Quim. Nova, Vol. 48, No. 3, e-20250045, 1-5, 2025 http://dx.doi.org/10.21577/0100-4042.20250045

REMOVAL OF DEPOSITS AND IMPROVEMENT OF SHELF LIFE IN CO_2-RICH MINERAL WATER BY OZONE-MICROBUBBLES

Un Hwa Choe[a,*], **Jong Hyon Choe**[b] **and Yong Jun Kim**[a]
[a]Department of Applied Physics, Kim Chaek University of Technology, 999003 Pyongyang, Democratic People's Republic of Korea
[b]Department of Food Engineering, Pyongyang Han Tok Su University of Light Industry, 95003 Pyongyang, Democratic People's Republic of Korea

Received: 12/22/2023; accepted: 04/30/2024; published online: 08/06/2024

The aim of this study was to effectively remove Fe^{2+} by using ozone microbubbles in bottled mineral water to prevent sediment from occurring during storage and increase shelf life. By considering the characteristics of mineral water with low solubility of ozone and high CO_2 content, a suitable ozone injection step was chosen and a new mineral water treatment method using microbubbles was proposed. As a result of the treatment of the bottled mineral water with ozone microbubbles, the concentration of the iron ion was reduced from 0.14 to 0.01 mg L^{-1}, and the shelf life increased to 360 days. During the treatment, the concentrations of K^+ and Na^+ were almost unchanged, and the deposition time was reduced to one-third compared to the natural oxidation.

Keywords: CO_2-rich mineral water; ozone-microbubble; shelf life; bottled mineral water; water treatment.

INTRODUCTION

The mineral waters have been widely used since long ago because of its abundance of natural minerals useful for human life. In recent years, the variety and production of bottled mineral waters have increased rapidly due to water pollution from various causes, depletion of drinking water sources and increasing human demand for health. An important issue in the production of bottled mineral water is that the physical and chemical characteristics, including hygienic safety and color and taste after bottle packaging, are not changed for a period of time. Therefore, studies were conducted to analyze the microbial status of bottled mineral water and to determine the cause of microbial development and growth, and to conclude that the bottling and storage process of mineral water affect the quantity and quality of microorganisms.[1-4]

It is not only microorganisms that affect the quality of mineral water. In mineral water, unstable components such as iron, manganese, and sulfur are also present, which are allowed to be removed.[5] Also, according to EU directive 2003/40/EC,[6] it is possible to use ozone-rich gases for the treatment of natural mineral water containing carbon dioxide. The results of the study show that limited treatment of filtration, oxidation, precipitation and ozone treatment should be performed so that the physicochemical properties of mineral waters along with microorganisms are not changed during the bottling process. The use of ozone gas in water treatment began about a century ago and was used to purify the dirty water by microorganisms.[7] Later, chlorine and chlorine dioxide were used to effectively treat contaminants, including pathogenic organics. Ozone was again widely used because of the generation of chlorinated halogenated purified products (especially trihalomethane, THMS) by chlorine. However, due to the low solubility of ozone in water, ozone gas injected into the liquid decomposes before reacting with pollutants in water, reducing the efficiency of the reaction.[8,9] In order to overcome this disadvantage of ozone gas, the gas dissolution effect is good and ozone microbubble treatment using improved oxidation process by hydroxyl radicals generated during bubble cracking has been widely carried out in recent years. Water treatment using ozone microbubbles resulted in an 8-34% higher treatment rate than that with pure ozone gas.[10] Ammonia, the main factor of water pollution, was treated with ozone microbubbles, which were very effective for the oxidation of ammonia.[11] Analysis of the effectiveness of dimethylphthalein (DEP) in water by treatment with ozone microbubbles in various reaction conditions showed that the mass transfer efficiency of ozone increased with increasing pH.[12] The effect of pH on ozone microbubble treatment was also studied by other researchers,[13-15] who concluded in agreement that the higher the pH, the better the microbubble treatment effect.

Starting from the need for treatment of mineral water, it is reasonable to use ozone gas (redox potential 2.07 V) for oxidation of Fe^{2+}, one of the unstable components. Among the inorganic materials in mineral water sources, Fe^{2+} that do not undergo sufficient oxidation can be oxidized to Fe^{3+} during storage of mineral water and become precipitates, which do not change the total iron content in mineral water, but may change the physical properties such as turbidity. Therefore, the deposition of mineral water by fully oxidizing Fe^{2+} before bottling can increase the shelf life of mineral water. This is not contrary to the rule (legislation) that the unstable components of mineral water, such as iron, manganese, sulfur, and arsenic, can be removed.[2] Results show that the ozone microbubble technique can be used to clean the Fe^{2+} present in mineral water, and that the pH of mineral water is problematic. Most mineral water, especially mineral water with CO_2 above 400 mg L^{-1}, has a pH below 7, which can also have a negative effect on ozone treatment of mineral water.[5] In addition, CO_2 gas, which is highly soluble in mineral water, makes it difficult for other gases to dissolve in mineral water. According to Henry's law of solubility the amount of gas dissolved in water depends on the partial pressure of the gas dissolved in the water, because in mineral water, CO_2 gas is already highly dissolved. Therefore, the effective oxidation and deposition of Fe^{2+} by using ozone gas in CO_2-rich mineral water requires a new method of ozone injection and injection conditions to suit the characteristics of mineral water.

The aim of the present study was to use ozone microbubbles to fully oxidize Fe^{2+} to reduce the reference value of drinking water, thus eliminating the occurrence of sediment during storage and increasing the shelf life by 360 days.

---

*e-mail: cuh80624@star-co.net.kp

Associate Editor handled this article: Eduardo H. S. Sousa

In this paper, the effect of the concentration of CO_2 gas in mineral water, the pH of mineral water on the deposition rate of Fe^{2+} and the injection stage of ozone gas were determined, and the change of other ions in mineral water during ozone microbubble treatment was considered.

EXPERIMENTAL

Preparation of mineral water samples

The mineral water samples used in the experiment were CO_2-separated from original mineral water containing natural CO_2. The amount of CO_2 in original mineral water is about 3990 mg L^{-1} at 15 °C, 0.1 MPa, and the pH of the mineral water is 5.71. The mineral waters are of HCO_3-Ca-Mg-Na type.

The amount of CO_2 in the mineral water was changed with the partial pressure of CO_2 in the mineral water, because the amount of CO_2 depends on the partial pressure of CO_2 in the mineral water.[16,17] CO_2 degassing from the original mineral water was performed using degassing cascade column.[18]

When the partial pressure of CO_2 was 0.1, 0.08, 0.06, 0.04, 0.02 MPa at the temperature of 14 °C, the amount of CO_2 in mineral water was changed to five values such as 3990, 2230, 1675, 1118 and 558 mg L^{-1}, respectively.

Natural oxidation

The CO_2-separated mineral water was oxidized and precipitated in an air-contacting oxidation column (80 m^3) for 3 days (Figure 1), and the mineral water sample was sprayed in a jet nozzle mounted at the top of the oxidation column and placed in contact with air. The mineral water sprayed from the jet nozzle passes through the sand filter bed and is transported to the settling tank through a valve.

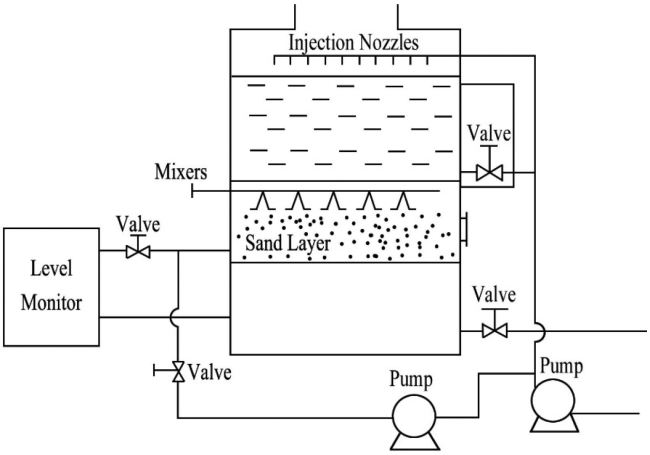

Figure 1. *Structure of the oxidation column*

Pure ozone gas oxidization

The experimental diagram is shown in Figure 2. The air inhaled to the ozone generator is purely oxygen through filtration, compression, water separation, and nitrogen separation steps. The passing pressure of oxygen gas in the plate is at a maximum of 0.6 atm and the amount of ozone gas produced in the ozone generator is 6-60 g h^{-1}. The experiments were carried out by varying the concentration of ozone gas generated from 0.5 to 5 g h^{-1}.

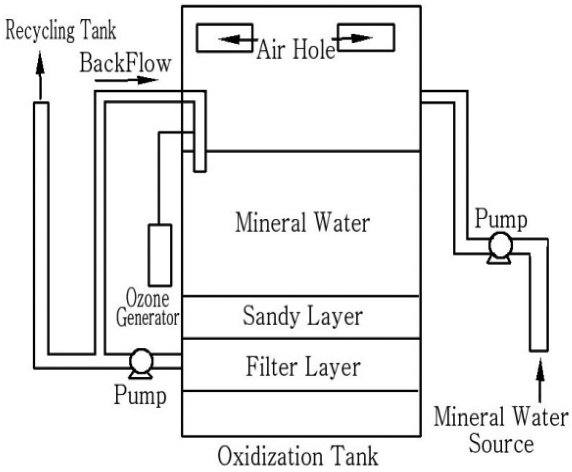

Figure 2. *Schematic of pure ozone gas treatment*

Ozone microbubbles oxidization

The experiment scheme is shown in Figure 3. The microbubble generator (MF5, Shanghai Xingheng Technology, Inc., China) was placed at 0.5 m from the upper liquid side of the reaction tank (80 m^3) and the ozone microbubbles generated in the generator were passed through the reaction tank. The pressure of mineral water injected into the microbubble generator was 7 atm, and ozone gas was spontaneously inhaled by the negative pressure generated inside the generator. Ozone microbubble treated mineral water was discharged through the sand filter bed and transported to the settling tank.

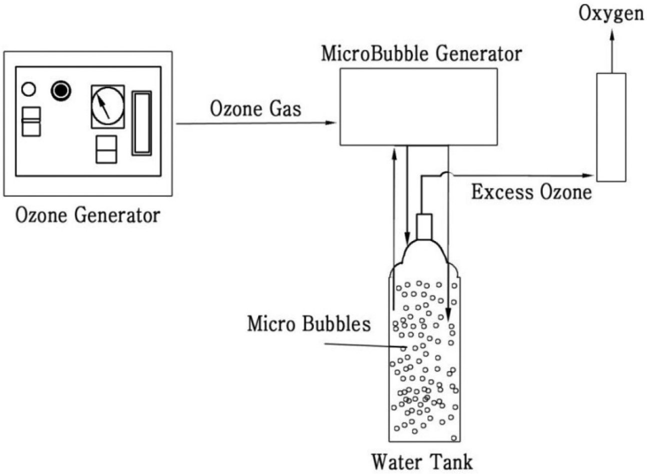

Figure 3. *Schematic of ozone micro bubbles treatment*

Methods of analysis

The concentration of gaseous ozone was measured by the iodine method.[19] The concentration of ozone dissolved in mineral water was measured by the indigo colorimetric method.[19] Determination method of Fe cation was carried in accordance with ISO 6332:1988[20] by spectrometric method using 1,10-phenanthroline using spectrometer (UV-160A, Shimadzu, Japan). The method for determining K and Na cations was conducted in accordance with the international standard ISO9964-1:1993[21] and the method for determining Ca cation was performed in accordance with the international ISO7980:1986[22] using atomic absorption spectrometer (PerkinElmer 5100 PC, USA). Determination method for free chlorine and total chlorine were performed in accordance with the international standard ISO7393-3:1990[23] by iodometric titration method for the determination of total chlorine. Alkalinity (HCO_3^- and CO_3^{2-}) values were determined by acidimetric titration with 0.01 mol L^{-1} HCl using an automatic titrator (DL53, Mettler Toledo, Switzerland). The settling time was determined as the time taken from the start of oxidation to the acceptable turbidity by extracting mineral water from the oxidation tank at a certain time interval and measuring its turbidity. The turbidity was measured using Hach 2100P (Hach Company, USA).

RESULTS AND DISCUSSION

Effectiveness of oxidation by ozone microbubbles

For mineral water with a CO_2 gas content of 558 mg L^{-1}, the changes in turbidity with time were observed for natural oxidation, pure ozone gas oxidation and ozone microbubble oxidation (Figure 4). Figure 4 shows that the turbidity of natural oxidized mineral water gradually decreases over time and takes 70 h to settle until it becomes an acceptable turbidity according to drinking water standards.

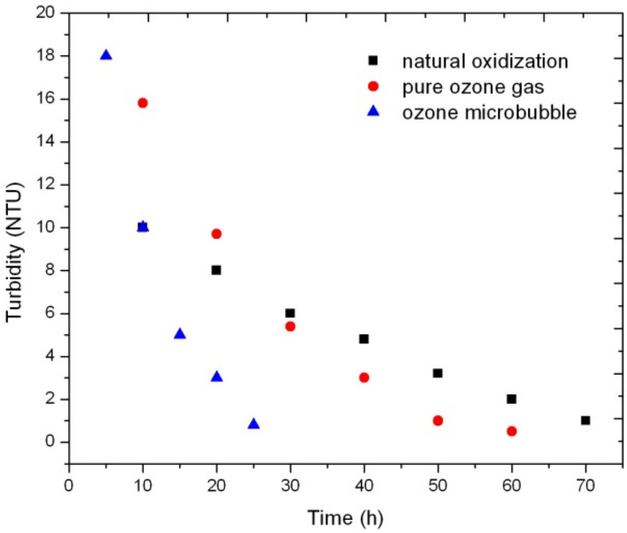

Figure 4. *Turbidity change with time for different oxidization methods*

In the case of pure ozone gas oxidation, the reference turbidity was satisfied for 50 h. The settling time for oxidation by ozone microbubbles was about 25 h. The effect of oxidation by ozone gas is better compared to natural oxidation; especially the effect of ozone microbubble oxidation is three times higher. The amount of residual ozone in the solution for the oxidation by ozone gas was 1 mg L^{-1}, and the amount of residual ozone in the oxidation by ozone microbubbles was 25.6 mg L^{-1}, which is about 52 times higher than the solubility of ozone gas at room temperature. This means that the concentration of dissolved ozone in oxidation by ozone microbubbles is higher and the ozone availability is higher compared to oxidation by ozone gas.

The internal pressure of the bubble, which has a large influence on the solubility, depends strongly on the size of the bubble. The Young-Laplace equation[24] can be used to calculate the internal pressure of bubbles.

$$p_g = p_l + \frac{4\sigma}{d_b} \tag{1}$$

where p_g is the gas pressure (Pa) inside the bubble and p_l is the pressure (Pa) of the bubble outer liquid; σ is the surface tension of bubbles (N m^{-1}), and d_b is the diameter of the bubble (m). According to Equation 1, the internal pressure of 1 μm bubble is 3.85 times larger compared to the internal pressure of 1 mm bubbles. Therefore, micro-bubbling of ozone gas decreases the surface area of the bubbles and increases the partial pressure of ozone gas; which increases the solubility of ozone gas.[19,25] Oxidation by ozone microbubbles generates more hydroxyl radicals because of the large mass transfer coefficient of ozone gas due to the increased contact cross-section of ozone gas and water. In addition, hydroxyl radicals are generated during the cracking of microbubbles, the redox potential of hydroxyl radicals is 0.73 eV higher than that of ozone gas, which also plays a role in enhancing the additional oxidation capacity of ozone gas.[24] Therefore, it can be seen that the oxidation process by ozone microbubbles increases the dissolution concentration of ozone and improves the production of hydroxyl radicals.

Effect of CO_2 concentration on ozone microbubble treatment

Figure 5 shows the turbidity variation measured at five-hour intervals from the start of ozone microbubble treatment in mineral water with different CO_2 gas concentrations. At this time, the size of ozone microbubbles is about 80 μm. When the CO_2 gas content is 1118 mg L^{-1}, the deposition time is about 25 h, about 35 h for 1675 mg L^{-1} and about 40 h for 2230 mg L^{-1}. It can be seen that the deposition time increases gradually with increasing CO_2 gas content.

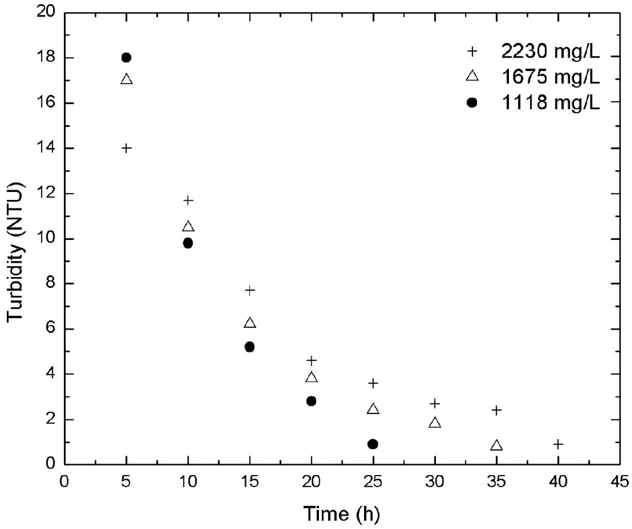

Figure 5. *Turbidity change with time in different concentration of CO_2 for ozone microbubbles treatment*

As can be seen from Figure 5, the CO_2 content in the mineral water certainly affects the ozone gas bubble treatment. The lower CO_2 concentration is, the more ozone gas is dissolved; thereby the oxidation of Fe^{2+} is accelerated and the deposition time gets short. In fact, according to Henry's solubility law, the mole fraction for water at 20 °C and 0.1 MPa is 7.07×10^{-4} for CO_2, whereas 1.885×10^{-6} for O_3, CO_2 is about 375 times larger than O_3. Therefore, it is more difficult to dissolve ozone gas in mineral water sources with high CO_2 solubility. The solubility of CO_2 and O_3 at the temperature of 20 °C are 0.942 and 0.39 L *per* L water, respectively;[19] the value for CO_2 is about 2.4 times larger than that for O_3.[19,26]

Gases with low values of the solubility are difficult to dissolve in water, and gases with high values of the solubility are prone to dissolve in water. Therefore, 3990 mg L^{-1} of CO_2 gas in mineral water source would prevent additional dissolution of O_3. With the removal of CO_2 gas from mineral water source, the amount dissolved in water increases, resulting in a decrease in deposition time. According to experiments, it is clear that the ozone microbubble injection step should be chosen as a step with sufficient CO_2-removal from mineral water.

Effect of pH on ozone microbubble treatment

In the case of ozone microbubble treatment, the variation of residual ozone concentration and pH with the change of CO_2 gas concentration in mineral water is given in Table 1.

Table 1. Residual ozone concentrations and pH values depending on CO_2 concentration in mineral waters

No.	CO_2 concentration / (mg L^{-1})	Residual ozone concentration / (mg L^{-1})	pH
1	3990	-	5.8
2	2230	4	6.2
3	1675	8	6.4
4	1118	12	6.5
5	558	25.6	6.9

As shown in Table 1, as the content of CO_2 in mineral water decreases, the pH increases and the residual ozone concentration increases. When the CO_2 content in original mineral water was 3990 mg L^{-1}, the pH was 5.8 and the residual ozone concentration was not observed, whereas the pH was 6.9 and the residual ozone concentration was 25.6 mg L^{-1}, when the CO_2 content in mineral water was 558 mg L^{-1}. This indicates that the decrease in CO_2 content of mineral water increases the solubility of ozone microbubbles, and at the same time increases the pH value of mineral water, which makes the water treatment effect by ozone microbubbles favorable.[8] Decomposition reaction of ozone in water varies in characteristic depending on the pH value. Under acidic conditions of solution ($pH < 7$), direct oxidation reactions with molecular ozone and microorganisms dominate, and at $pH \sim 7$, indirect reactions with radicals that occur when ozone is dissolved in water and direct reactions occur simultaneously. In the case of $pH > 7$, organic compound does not react with molecular ozone, and continuous decomposition of ozone occurs with increasing pH value. In Figure 4, the good effect of ozone microbubble treatment with a concentration of 558 mg L^{-1} in mineral water is seen as an increase in the solubility of ozone microbubbles with a decrease in CO_2 content, while the pH of mineral water is 6.9 (Table 1), which indicates that the generation of hydroxyl radicals with direct reaction of ozone molecules occurs explosively and the oxidation effect by ozone is improved. This is in good agreement with the results reported in the literature.[27-30] Bityukova *et al.*[27] reported that mineralized waters have acidic pH due to carbonatisation of the bottled waters and Kopylova *et al.*[28] reported that the presence of CO_2 accounts for the relatively low pH. Similar conclusions were made by Hoigne and Bader,[29] and Mansouri *et al.*[30]

From the above experimental results and discussions, it can be seen that the ozone injection step, which is reasonable for the effect of water treatment by ozone microbubbles in mineral water with high CO_2 content, is a step in which the content of CO_2 is controlled so that the pH value of mineral water is about 7 or above 7. In the mineral water used in this paper, its value was 558 mg L^{-1}.

Effect of ozone microbubble treatment on ion concentration in mineral water

The main components of the ozone microbubble treated mineral water with 558 mg L^{-1} CO_2 concentration are analyzed in Table 2.

As shown in Table 2, the concentrations of K^+ and Na^+ were almost unchanged before and after the ozone microbubble treatment, and the concentration of Ca^{2+} decreased by half. This indicates that the oxidation process of mineral water by ozone microbubbles does not change the amount of ions that are beneficial to the human body. The concentration of Fe was decreased from 0.14 to 0.01 mg L^{-1}, because most of Fe^{2+} was sufficiently oxidized and precipitated with $Fe(OH)_3$ by ozone microbubbles.

Table 2. Results of the analysis of important components of ozone microbubble treated mineral water

Component	Fe / (mg L^{-1})	Na / (mg L^{-1})	K / (mg L^{-1})	Ca / (mg L^{-1})	HCO_3^- / (mg L^{-1})	Cl^- / (mg L^{-1})
Before	0.14 ± 0.007	45.3 ± 2.27	12.2 ± 0.61	117.4 ± 5.87	707.6 ± 35.38	63.03 ± 3.15
After	0.01 ± 0.0005	46.3 ± 2.32	11.9 ± 0.60	56.7 ± 2.84	695.4 ± 34.77	62.6 ± 3.13

CONCLUSIONS

Ozone microbubbles can be used to improve the oxidation of CO_2-rich mineral water. The injection of ozone microbubbles into mineral water with CO_2 of 3390 mg L^{-1} did not show a good treatment effect. It is due to the effect of pH on ozone treatment and CO_2 dissolved in mineral water.

The separation of CO_2 from mineral water and injection of ozone microbubbles enhance the solubility of ozone gas in mineral water. Optimal injection step of ozone microbubbles should be chosen so that the pH value of mineral water is about 7 or above 7. For a residual CO_2 of 558 mg L^{-1}, pH value of mineral water is 6.9 and ozone microbubble treatment reduced the deposition time by 1/3 compared to natural oxidation, and the concentration of iron ions decreased from 0.14 mg L^{-1} before treatment to 0.01 mg L^{-1} after treatment. At this time, the shelf life increased from 30 to 360 days. This is because the solubility of microbubbles is high and oxidation due to the generation of hydroxyl radicals is improved. Ozone microbubble treatment method for mineral water with high CO_2 content can be used for wastewater treatment with high harmful gas content.

ACKNOWLEDGMENTS

The authors warmly thank Prof. I. Y. Kang for kind help.

REFERENCES

1. Tsai, G.; Yu, S.; *Int. J. Food Microbiol.* **1997**, *37*, 137. [Crossref]
2. Franca, L.; Lopez-Lopez, A.; Rossello-Mora, R.; da Costa, M. S.; *Environ. Microbiol.* **2015**, *17*, 577. [Crossref]
3. da Silva, M. E. Z.; Santana, R. G.; Guilhermetti, M.; Camargo Filho, I.; Endo, E. H.; Nakamura, T. U.; Nakamura, C. V.; Dias Filho, B. P.; *Int. J. Hyg. Environ. Health* **2008**, *211*, 504. [Crossref]
4. dos Santos, R. V.; Rigotto, C.; Staggemeir, R.; Vecchia, A. D.; Henzel, A.; Spilki, F. R.; *Beverages* **2015**, *1*, 140. [Crossref]
5. Guler, C.; Alpaslan, M.; *Clean: Soil, Air, Water* **2011**, *39*, 947. [Crossref]
6. EU Directive 2003/40/EC: *Council Directive of 16 May 2003 Establishing the List, Concentration Limits and Labeling Requirements for the Constituents of Natural Mineral Waters and the Conditions for Using Ozone-Enriched Air for the Treatment of Natural Mineral Waters and Spring Waters*; Official Journal of the European Union, L126/34, 2003.

7. Gottschalk, C.; Libra, J. A.; Saupe, A.; *Ozonation of Water and Waste Water: A Practical Guide to Understanding Ozone and its Applications*, 1st ed.; Wiley-VCH: Weinheim, 2000.
8. Beltrán, F. J.; *Ozone Reaction Kinetics for Water and Wastewater Systems*, 1st ed.; CRC Press: Boca Raton, 2003.
9. Sander, R.; *Atmos. Chem. Phys.* **2015**, *15*, 4399. [Crossref]
10. Azuma T.; Otomo, K.; Kunitou, M.; Shimizu, M.; Hosomaru, K.; Mikata, S.; Mino, Y.; Hayash, T.; *Sep. Purif. Technol.* **2012**, *212*, 483. [Crossref]
11. Khuntia, S.; Majumder, S. K.; Ghosh, P.; *Ind. Eng. Chem. Res.* **2013**, *52*, 318. [Crossref]
12. Jabesa, A.; Ghosh, P.; *J. Environ. Manage.* **2016**, *180*, 476. [Crossref]
13. Wen, G.; Liang, Z.; Xu, X.; Cao, R.; Wan, Q.; Ji, G.; Lin, W.; Wang, J.; Yang, J.; Huang, T.; *Water Res.* **2020**, *185*, 116218. [Crossref]
14. Khuntia, S.; Majumder, S. K.; Ghosh, P.; *Chem. Eng. Res. Des.* **2015**, *98*, 231. [Crossref]
15. Khuntia, S.; Majumder, S. K.; Ghosh, P.; *Chemosphere* **2014**, *97*, 120. [Crossref]
16. Chang, R.; Thoman Junior, J. W.; *Physical Chemistry for the Chemical Sciences*, University Science Books: Herndon, 2014.
17. Lide, D. R.; *CRC Handbook of Chemistry and Physics*, 89th ed.; Taylor & Francis: New York, 2008.
18. Moran, D.; *Aquacultural Engineering* **2010**, *43*, 29. [Crossref]
19. Rice, R. C.; Netzer, A.; *Handbook of Ozone Technology and Applications*, vol. 1, 2nd ed.; Ann Arbor Science: Michigan, 1985.
20. ISO6332:1988 (E): *Water Quality - Determination of Iron - Spectrometric Method Using 1,10-Phenanthroline*, ISO, 1988.
21. ISO9964-1:1993: *Water Quality - Determination of Sodium and Potassium - Part 1: Determination of Sodium by Atomic Absorption Spectrometry*, ISO, 1993.
22. ISO7980-1:1986: *Water Quality - Determination of Calcium and Magnesium - Atomic Absorption Spectrometric Method*, ISO, 1986.
23. ISO7393-3:1990: *Water Quality - Determination of Free Chlorine and Total Chlorine - Part 3: Iodometric Titration Method for the Determination of Total Chlorine*, ISO, 1990.
24. Zheng, T.; Wang, Q.; Zhang, T.; Shi, Z.; Tian, Y.; Shi, S.; Smale, N.; Wang, J.; *J. Hazard. Mater.* **2015**, *287*, 412. [Crossref]
25. Terasaka, K.; *J. Oleo Sci.* **2010**, *10*, 323. [Crossref]
26. De Moel, P. J.; Verberk, J. Q. J. C.; Van Dijk, J. C.; *Drinking Water Principles and Practices*, World Scientific: New Jersey, 2007.
27. Bityukova, L.; Petersell, V.; *J. Geochem. Explor.* **2010**, *107*, 238. [Crossref]
28. Kopylova, Y. G.; Lepokurova, O. E.; Tokarenko, O. G.; *Water Resour.* **2009**, *36*, 577. [Crossref]
29. Hoigne, J.; Bader, H.; *Water Res.* **1983**, *17*, 173. [Crossref]

30 Mansouri, L.; Mohammed, H.; Tizaoui, C.; Bousselmi, L.; *Desalin. Water Treat.* **2013**, *51*, 6698. [Crossref]