Removal of Dissolved Metal Ions from Water by Plasma Oxidized Precipitation Method

サイマ, カノム

出版情報：Kyushu University, 2023, 博士（学術）, 課程博士
バージョン：
権利関係：

氏　　名　：Sayma Khanom
Name
論 文 名　：
Title　Removal of Dissolved Metal Ions from Water by Plasma Oxidized Precipitation Method
（プラズマ酸化沈殿法による水中溶存金属イオンの除去に関する研究）

区　　分　：甲
Category

論　文　内　容　の　要　旨

Thesis Summary

Non-thermal plasma or low-temperature plasma is a green technology and has been studied for water treatment. But most studies have focused on using low-temperature plasmas to be inactivated microorganisms and to decompose organic compounds for wastewater treatment. However, low-temperature plasmas using oxygen, or any other gas have not yet been tested to remove metal ions from water, which is the most complex issue of today's contamination problems. When the dielectric barrier discharge (DBD) occurs using oxygen gas, energetic free electrons and a variety of active oxygen species are produced in the electrode gap. These active oxygen species would also oxidize metal ions in liquid effectively and these metal oxide deposits can be removed from the water easily using filtration or deposition.

Chapter 1 explains the background of the research and the purpose of the research. This chapter describes briefly both conventional methods and current technology that are normally used for water treatment. Advanced oxidation processes (AOPs) exhibit advantages over conventional treatment methods because of the generation of strong oxidants. Among the AOPs, electrical discharge plasma is widely employed for wastewater treatment. Active oxygen species such as oxygen radicals, OH radical and ozone, which have been used for AOPs, would also oxidize metal ions in liquid. 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. In the this study the removal of metal ion from tap water is attempted by the ozone oxidation method using the DBD plasma and identify its removal effect on plant growth.

Chapter 2 describes the current studies of water treatment by plasma. It also explains the negative effects of heavy metals on the environment and the need for improvement in the current technology for water purification.

Chapter 3 explains the experimental apparatus used in this research and described the procedure of that was done in this experiment. First, the structure and configuration of the atmospheric pressure plasma device using the torch-shape dielectric barrier discharge (DBD) and the characteristics, i.e. gas, temperature, water parameter, amount of active oxygen produced by atmospheric oxygen plasma, were explained. Zinc (Zn) ion in water is produced by 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 8.0 V is applied to one electrode, and then the zinc ion dissolves in water. The ozone oxidation of the dissolved zinc ion is performed by the simple ozone bubbling in the water containing the zinc ion. The ozone is generated by the torch-shaped dielectric barrier discharge (DBD) using the pure oxygen gas with a flow rate of 1.0 L/min. When the high voltage with 5.0 kHz is applied to the discharge electrode, the barrier discharge occurs on the inner surface of the tube, and the oxygen plasma is generated.

Next the process that was followed for making the metal ion water. Then described the method for developing deposits in water by plasma irradiation and measured the removal rate of metal ion from water. The produced ozone is transported into the water vessel and is dissolved in water using a bubbler. The dissolved ozone concentration is controlled by the discharge voltage of the DBD. Effect of the oxidation of the zinc is evaluated by the concentration of the zinc oxide, which deposits on the bottom of the water. The weight of the dried deposit is measured using the precision measure and then calculate the removal rate from the deposit. To specify the composition of the deposit, the produced samples of precipitates are measured using the FTIR with the ATR mode, and the obtained spectra are compared with the typical spectra of zinc oxide. This chapter also describes the methods for the preparation of making different treated water and their application as irrigation on plant. To identify the effect on plant growth gene expression analysis of plant

leaves is also introduced here.

Chapter 4 explains the results of the metal ion dissolved water treatment by oxygen plasma. When the high voltage with 5.0 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 DBD plasma and is ejected from the opening edge of the tube by the oxygen gas flow. From this study, it is identified that the removal rate of the zinc oxide deposit increases initially and then decreases with the treatment period. The maximum removal rate (29%) of zinc ion from water is achieved at the treatment period of 10 min, where pH is lower (7.4). The production of the zinc deposit increases with the dissolved ozone concentration till 0.41 ppm. Initially, the amount of the deposit increases with the ozone treatment period due to the production of both ZnO and $Zn(OH)_2$. After that, the production of $Zn(OH)_4^{2-}$ increases even when the total removal rate of the deposit decreases. When the treatment period becomes around 10 min, since zinc ions consume the OH^- 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 all the zinc ion changes into deposits, and then OH^- starts to increase and pH increases. The ZnO deposit becomes ionized and again dissolves in the water forming $Zn(OH)_2$ and $Zn(OH)_4^{2-}$. IR spectrum peaks also indicate that ZnO has further been oxidized to the zinc hydroxides by the long-term penetration of the oxygen plasma. Therefore, to remove zinc ion from water forming metal oxide deposits, 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 zinc oxides' deposit decreases. The pH of the zinc dissolved water treated by ozone depends on both zinc ion and ozone concentration in water.

This chapter also describes the findings of lead ion removal from water. In this study, Lead (Pb) ion in water is produced by electrolysis using two cylindrical electrodes with 5 mm in diameter and 30 mm in length, which are made of pure lead. The amount of water used in this experiment is 0.2 L and there is no water flow in the water vessel. The concentration of the gaseous ozone is controlled by changing the discharge voltage. The effect of the oxidation of the lead is evaluated by the concentration of the lead oxide, which deposits on the bottom of the water. The weight of the dried deposit is measured using the precision measure and then calculate the removal rate from the deposits. In order to specify the composition of the deposit, the produced samples of deposits are measured using Raman spectroscopy, and the obtained spectra are compared with the typical Raman spectra of lead oxide. Results obtained from this experiment show that removal rate of the deposit increases initially and then decreases with the treatment period. The maximum removal rate (13%) of lead ion from water is achieved at the treatment period of 10 min, where O_3 concentration is 1.52 ppm and pH is 9.7. In this study, first yellow colored β-PbO (Massicot) deposit is produced, then reddish yellow colored α-PbO (Litharge) deposit is produced. After that bright orange to red colored Pb_3O_4 (Tri lead Tetroxide) deposit is formed. Then dark brown to black colored PbO_2 (Lead dioxide) deposit is formed. Until 10 min irradiation period of ozone lead ion reacts with oxygen and forms lead oxide deposits. Until 30 min of ozone penetration period some lead oxide deposits may be again dissociated to form some dissolve lead oxide/lead hydroxides, which results shows decreasing the removal rate. From 60 to 120 min treatment period, with increasing ozone in the water lead oxide deposits again increases and reaches maximum removal rate like 10min treatment period. But with increasing treatment time the composition of lead oxide deposits changes which can be identified both from the color and the Raman spectrum. From the Raman spectra, the generation properties of lead oxide compounds are recognized. The Raman spectrum of α-PbO, β-PbO and Pb_3O_4 is identified except PbO_2. But the dark brown to black colored deposit indicates the presence of PbO_2. Therefore, to remove lead ion from water forming lead oxide deposits, the penetration amount of the active oxygens to the water must be controlled to 1.52 ppm and pH should be controlled at 9.7.

Chapter 5 explains the removal effects of metal ions from water by oxygen plasma on plant growth. In this study, three different water along with control (tap water) are used as irrigation water to observe the effect on plant growth. *Arabidopsis thaliana* is used as a model plant for this experiment. $Zn+O_3$(10mins) and $Zn+O_3$ (30mins) are produced through 10mins and 30mins of oxygen plasma irradiation on Zn water, respectively. Results obtained from this experiment show that all the growth parameters like plant height, seed weight, leaf area index of the *Arabidopsis plant* showed that $Zn+O_3$ (10min) gives the best performance followed by control and the worst performance given by $Zn+O_3$ (30min) followed by Zn water. Gene expression analysis shows that cell wall strengthening occurs in Zn water treatment and the defense response of plant improves in both $Zn+O_3$ (10min) and $Zn+O_3$ (30min) treatment. Therefore, 10min O_2 plasma treated of zinc water $Zn+O_3$ (10min) can recover the zinc effect on the growth of Arabidopsis plants.

Chapter 6 summarizes the results of this study. So, it can be concluded that plasma application will be effective in water treatment for the removal of metal ions.