# Decomposition of Cu-EDTA in wastewater using pulsed streamer discharge

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**Abstract:** The pulsed streamer discharge is a nonthermal plasma technique that generates extremely reactive species which are more likely able to degrade the heavy metal complexes from wastewater. In this study, we propose a novel method to decompose Cu-EDTA using the pulsed streamer discharge from a simple point electrode. The decomposition of Cu-EDTA is characterized by high-performance liquid chromatography and UV-Vis spectrophotometer. In addition, an estimation of the generated reactive oxygen and nitrogen species is reported.

**Keywords:** Wastewater treatment, Cu-EDTA, Pulsed streamer discharge.

## 1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is a complexing agent that is being used in electroplating, printing, and dyeing industries, to enhance the solubility and stability of the heavy metal ions [1]. Reacting with the heavy metal ions, EDTA forms metal complexes that possess great potential threats to the human body by accumulating in the cells and damaging vital organs, and to the environment by degrading the soil quality. As these metal complexes are chemically stable, it is extremely challenging for the traditional methods to decompose them. Therefore, there is an urgent requirement of alternative methods for eliminating the heavy metal complexes.

Since the last decade, advanced oxidation processes (AOPs) have been used for decomposing metal complexes including Cu-EDTA, Pb-EDTA, Ni-EDTA, etc. based on the consideration that the chelate bonds between complexing agents and heavy metals are broken accompanied by the release of free heavy metal ions. However, a few limitations also emerged during those processes. Nowadays, electrical discharge plasma is widely employed for wastewater treatment. In the strong electric field region, gases are excited and ionized and form non-thermal plasma (NTP), where the generated reactive species ($\cdot$O, $\cdot$OH and $O_3$, etc.) attack the pollutant molecules, resulting in their degradation. However, a few studies have been carried out on the decomposition of heavy metal complexes by the NTP.

Previous studies [2-4] have reported Cu-EDTA decomposition by using dielectric barrier discharge assisted by alkaline precipitations and reported the effects of input energy, initial concentration, solution pH, feeding gas flow rate, etc. They triggered NTP in a Plexiglass cylinder and then transferred the generated substances into the sample. However, their decomposition processes were based on the generation of the long lived reactive species, and the discharge plume was not directly in contact with the liquid. In this study, we treated wastewater containing Cu-EDTA by using pulsed streamer discharge with a simple needle to ground electrode system, where the generated reactive species directly touched the liquid surface. The effects of the discharge on the solution pH and conductivity are discussed, and the decomposition rate and energy efficiency are calculated. In addition, the changes in Cu-EDTA concentration and UV-Vis absorption spectra due to the discharge treatment are discussed. Finally, an estimation of the generated reactive nitrogen and oxygen species (RONS) during the decomposition process is made.

## 2. Experimental

### 2.1 Discharge setup and chemicals

Figure 1 shows the discharge configuration used in this study where a stainless steel needle with outer diameter 1.2 mm is placed at 5 mm above the liquid surface. A ring electrode with outer diameter 30 mm and inner diameter 25 mm is inserted in the liquid as the ground. A pulsed voltage source (SUEMATSU ELECTRONICS) is used to generate the discharge from the needle tip. The voltage and discharge current waveforms were observed by an oscilloscope (IWATSU, DS-5624A) via a high voltage probe (Tektronix, P6015A) and a 0.1-V/A current probe (Pearson, 2878), respectively. The Cu-EDTA stock solution was prepared in the laboratory by mixing $CuSO_4.5H_2O$ and EDTA-2Na solutions with a molar ratio of 1:1, and prior to use, the working solution of 0.3 mmol/L was obtained by diluting it with deionized water. The processed volume of the liquid is 50 ml in this study.

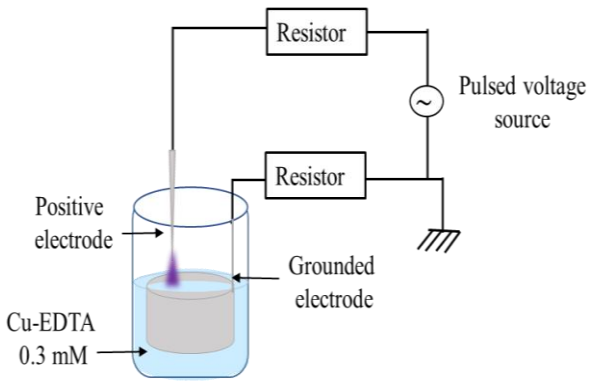


Figure 1. Schematic of the discharge setup

### 2.2 Analysis and characterization method

The high performance liquid chromatography (HPLC, JASCO) with UV-detector (JASCO, UV-2075 plus) and a C18 analytical column (Unifinepak) was used to detect the concentration of Cu-EDTA. The mobile phase was the mixture of chromatographically pure methanol and 0.02 M tetra butyl ammonium bromide solution with deionized water with a volume ratio of 1:1. The flow rate was 1.0 mL $min^{-1}$ and the detection wavelength was 254 nm. The Cu-EDTA removal rate and energy efficiency were calculated as equations (1) and (2), respectively, based on the evolution of the concentrations.

$$Removal\ rate = \frac{C_{initial} - C_t}{C_{initial}} \times 100\% \quad (1)$$

$$Energy\ efficiency = \frac{m_{Cu}}{P.t} \times 100\% \quad (2)$$

where $C_{initial}$ and $C_t$ are Cu-EDTA concentrations at the treatment time 0 min and t min, respectively, $m_{Cu}$ is the amount of removed Cu, $P$ is the discharge power.

The absorption spectrums of Cu-EDTA solution, $NO_2^-$, $H_2O_2$, and $NO_3^-$ were obtained using a UV-vis spectrophotometer (JASCO, V600) with a quartz cell. The pH and conductivity of the Cu-EDTA solution before and after the treatment were measured by a pH/COND meter (Horiba, D-54) using a pH probe (Horiba, 9615S) and a conductivity probe (Horiba, 9382), respectively.

## 3. Results and discussion

### 3.1 Degradation of Cu-EDTA

Figure 2 depicts an example of typical waveforms of the pulsed voltage and the discharge current at 15 kV. The voltage waveform has a pulse width of 50 ns and a rise time of 20 ns. The pulse energy obtained from the product of the pulsed voltage and the discharge current was 3.33 mJ, and the repetition rate was 300 pps. Upon applying the voltage to the positive needle, the discharge was triggered directly to the liquid surface up to 90 minutes. It is considered that when discharge is triggered, reactive species including ·OH and $H_2O_2$ are generated in the gas phase, and they transfer to the liquid surface. Figure 3 shows the HPLC chromatograms of Cu-EDTA at treatment times 0, 30, 60, and 90 min. The peaks detected at the retention time of 3.35 min are Cu-EDTA, and it is evident in the figure that the peak intensity decreases as the treatment time elapses. The blue peak stands for the untreated Cu-EDTA, and has the maximum peak intensity, whereas the 90 min treated peak (grey line) has the lowest intensity. The removal rate of Cu-EDTA, and the energy efficiency with respect to the treatment time are represented in figure 4. It is observed that the Cu-EDTA removal rate increases up to 33.7% within 90 min of treatment. On the other hand, energy efficiency decreases with a higher energy input. The maximum energy efficiency reached 0.2848 g $kWh^{-1}$ within 30 min of treatment at an input power of 0.99 W. However, compared to the previous results our energy efficiency is in good term although our discharge system is not optimized.

Furthermore, the effects of discharge on the pH and electroconductivity of Cu-EDTA solution were observed.

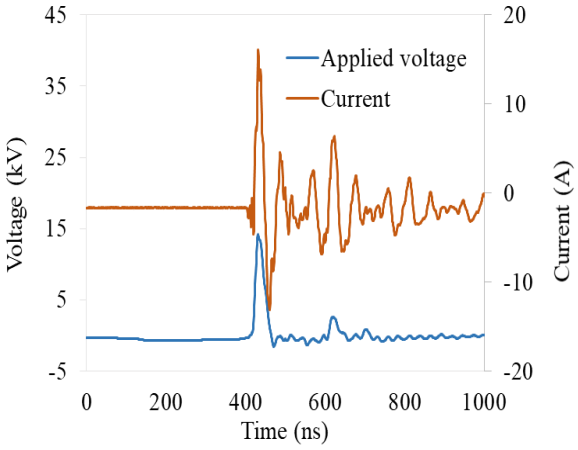


Figure 2. Typical waveform of pulsed voltage and discharge current

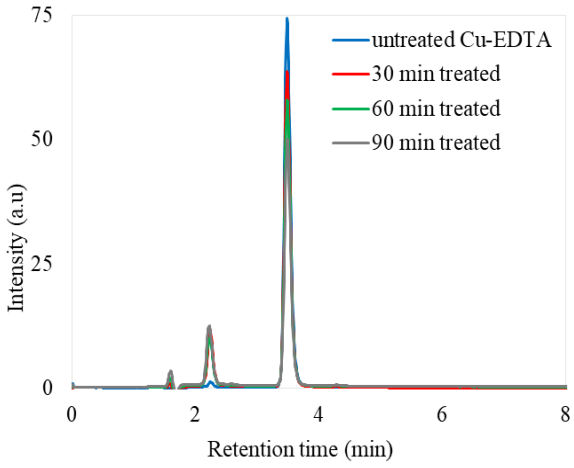


Figure 3. HPLC chromatograms of plasma treated and untreated Cu-EDTA

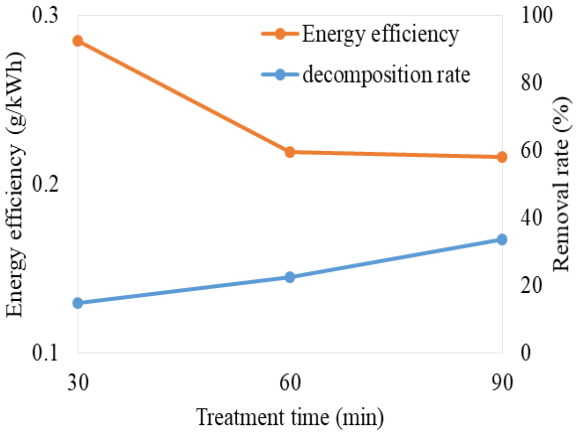


Figure 4: Cu-EDTA removal rate and energy efficiency with respect to the treatment time

It was found that the electroconductivity of the solution gradually increases from 108 $\mu Scm^{-1}$ to 186 $\mu Scm^{-1}$, and pH decreases from 4.26 to 4.0 after 90 min of plasma

treatment. The results are considerate as during the plasma treatment reactive species are generated and they are supposed to penetrate the liquid surface and Cu(II) ions are also assumed to be released.

### 3.2 UV-Vis spectrum of untreated Cu-EDTA and plasma treated Cu-EDTA

The UV-Vis absorption spectra of Cu-EDTA before and after the plasma treatment were measured in order to observe the light absorption in untreated and treated Cu-EDTA. The results are shown in figure 5. The blue line shows the absorbance for untreated Cu-EDTA, and red, grey, and green ones stand for 30, 60, and 90 min treated Cu-EDTA, respectively. From the figure, it is observed that the untreated Cu-EDTA has a wide absorption spectrum. After 30, 60, and 90 mins treatment, the intensity of the wide spectrum reduces, and there is a new peak at about 208 nm, 215 nm, and 220 nm, respectively. It is assumed that as time elapses, more and more reactive species are emitted due to the discharge, and they may react with the $N_2$ and $O_2$ present in the air as well as with the Cu-EDTA in the liquid. Therefore, the intensity of the Cu-EDTA spectrum reduces and the absorbance peak increases.

In order to confirm the generated reactive species during the decomposition of Cu-EDTA using pulsed streamer discharge in air, we measured the absorption spectra of $NO_2^-$, $NO_3^-$, and $H_2O_2$ to perform a curve fitting routine. Oh *et al.* [5] has shown the curve-fitting of the UV–vis spectra of plasma activated water using the reference spectra of $H_2O_2$, $NO_2^-$, $NO_3^-$ and $O_2$. Based on that idea, we made a curve fitting routine for Cu-EDTA. Figure 6 shows the UV–vis spectra of $H_2O_2$, $NO_2^-$, and $NO_3^-$, which are used to curve fit. Fitting these spectra with the Cu-EDTA spectra shown in figure 5, we found the followings:

(a) Treated Cu-EDTA peaks below 220 nm, and shoulders between 220 to 240 nm are fitted with the $H_2O_2$, $NO_2^-$, and $NO_3^-$ spectra.
(b) The absorption falling part between 240 and 280 nm is fitted with the $H_2O_2$, and $NO_3^-$ spectra.
(c) The absorbance after 280 nm fits with the $NO_3^-$ spectra.

Figure 7 shows a comparative analysis of the curve fitted spectrum along with the treated Cu-EDTA spectra. The curve fitted spectrum is obtained by summing up the reference spectra of RONS and the untreated Cu-EDTA. The concentration of $H_2O_2$, $NO_2^-$, and $NO_3^-$ used for obtaining the reference spectra are- (a) 0.015% of $H_2O_2$, (b) about 7 $mgL^{-1}$ of $NO_2^-$, and (c) about 8.5 $mgL^{-1}$ of $NO_3^-$. From the figure it is observed that the spectrum is in good relation with the treated Cu-EDTA spectra although the absorbance intensity differed. The difference in the absorbance may occur as the actual amount of reactive substances generated during the experiments may vary. In addition, while obtaining the $H_2O_2$ reference spectrum, it was observed that a higher concentration of $H_2O_2$ led to the widening of the absorbance shoulder. Since the curve fitted graph is almost consistent with the treated Cu-EDTA, it is considerate that the amount of $H_2O_2$ in the liquid is comparatively lower. However, a detailed study is necessary to find out the actual amount of the generated species and their roles on the decomposition process of Cu-EDTA.

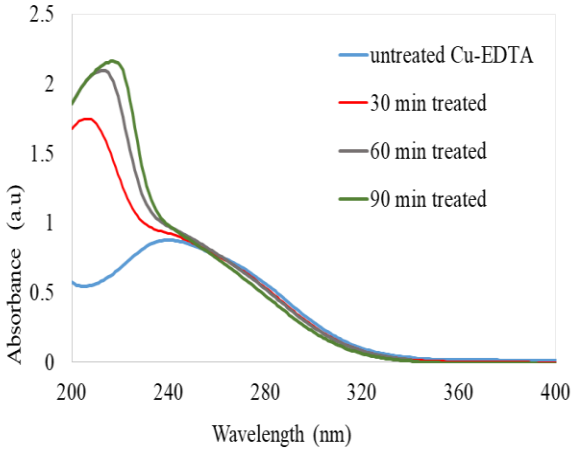


Figure 5. UV-Vis evolution of treated and untreated Cu-EDTA

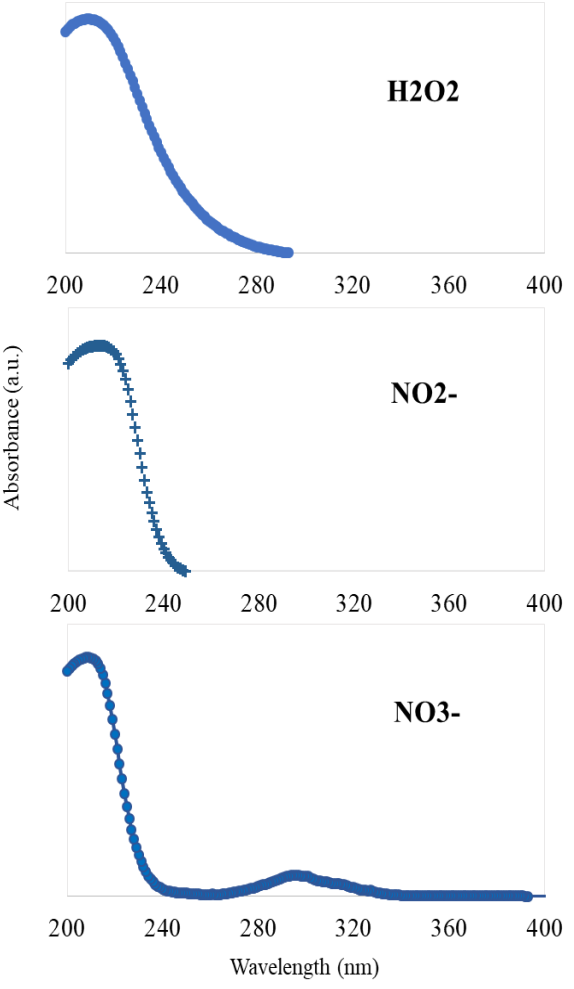


Figure 6. UV–vis absorption spectra for $H_2O_2$, $NO_2^-$, and $NO_3^-$

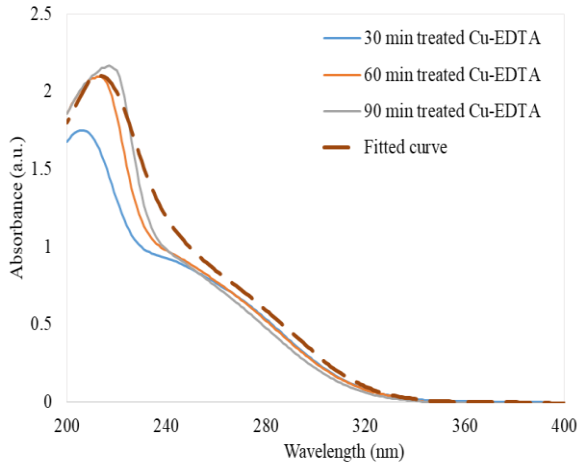


Figure 7. Comparison of the curve fitted spectrum and treated Cu-EDTA spectra

## 4. Conclusion

In this work, a simple plasma oxidation process for the degradation of Cu-EDTA in wastewater has been proposed where discharge occurs at the gas phase, and touches the liquid directly. The proposed technique has the advantages of being simple yet direct NTP method over the other existing methods with complex reactor arrangement. In this study, 33.7% Cu-EDTA decomposition is achieved with 90 min of treatment. In addition, the maximum energy efficiency of 0.2848 g $kWh^{-1}$ is obtained with 30 min of treatment. The UV-Vis spectrum of the treated Cu-EDTA confirmed the decrease in Cu-EDTA spectrum intensity, and the appearance of new peaks give the idea of generated reactive species. Furthermore, the relative amount of $H_2O_2$, $NO_2^-$, and $NO_3^-$ generated during the NTP treatment is estimated. However, their contribution to the decomposition process, and the decomposition pathway needs to be studied further.

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