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## Research Article

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# Removal of Metal Ions from Water Using Oxygen Plasmas

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## ABSTRACT

Zinc ion dissolved in water is attempted to be removed by generating the oxides of zinc using the oxygen gas in DBD plasma system. The removal rate of zinc oxides' production (ZnO and Zn(OH)<sub>2</sub>) were measured at different treatment periods by the oxygen plasma penetration in water. The removal rate of the deposit increases initially and then decreases with the treatment period. The maximum removal rate (29%) of zinc from water is achieved at the treatment period of 10 min, where pH is minimum. From FTIR the generation properties of zinc oxide can be recognized. Initially the amount the deposit increases with the ozone treatment period due to production of both ZnO and Zn(OH)<sub>2</sub>. After that, the production of Zn(OH)<sub>4</sub><sup>2-</sup> increases even when the total removal rate of the deposit decreases. Therefore, to remove zinc ion from water forming metal oxide deposit, the penetration amount of the active oxygens to the water must be controlled to keep the pH lower than around 7.5. Because with increasing pH amount of removal rate of ZnO deposit decreases. The pH of the zinc dissolved water treated by ozone depends on both zinc and ozone concentration in water.

## Introduction

Metal contamination is one of the most complex issues of today's contamination problems. Excess amount of heavy metal ions dissolved in tap water induces many serious problems on the health of living bodies including human<sup>1,2,3,4</sup>. There are two main sources of heavy metals in water-natural and anthropogenic. Natural sources comprise volcanic activities, soil erosion, activities of living organisms, and weathering of rocks and minerals, whereas anthropogenic sources include landfills, fuel combustion, street run-offs, sewage, agricultural activities, mining, and industrial pollutants, such as textile dyes<sup>5</sup>. In recent years, drastic increases in pollutants in water resources have been detected<sup>6</sup>. However, there is no effective and reasonable technique to remove heavy metal ions from the water.

Heavy metals are a group of trace elements that include metals and metalloids, such as arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, tin, and zinc. They have a relatively high density of over  $4 \times 10^6$  mg/L. The metal ions are known to contaminate the soil, atmosphere, and water systems and are poisonous even in very low concentrations. Widespread

uses of metals, the legacies of past contamination, and new technologies continue to pose important ecological risks for aquatic environments across the earth<sup>7</sup>. Especially, metal ions taken up by plants accumulate on each part of plants, and cause health problems on animals those ingest the plants<sup>8,9,10,11</sup>. Several methods have been used to remove heavy metals from contaminated water. They include chemical precipitation, ion exchange, adsorption, membrane filtration, reverse osmosis, solvent extraction, and electrochemical treatment<sup>12,13,14,15,16,17</sup>. Many of these methods suffer from high capital and operational costs. The rapid growth in world population brings with it the need for improvement in the current technology for water purification, in order to provide adequate potable water to everyone.

Advanced oxidation processes (AOPs) exhibit advantages over conventional treatment methods because of the generation of strong oxidants<sup>18,19,20</sup>. Among the AOPs, electrical discharge plasma is widely employed for wastewater treatment. Non-thermal plasma or low-temperature plasma is green technology and has been studied for water treatment<sup>21,22,23,24</sup>. Most studies have focused on using low-temperature plasmas to be inactivated microorganisms and to decompose organic compounds for wastewater treatment<sup>25,26,27</sup>. For water treatment, dielectric barrier discharge (DBD) have been commonly generated with the coaxial electrode configuration. When the DBD occurs using atmospheric air, energetic free electrons, ultraviolet (UV) light and variety of active species are produced in the electrode gap<sup>25</sup>. These species have short lifetime unlike other chemical reagents for water treatment.

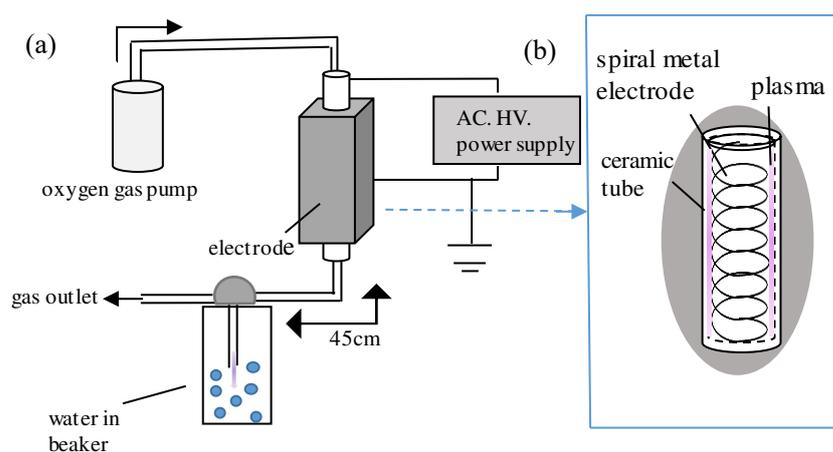
Oxidation of the heavy metal ions using oxidation reagents sometimes produces deposits of metal oxide<sup>28,29,30</sup>. These metal oxide deposits can be removed from the water easily using filtration or deposition<sup>31,32</sup>. Active oxygen species such as oxygen radicals, OH radical and ozone, which have been used for AOPs, would also oxidize metal ions in liquid effectively. Among these species, ozone is one of the relatively stable active species. The ozone treatment of the tap water, which has been developed and put to practical use, would be also effective for the removal of metal ions from the water. This method is considered to be a new experiment where attempts are being made to eliminate metal ions from water using oxygen in DBD plasma method. However, low-temperature plasmas using oxygen, or any other gas has not yet been tested to remove metal ions from water treatment. In the present study, removal of metal ion from tap water is attempted using the ozone oxidation method using the DBD plasma. In this experiment, the zinc ion in water, as a typical example of metal ions dissolved in water, is attempted to be removed generating the zinc oxide (ZnO) using the ozone oxidation treatment.

## **Experimental methods**

Zinc ions in water is produced by the electrolysis using cylindrical electrodes with 5 mm in

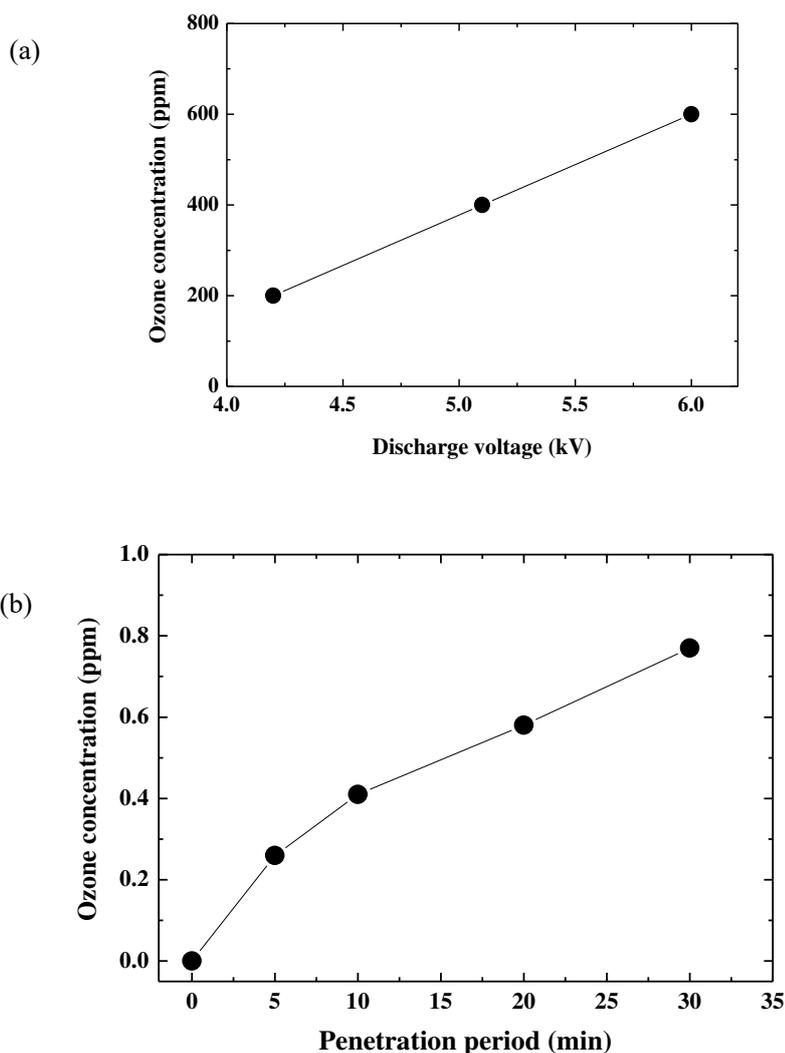
diameter and 30 mm in length, which are made of pure zinc. Amount of water used in this experiment is 0.2 L. The DC voltage at 8 V is applied to one electrode, and then the zinc ion dissolves in water. The density of zinc ion is obtained using the measurement reagent. The ozone oxidation of the dissolved zinc ion is performed by the simple ozone bubbling in the water containing the zinc ions, as shown in Fig. 1(a). The amount of water is 0.2 L and there is no water flow in the water vessel. The ozone is generated by the torch-shaped dielectric barrier discharge (DBD) using the pure oxygen gas with the flow rate of 1.0 L/min. The barrier discharge plasma torch used in this experiment has the shape of a cylindrical tube with dimensions of 100 mm in length and 4 mm in inner diameter, which is made from porous alumina. The cylindrical spiral-type discharge electrode is set along the inner wall of the alumina tube, and the copper film as grounded electrode is wound on the outer of the alumina tube, as shown in Fig. 1(b). When the high voltage with 5 kHz is applied to the discharge electrode, the barrier discharge occurs on the inner surface of the tube, and the oxygen plasma is generated.

The ozone is produced by high energy electrons in the plasma and is ejected from the opening edge of the tube by the oxygen gas flow. The produced ozone is transported into the water vessel and is dissolved in water using a bubbler. The concentration of the gaseous ozone ejected from the DBD device is measured using the gas detection tube and is controlled by changing the discharge voltage, as shown in Fig. 2(a). This concentration range is almost same as that used for the practical ozone treatment of the tap water. Since the zinc ion dissolved in water interferences with the measurement reagent of the ozone titration, the ozone concentration dissolved in the pure water is measured as an index of the ozone concentration in the zinc ion water, as shown in Fig. 2(b).



**Figure 1.** (a) Schematic diagram of the experimental apparatus, and (b) discharge electrode inside tube.

Effect of the oxidation of the zinc is evaluated by the concentration of the zinc oxide, which deposits on the bottom of the water. After the water is treated by ozone or oxygen plasma, the water is moved to a conical tube with the capacity of 15 ml is centrifuged, then the deposit accumulates on the bottom. The deposit is extracted from the water and dried up. The weight of the dried deposit is measured using the precision measure and then calculate the removal rate from the deposit. In order to specify the composition of the deposit, IR absorbance spectra of the deposit is measured using the FTIR, and the obtained spectra are compared with the typical spectra of zinc oxide.



**Figure 2.** (a) Gaseous ozone concentration as a function of the discharge voltage of DBD, and (b) Ozone concentration in water at different penetration period of ozone in water.

## Results and discussion

### Discharge of zinc in water

Under normal conditions, zinc (Zn) does not react with water. In the high temperature circumstance of 600-800°C, the zinc reacts with water to produce zinc oxide and hydrogen gas, as

shown in the equation:  $Zn + 2H_2O \rightarrow ZnO + H_2$ . The zinc oxide indicates yellow color at higher temperature, and white color at lower temperature.

In this study, the pure zinc electrode is used for the electrolysis of zinc ion in water. In a beaker a pair of zinc electrode is soaked in water of 0.2 L, and the DC voltage of 8V is applied to an electrode for 60 min. The concentration of zinc ion in water was around 39 ppm. When electrical discharge occurs on the zinc electrode, the pH of the water increases with the discharge period according to following equations:



Reaction in Eq. (2) requires the higher pH condition. When the zinc discharge period increases, the pH of the water increases owing to the production of the  $OH^{-}$ .

### Ozone reactions in water

When low-temperature plasma is formed using the DBD, high energetic free electrons, ultraviolet (UV) light and variety of active species are produced in the electrode gap [39]. Among these species, ozone is one of the most chemically stable and active species. The reactions to generate ozone in gas phase are expressed in Eq. (3) and (4). In this study, the ozone generated in the gas phase is supplied in water for 120 min with the simple bubbling method. Ozone concentration in water was measured as a function of the penetration period, as shown in Fig. 2(b). It is found that ozone concentration is increased with increasing treatment period.



In the water, ozone reacts with water molecule and the hydroxyl radical is produced as Eq. (5). The hydroxyl radical has very high reactivity and changes to hydroxide ion by receiving an electron from ions and molecules dissolved in water as impurities as Eq. (6). The hydroxide ion is stable in water.

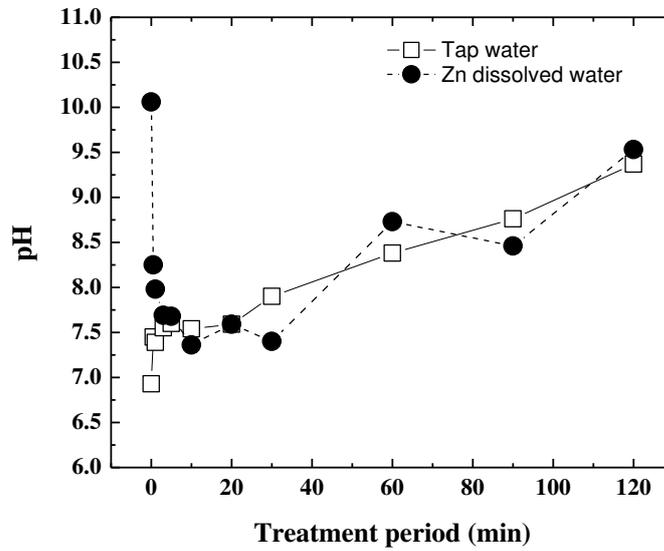


The ozone dissociates to oxygen molecule and excited neutral atomic oxygen as Eq. (7). Also, the atomic oxygen changes to oxygen ion in water as Eq. (8).



These active oxygen species in the water would be the factor for the zinc oxides' production ( $Zn(OH)_2$  and  $ZnO$ ) from the zinc ion. The zinc oxide tends to coagulate and becomes deposit in water. Since the  $OH^*$  combines into the  $H_2O_2$ , the  $H_2O_2$  concentration in the water is measured as

the index of the OH\* generation. In this experiment no H<sub>2</sub>O<sub>2</sub> is found in the zinc dissolved water.

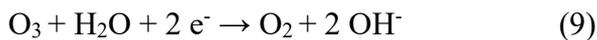


**Figure 3.** pH values of tap water and Zn dissolved water at different ozone treatment period.

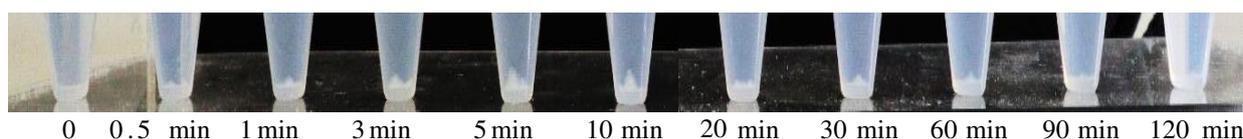
#### pH of water

The pH value of the water is one of the major factors for the deposition of metal oxides. Deposition of some metal oxides such as zinc and lead strongly depend on the pH value of the water. A significant role in the pH change can be attributed to positive and negative charges created in the DBD plasma that reach the water surface. The pH of tap water and Zn dissolved water were investigated changing the ozone penetration period till 120 min, as shown in Fig. 3.

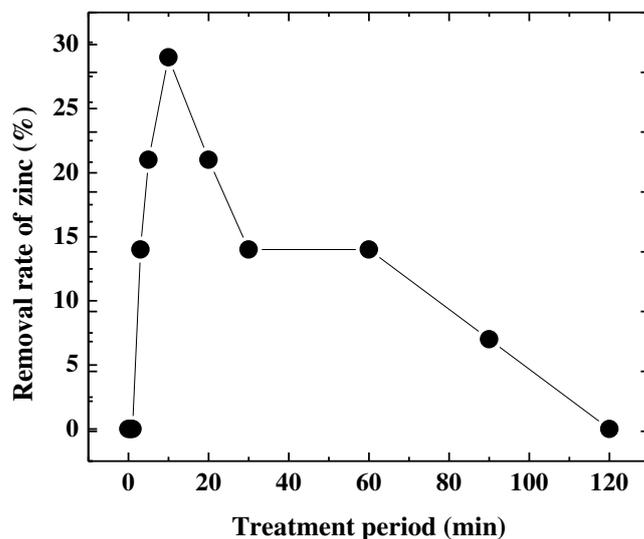
The pH value of the ozone dissolved tap water till 10 min of the ozone penetration period increases rapidly owing to rapid increase of the ozone concentration. The pH increases monotonically with the ozone treatment period after 10 min of the ozone treatment period. When ozone dissolves in water, some portion of the ozone reacts with H<sub>2</sub>O, and hydroxyl ion (OH<sup>-</sup>) and oxygen O<sub>2</sub> are generated, as shown in Eq. (9). Electrons on the left side of the equation can be supplied from impurity in the tap water. Then, ozone dissolved water becomes alkaline condition.



In this experiment, when the oxygen plasma treatment period of the zinc dissolved water increases from 0 to 30 min, the pH of the zinc dissolved water changes from 10 to 7. Decrease of pH in Zn dissolved water occurs due to the Zn ion consumes the hydroxyl ions those are generated by the



**Figure 4.** Deposits of Zn oxide compounds in water varying the ozone treatment period.



**Figure 5.** Removal rate of Zn ion from water at different treatment period.

reaction of ozone with water. After 10 min, the pH of the Zn dissolved water increases with the ozone treatment period. The pH of the zinc dissolved water treated by ozone depends on both zinc and ozone concentration in water.

Opposite tendency of pH decreasing in water using oxygen plasma application were reported by different researchers<sup>33,34,35,36</sup>. Plasma acid – hydrogen cation  $H^+$  and superoxide anion  $O_2^-$  is the cause of water acidification following plasma-treatment<sup>33,34,35</sup>. In a direct system, the production of  $H^+$  ions can be a result of ion exchange mechanisms and the main conjugate base of the plasma treated water in oxygen is the superoxide radical. Thus, plasma acid may consist of hydrogen cation  $H^+$  and superoxide anion  $O_2^-$  as the cause of water acidification following plasma-treatment<sup>33,34,35</sup>. In this study the changing in pH of water does not follow the previous studies. This may be due to attempts to remove metal oxide by indirect or remote plasma irradiation process.

#### Ozone oxidation of zinc metal ion

When the zinc ion dissolved in water contacts with ozone, white deposit of oxides of zinc are produced with the treatment period. Figure 4 illustrates the photograph of the white deposit in a water, which is generated by the oxygen plasma penetration to the zinc ion dissolved water varying the ozone treatment period from 0 (without treatment) to 120 min. After the ozone treatment, the

deposit is observed on the bottom of the tube. To investigate the tendencies of the production of zinc oxides in the water, the dried weight of the deposit obtained from the water is measured changing the oxygen plasma treatment period. Obtained deposit contains oxides of zinc, ZnO and Zn(OH)<sub>2</sub>. ZnO tends to deposit with lower pH, and Zn(OH)<sub>2</sub> deposits with higher pH. With lower pH circumstance, zinc ion and oxygen ion produce the zinc oxide deposit as Eq. (10). When the pH increases, concentration of hydroxide ion increases. The zinc ion reacts with hydroxide ion and then zinc hydroxide is produced as Eq. (11).

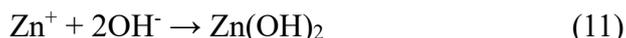
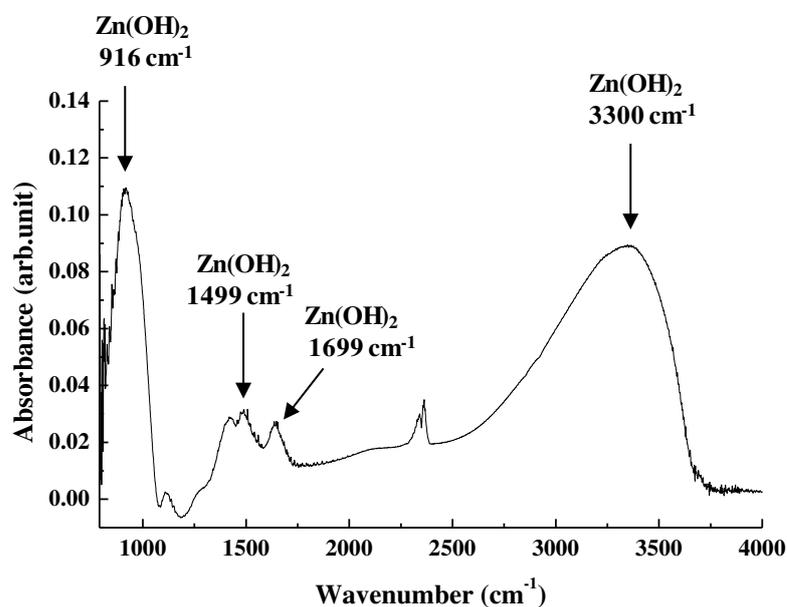


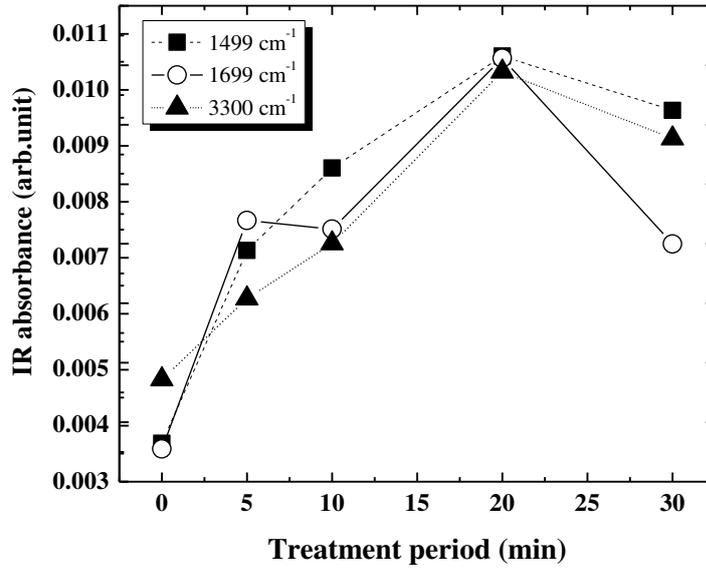
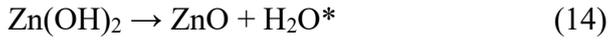
Figure 5 indicates the removal rate of the zinc ion deposit produced in the zinc ion water changing the ozone treatment period. Removal rate of zinc increases with the treatment period almost linearly till 10 min. After 10 min the removal rate of zinc decreases with increasing the treatment period. The ozone treatment for 10 min shows maximum removal rate (29%) of the zinc ion deposit, which is most suitable condition to produce the zinc oxide deposit. The dissolved ozone concentration is controlled by the discharge voltage of the DBD. The production of the zinc deposit increases with the dissolved ozone concentration till 0.41 ppm. When the treatment period increases till 10 min, reactions (12) - (14) occur. Since zinc ions consume the hydroxyl ions those are



**Figure 6.** Typical IR absorbance spectrum of zinc oxide compounds deposit.

generated by the reaction of ozone with water in eq. (9), pH of the water decreases. Then ZnO is dominant in the deposit.



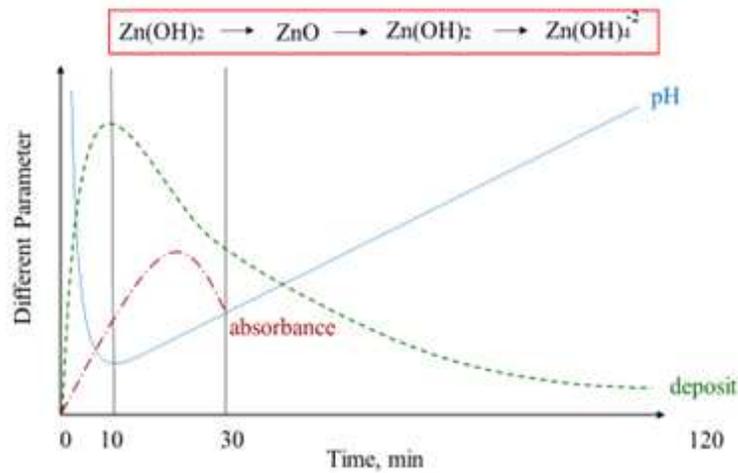


**Figure 7.** IR light absorbance by  $\text{Zn(OH)}_2$  contained in the deposit at different treatment period.

When the treatment period becomes around 10 min, almost of the zinc ion changes to deposit, then  $\text{OH}^-$  starts to increase according to the eq. (9). When the treatment period increases longer than 10 min and ozone is kept injected in the water even after removal of zinc ion from the water,  $\text{OH}^-$  increases and then pH of the water increases. The zinc oxide deposit becomes ionized and again dissolves in the water forming  $\text{Zn(OH)}_2$  and  $\text{Zn(OH)}_4^{2-}$ .  $\text{Zn(OH)}_4^{2-}$  is due to the super oxidation of the zinc oxide combining with  $\text{OH}^-$ , as shown in the eq. (15) and (16), under alkaline condition with pH higher than around 9. Therefore, to remove zinc ion from water forming metal oxide deposit, the penetration amount of the active oxygens to the water must be controlled to keep the pH lower than around 7.5. After 120 min of ozone penetration period, the zinc concentration is 10 ppm which is approximately  $1/4^{\text{th}}$  of the initial zinc concentration (39 ppm).



Figure 6 illustrates typical IR spectrum of the deposit extracted from the zinc ion dissolved water treated by the oxygen plasma penetration. Significant spectral peaks are assigned by the OH bonds in the zinc hydroxide. The zinc hydroxide in the deposit can be the  $\text{Zn(OH)}_2$ . This result indicates



**Figure 8.** Schematic diagram of zinc oxide compounds with different parameter.

that the ZnO, which is generated by the oxidation of zinc ion, has further been oxidized to the zinc hydroxides by the long-time penetration of the oxygen plasma. However, in this experiment, the zinc oxide peak is out of range of the FTIR spectrum. These obtained peaks are similar to those of the zinc hydroxide that is synthesized in water<sup>35,36</sup>. Therefore, the deposit, which is produced by the ozone oxidation of the zinc ion dissolved water, contains several oxides such as the zinc oxide, Zn(OH)<sub>2</sub> and Zn(OH)<sub>4</sub><sup>2-</sup>. Also, from the obtained IR spectra, the significant peak of byproduct of the ozone treatment has not been observed on the spectrum.

According to the Lambert-Berr's law, the zinc oxide amount is proportional to the IR light absorbance of the zinc oxide. Figure 7 shows the IR light absorbance by the Zn(OH)<sub>2</sub> contained in the deposit changing the treatment period, which is obtained from the peak height of the IR spectral peak of the deposit at around the wavenumber of 1499, 1699 and 3300 cm<sup>-1</sup>. The amount of the Zn(OH)<sub>2</sub> in the deposit increases monotonically with the oxygen plasma treatment period up to 20 min and then decreases. Production characteristics of the zinc oxide can be clarified from the different tendencies of depositions shown in Figs. 5 and 7, which indicate generation properties of the zinc oxide+Zn(OH)<sub>2</sub>, Zn(OH)<sub>2</sub> and the Zn(OH)<sub>4</sub><sup>2-</sup>, respectively. The difference in the amount of deposits in these figures indicates the production tendency of zinc oxide. At 30 min the IR light absorbance decreases due to decrease of the Zn(OH)<sub>2</sub> in the deposit. The amount of the Zn(OH)<sub>4</sub><sup>2-</sup> increases constantly with the ozone penetration period, even when the total rate of the removal deposit decreases.

From this experiment, the maximum removal rate of zinc oxide compound deposits found at 10min ozone penetration period where pH is minimum, as shown in Fig. 8. When the treatment period becomes around 10 min, since zinc ions consume the OH<sup>-</sup> those are generated by the reaction

of ozone with water, pH of the water decreases. Then ZnO is dominant in the deposit. When the treatment period increases longer than 10 min, almost of the zinc ion changes into deposit, and then OH<sup>-</sup> starts to increase and pH increases. The zinc oxide deposit becomes ionized and again dissolves in the water forming Zn(OH)<sub>2</sub> and Zn(OH)<sub>4</sub><sup>2-</sup>. IR spectrum peaks also indicates that ZnO has further been oxidized to the zinc hydroxides by the long-term penetration of the oxygen plasma.

## Conclusions

Removal of zinc ion from water was attempted using the nonthermal oxygen plasma dissolved in water. Zinc ion in water can be removed from water as the zinc oxide deposit. The maximum removal rate (29%) of zinc from water is achieved at the treatment period of 10 min, where pH is minimum. Therefore, to remove zinc ion from water forming metal oxide deposit, the penetration amount of the active oxygens to the water must be controlled to keep the pH lower than around 7.5. Because with increasing pH amount of deposit of ZnO decreases. The pH of the zinc dissolved water treated by ozone depends on both zinc and ozone concentration in water. Actually, precise control of the pH is not easy.

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## **Figure Legends**

**Figure 1.** (a) Schematic diagram of the experimental apparatus, and (b) discharge electrode inside tube.

**Figure 2.** (a) Gaseous ozone concentration as a function of the discharge voltage of DBD, and (b) Ozone concentration in water at different penetration period of ozone in water.

**Figure 3.** pH values of tap water and Zn dissolved water at different ozone treatment period.

**Figure 4.** Deposits of Zn oxide compounds in water varying the ozone treatment period.

**Figure 5.** Removal rate of Zn ion from water at different treatment period.

**Figure 6.** Typical IR absorbance spectrum of zinc oxide compounds deposit.

**Figure 7.** IR light absorbance by Zn(OH)<sub>2</sub> contained in the deposit at different treatment period.

**Figure 8.** Schematic diagram of zinc oxide compounds with different parameter.

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Sayma Khanom performed the experiments and compiled the manuscript. Nobuya Hayashi contributed to the conception and design of the research. Both authors discussed and edited the manuscript.

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## **Additional Information**

### **Competing Interests**

The authors declare no competing interests.

# Figures

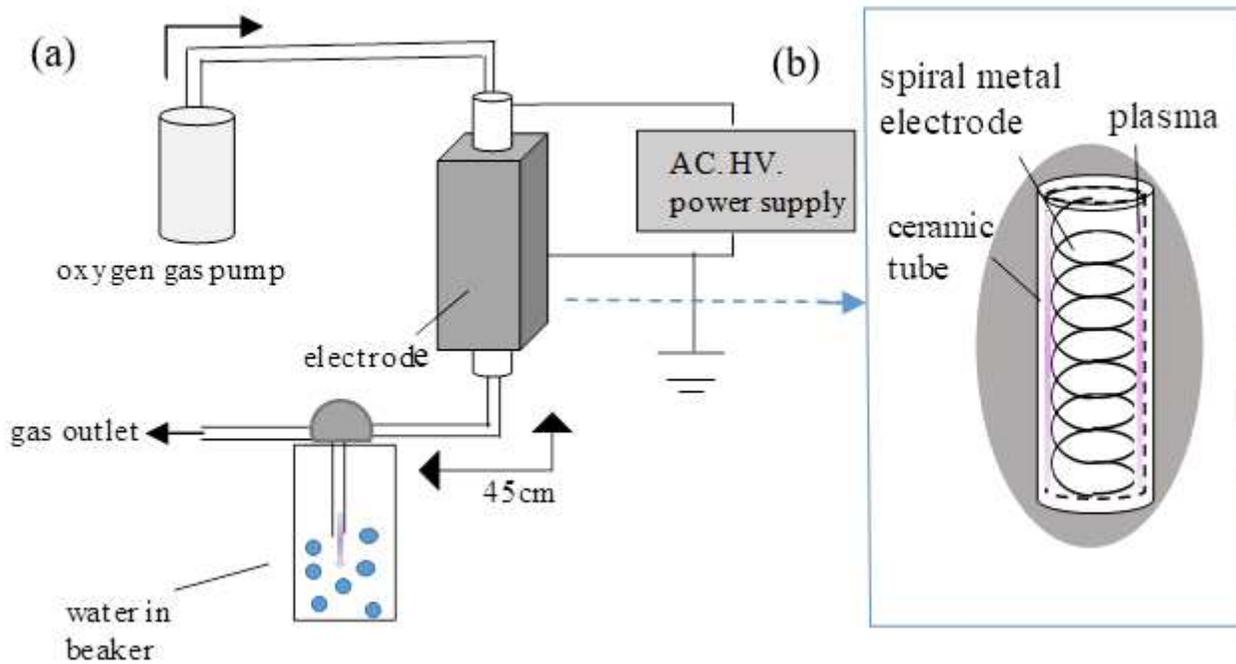


Figure 1

(a) Schematic diagram of the experimental apparatus, and (b) discharge electrode inside tube.

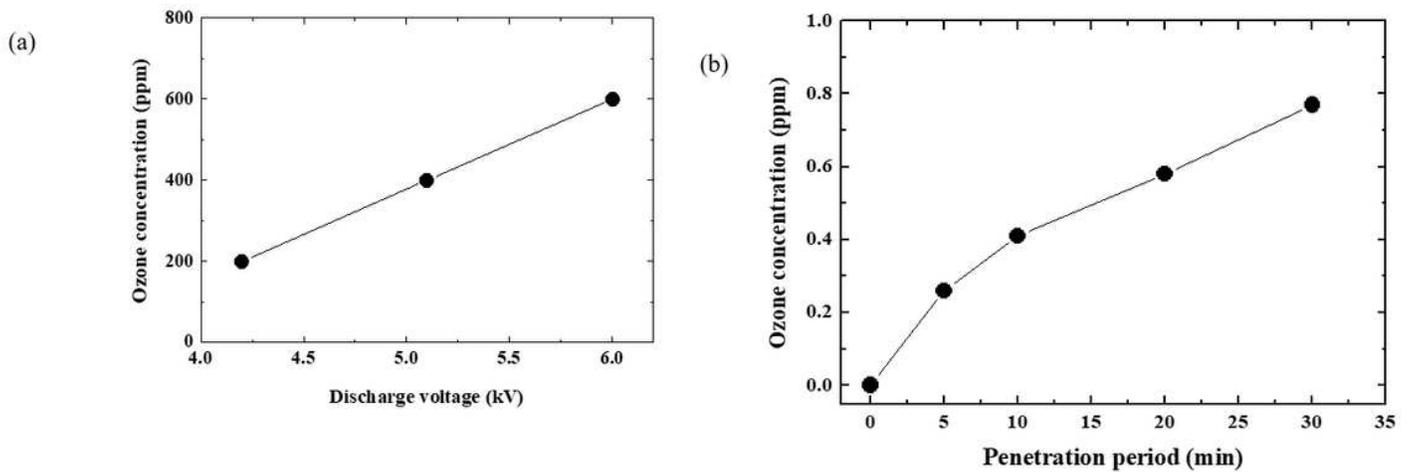


Figure 2

(a) Gaseous ozone concentration as a function of the discharge voltage of DBD, and (b) Ozone concentration in water at different penetration period of ozone in water.

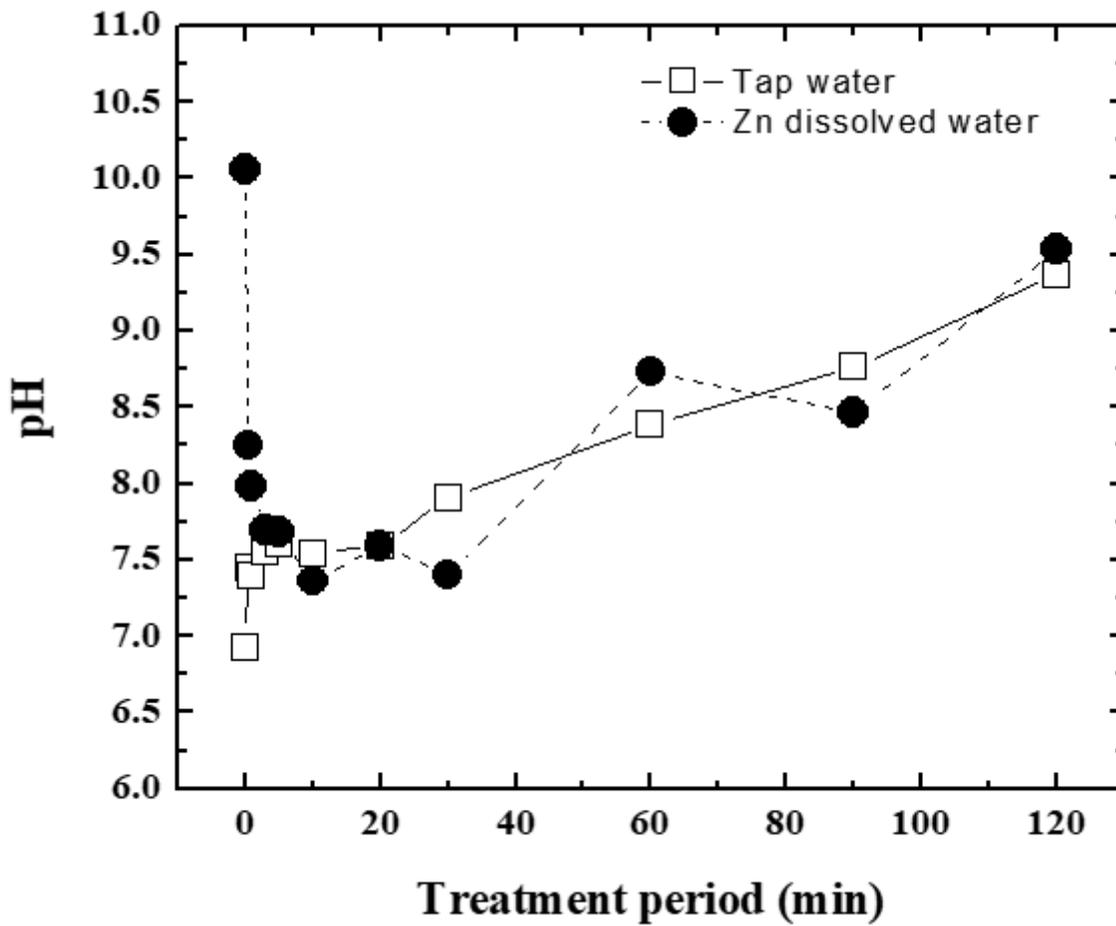


Figure 3

pH values of tap water and Zn dissolved water at different ozone treatment period.

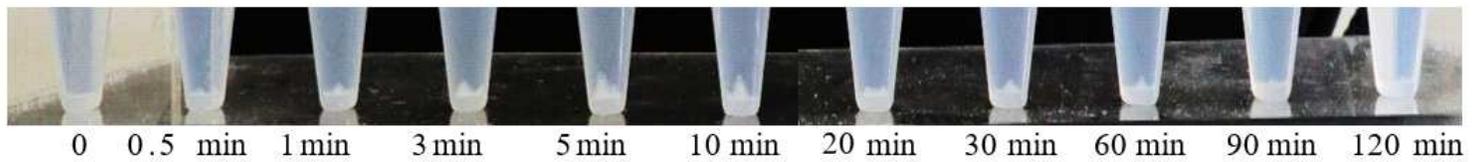


Figure 4

Deposits of Zn oxide compounds in water varying the ozone treatment period.

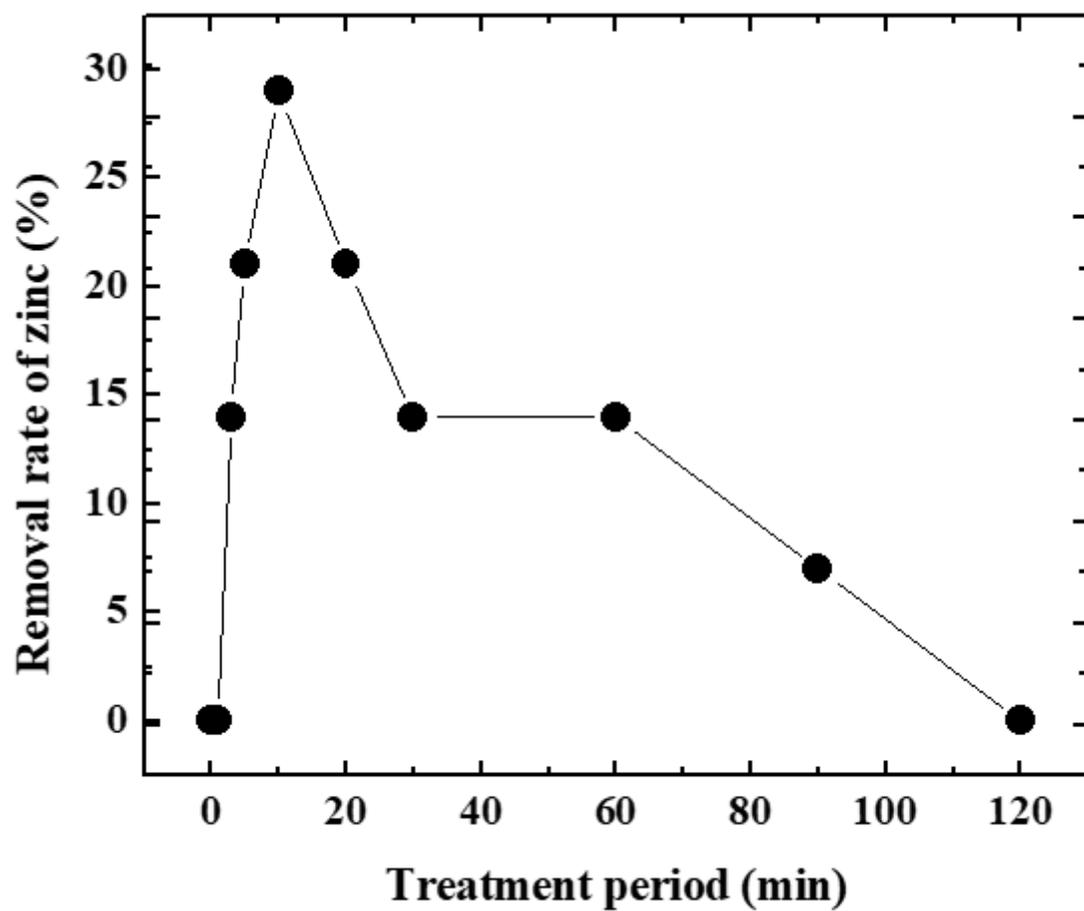


Figure 5

Removal rate of Zn ion from water at different treatment period.

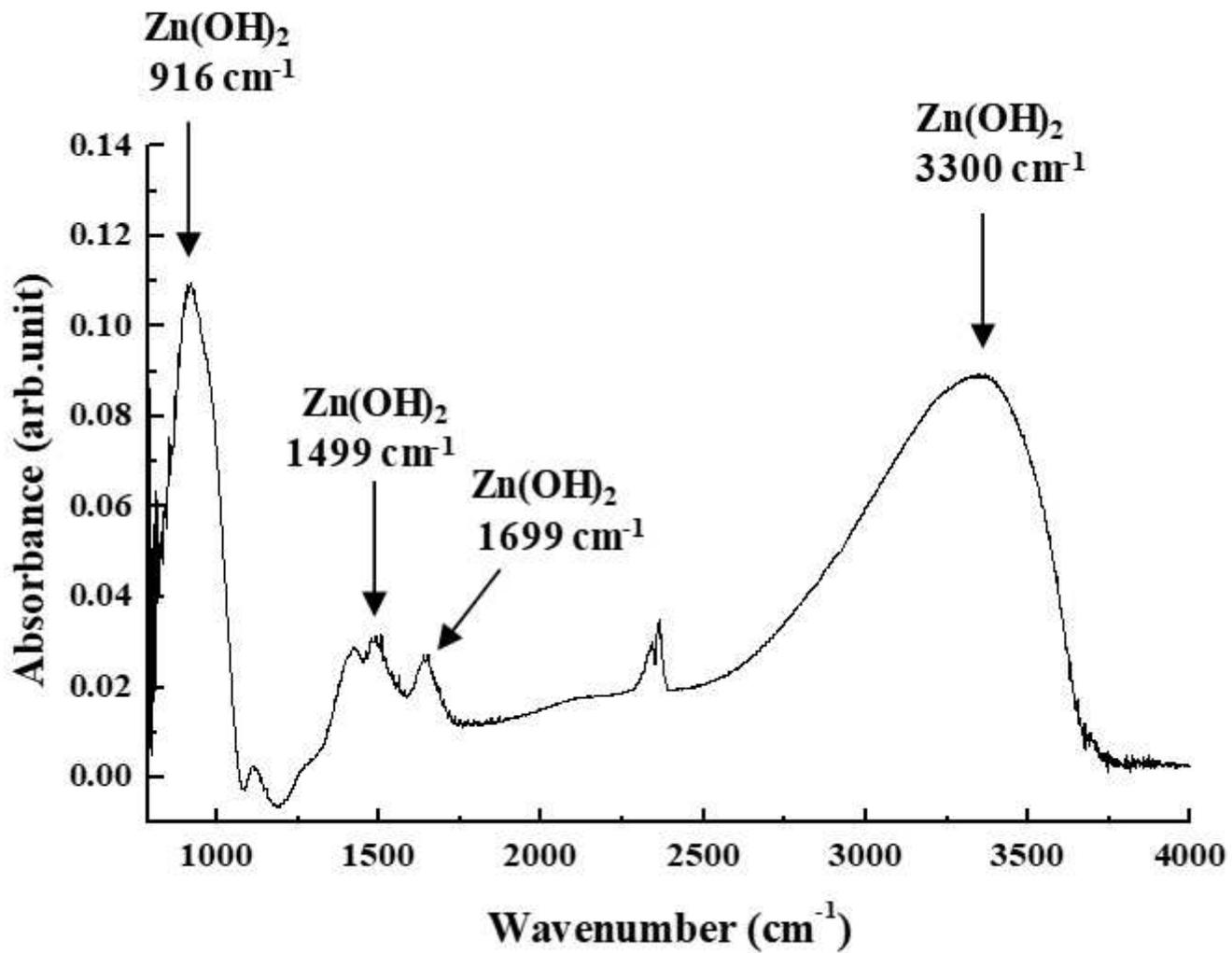


Figure 6

Typical IR absorbance spectrum of zinc oxide compounds deposit.

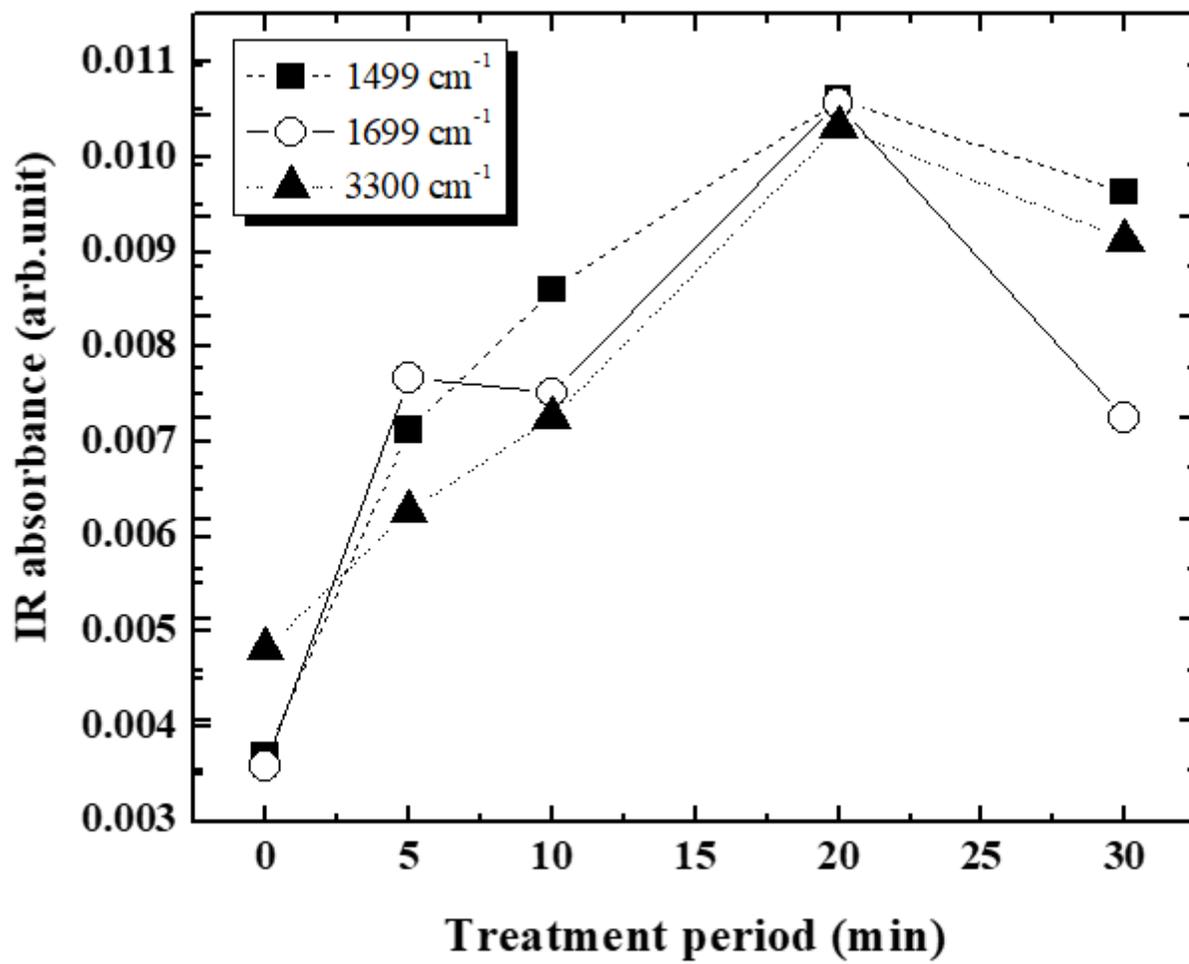


Figure 7

IR light absorbance by Zn(OH)<sub>2</sub> contained in the deposit at different treatment period.

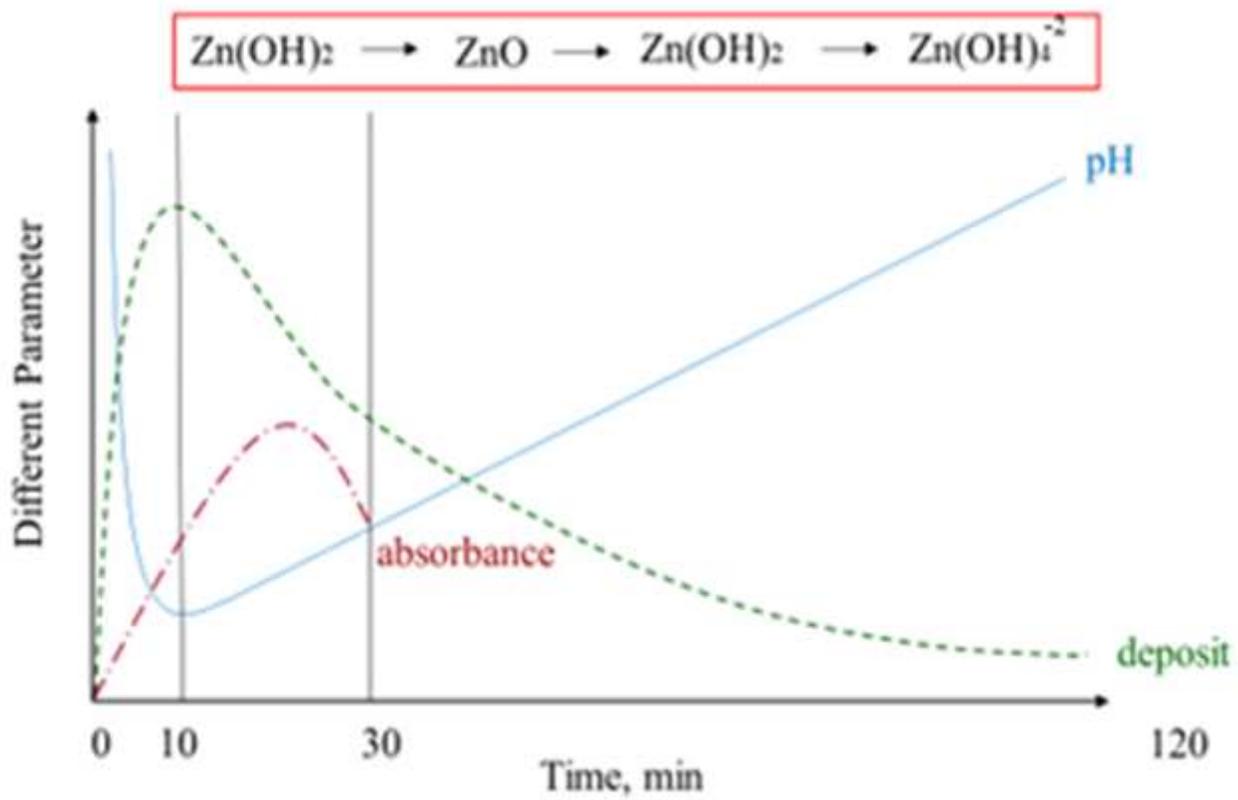


Figure 8

Schematic diagram of zinc oxide compounds with different parameter.