow can be used for degassing the flow as well. This system is advantageous with low maintenance cost and has a simple contactor layout as dissolution and reaction units are separated. However, compared to bubble diffusers, a booster pump has a comparably higher energy cost.

The third method uses a pump with diffusers or a disc with nano-sized pores. This is the one of most commonly used methods for generating gas bubbles. There is a safety hazard with the pump when using large quantities of ozone; however, this issue would still be a concern when using a nozzle. The disadvantage of a nozzle is that it is often expensive.

Ceramic diffusers are commonly used for aeration in waste water. These ceramic pores are made of carbon-based material and can be used to generate nanobubbles by simply submerging them in water and allowing desired quantities of gas to flow through the small pores. Because the pores are so small, the gas bubbles become nanobubbles. This method requires minimal energy and is much less complex than other methods. Because of its simplicity, this technology can be easily adapted into any system. According to Ahmed *et al.* (2017), it can be used ‘easily, instantly, and can be applied in-situ including underground, rivers, oceans, and soil liquid phases for water treatment, purification, remediation, pathogen mitigation, food processing, or agricultural applications’. A ceramic diffuser with pores that have a size of 20 μm produces microbubbles with an average diameter between 0·51 and 0·65 mm (Siswanto *et al.*, 2014). A ceramic diffuser with a pore size of 100 nm can produce nanobubbles with diameters between 160 and 330 nm (Ahmed *et al.*, 2017). It will be difficult to fabricate large ceramic nanodiffusers. Hence, Figure 7 shows a suggested method of such implementation of ozone nanodiffuser into a drinking water treatment plant. Several carbon-based ceramic nozzles are mounted on a stainless-steel box. These nozzles are made of a porous material and

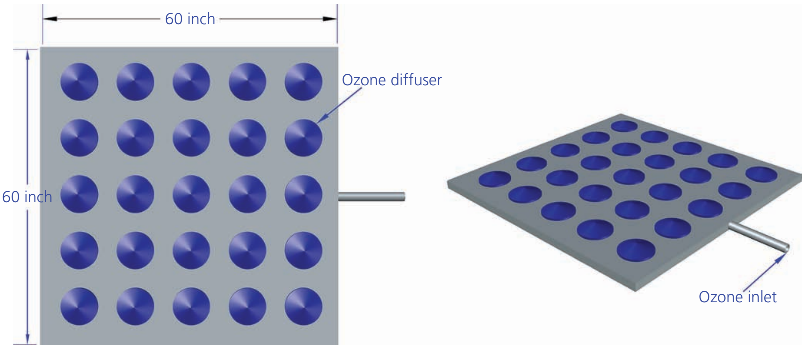

Figure 7. Nozzle diagram. 1 inch = 25·4 mm

generate nanobubbles when pressurised gas flows through them. This, however, would need further research before implementation, including possible enhancers such as coatings and electrical potential.

State-of-the-art nano-ozone for drinking water treatment

Nano Gas Technologies (NGT, 2017), a company that already uses nanobubbles to treat water, specialises in oil waste water treatment. They use nanobubbles to increase the amount of dissolved gas in water. Because nanobubbles are so small, they change the properties of Henry's law and more gas can be dissolved than predicted by the law. Nanobubbles also have the ability to change the density of water. This is important to separate oil from water. Most of the oil floats on top of the water, but the suspended oil particles settle at the bottom of the tank due to the low-density nanobubble-saturated water. This would normally take days or weeks, but, due to the nanobubbles, the water particles settle to the bottom in a matter of minutes.

Several companies have already begun to use ozone to treat waste water. There are different methods in which ozone is used. One method used by the Southern Delivery System (SDS, 2017) in a Colorado water treatment plant uses a three-step process. Ozone is used in the first step to remove coagulated solids. The second step uses activated carbon filters to remove ammonia and manganese. Chlorine is used in the final step to disinfect the water (ACC, 2017).

Ozone is currently being used in New Jersey and many water treatment plants in the USA. Figure 8 shows the typical steps involved in drinking water treatment plants, and Figure 9 shows the typical method of introducing ozone by using macrodiffusers. These macrodiffusers can be replaced and retrofitted by the nanoceramic diffuser shown in Figure 7. Ozone is generated and monitored within the cells of the contactor. Within the contactor, there are several cells which are monitored by an ozone analyser. After ozone oxidises the inorganic, organic and microbiological contaminants, the ozone concentration reduces with time. The rate of degradations depends on the water chemistry, pH and temperature. The remaining ozone is removed by an ozone destruction unit and vented to the atmosphere.

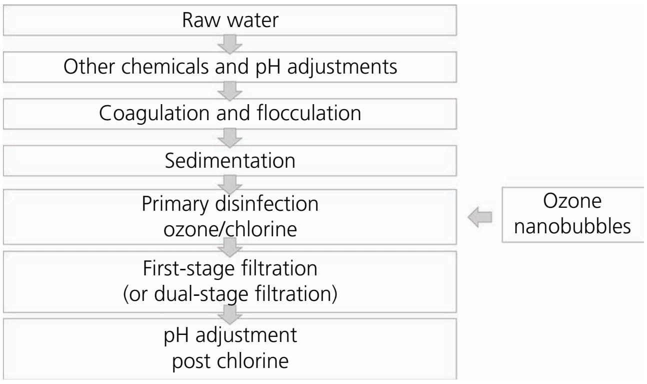

Figure 8. Typical steps involved in drinking water treatment

A cost–benefit analysis of nano-ozone for drinking water treatment plants

The following section illustrates the effectiveness of the use of ozone as nanobubbles in water treatment plants. Analysis is considered based on two aspects: first, with consideration of ozone diffusivity, and then based on the obtained experimental results.

Considering diffusivity of ozone

Using the information on the diffusivity of ozone described before and using 80 standard cubic feet per minute (SCFM) ($2{\cdot}265\ \mathrm{m^3/min}$) of ozone at 1 atm and 20°C in a typical water treatment plant, one can find the ratio of macrobubbles to nanobubbles. Table 1 presents the equivalent surface area of bubble sizes varying from 1 mm to 1 µm to 100 nm for equal volumes, where $\Sigma V_{1\ \mathrm{mm\ bubbles}} = \Sigma V_{1\ \mu\mathrm{m\ bubbles}} = \Sigma V_{100\ \mathrm{nm\ bubbles}} = 2{\cdot}265\ \mathrm{m^3}$.

By using Equation 1 ($r = 2S(C' - C_0)(DT/\pi)^{1/2}$), assuming parameters C' and D and an equal contact time for all the bubbles within the water and assuming unsaturated water throughout the diffusion and that all the nanobubbles are not impacted by the ozone saturation in the water, the diffusion ratio of 1 mm, 1 µm and 100 nm bubbles is $1{:}10^{12}{:}10^{16}$. If the system generates 1 mm ozone bubbles, then the total requirement is $2{\cdot}265\ \mathrm{m^3/min}$. If the

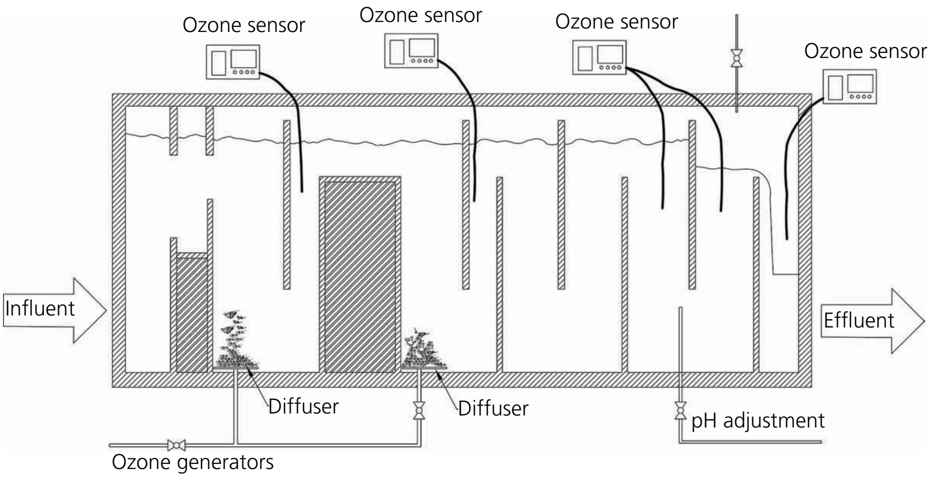

Figure 9. Typical method of introducing ozone using macrodiffusers

Table 1. Total surface area of the bubbles (1 mm, 1 μm and 100 nm) for a volume of 2·265 m^3

Bubble diameter: mm	Volume: mm^3	Surface area of bubble: mm^2	Total number of bubbles	Total surface area: m^2
1	$5·89 \times 10^{-1}$	3·14	$3·85 \times 10^{9}$	$1·21 \times 10^{4}$
0·001	$5·89 \times 10^{-10}$	$3·14 \times 10^{-6}$	$3·85 \times 10^{18}$	$1·21 \times 10^{16}$
0·0001	$5·89 \times 10^{-13}$	$3·14 \times 10^{-8}$	$3·85 \times 10^{21}$	$1·21 \times 10^{20}$

system generates 100 nm (at 100% efficiency) nanobubbles, then the required volume is $2·265 \times 10^{-16}$ m^3/min. However, nanobubble generation systems are not 100% efficient. Hence, with a 0·01% generating efficiency of nanobubbles and if all the other bubbles are 1 mm bubbles, the total required ozone will be reduced to $2·265 \times 10^{-12}$ m^3/min. Hence, the cost of the water treatment using ozone will be reduced if companies started using nano-ozone bubbles.

Based on the experimental results

Based on real applications, Figure 2 indicates the amount of ozone dissolved in water when using a nanobubble diffuser after running ozone for 3 min at the same flow rate in a chamber filled with 20 litres of water. The amount of ozone dissolved by a regular diffuser was 42·28 mg/l, and the ozone dissolved in water by using a nanodiffuser was 52·79 mg/l. Assuming that ozone takes an hour to stabilise in water, the two levels are 10·29 mg/l with a regular diffuser and 47·80 mg/l using a nanobubble diffuser. Hence, it is clear that nano-ozone bubbles retain ozone in water for roughly four times longer that using a regular diffuser. Hence using nanobubbles ozone requirement is reduced by four times. Table 2 shows a summary of data on ozone concentration in water with the use of a regular diffuser and as ozone nanobubbles.

Consider the typical water plant using 80 SCFM (2·265 m^3/min) of ozone and assuming the plant running for 24 h a day, 7 d a week and 365 d a year; 42 048 000 cubic feet or 1 190 000 m^3 of ozone is required per year, which means, with the density of ozone as 2·14 kg/m^3, a total of 2 500 000 kg of ozone per year is required. Based on this information and using a typical ozone generator requiring approximately 2·0 kWh of energy per kilogram of ozone and assuming that 1 kWh costs \$0·10, 1 kg of ozone would cost \$0·2. Thus, the total cost of using a regular diffuser will be \$500 000 (=2 500 000 kg × \$0·2/1 kg) per year. However, by installing a nano-ozone bubble diffuser, the total cost would be four times less, which is \$125 000 per year and will save \$375 000 per year.

Summary and conclusions

Use of ozone is one of the commonly used and effective methods of disinfecting drinking water. However, the short half-life of ozone prevents using ozone during drinking water delivery. This study used nanobubbles to increase ozone retention time in the water.

Table 2. Ozone concentration in water with use of regular and nanobubble diffusers

Diffuser type	Ozone concentration: mg/l In the beginning (time = 0 min)	Ozone concentration: mg/l After stabilisation of ozone concentration (time = 1 h)	Summary
Regular	42·28	10·29	Nano-ozone bubbles retain ozone in water for roughly four times longer that using a regular diffuser
Nanobubble	52·79	47·80	

Using nanobubbles as an ozone delivery mechanism proved many advantages such as increased retention time water, the increased surface area of bubbles increasing the contact area, increasing solubility due to high mass transfer area and reducing the decomposition of ozone in water. The research showed an ozone concentration of 52·79 mg/l at 20°C, which is much higher than that obtained from conventional methods. This will reduce ozone waste and decrease the cost of ozone production. Nanobubbles decelerate the decomposition of ozone in water, where calculated theoretical and experimental results showed a substantial advantage. The slow release of ozone into the water will be an added advantage during water distribution, where any intruding contaminants or pathogens during transmission and distribution will be oxidised by the ozone retained in nanobubbles. Due to the flexibility of nanobubble generation technology, this technology is capable of being retrofit to existing water treatment plants.

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