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Plasma-enhanced Degradation of Chlorinated Compounds

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Abstract: Degradation of halogenated organic compounds is now becoming an urgent technology due to their persistent toxicity to human beings and wildlife. This paper discusses the potential of plasma in the application of degradation. The release of inorganic chloride ions was regarded as an indicator of the degradation evaluation. The results show that the concentration of chloride ions exponentially increase with treatment time. The time-resolved spectra of the plasmas were also briefly introduced, which could be a useful tool to understand the degradation mechanism.

Keywords: Degradation, plasma, halogenated organic compounds, visualization, spectrum

1. Introduction

Halogenated organic compounds (HOCs) are used in varieties of industrial applications and they have been also used to produce different consumer products, such as pesticides, solvents, electrically insulating coatings, and plastics, which indicates the high consumption of HOCs in the world. However, due to the toxicity and persistence properties of HOCs, it is easy for the bioaccumulation, thus the spread of HOCs becomes a big challenge for human beings and wildlife. They are reported to be even found in the water supply and food chain [1]. Moreover, the high bond energy of the C-X (e.g. C-F, C-Cl, C- Br, C-I) causes a big challenge for dehalogenation. To date, the developments of dehalogenation technologies (catalytic methods [2], biological approaches [3], etc.) provide alternative solutions. During these cases, additional pathways are introduced which will reduce the reaction difficulty.

For example, photons with high energy can be emitted to induce an electron transfer state, thereby providing excessive electrons to achieve the release of inorganic chloride ions. However, these technologies require a relatively complex procedure to achieve useful performance [4]. Biological approaches are also promising, however, the transfer of HOCs through cell membranes is still less effective. Nevertheless, it requires a suitable environment for selected bacteria. The intermediates might also be a potential risk to the environment. Therefore, the development of degradation of chlorinated compounds with flexible operation and universal device support is expected. Plasma has been widely studied and it can be classified due to different working media, morphologies, and generation methods. During all cases, intense ionization and dissociation are accompanied, thereby degradation of chlorinated compounds by chemical reduction with the release of inorganic chloride ions can be achieved.

This study presents the experimental results of the degradation of monochloroacetic acid by repetitive plasma. The release of the chloride ions from the solution was recorded and compared with different working conditions. The spectrum of plasma emission was also analyzed.

2. Methodology

2.1 Experimental setup

Fig.1 shows the schematic diagram of the experimental setup for plasma generation and visualization. A tungsten needle electrode with a diameter of 1 mm and a tip radius of 30 μm was set in a quartz cell. The grounded electrode is a stainless-steel plate. The needle electrode was connected to a pulsed power supply. The applied voltage was adjustable in the range of ± 30 kV, and then a pulsed current with flexible duration and a rise time of about 200 ns was generated through a DC capacitor bank of 666 pF. A current-limit resistor of 2 kΩ was connected to the needle in series. A by-pass resistor of 20 kΩ was connected to the needle in parallel to cut the wave tail of the current.

The voltage across the electrode and the current of the plasma were recorded by an oscilloscope (LeCroy WS 510), with a voltage probe (LeCroy, PPE 20 kV), and a current coil (Bergoz, FCT-016-1.25 WB). A delay generator (Stanford Research Systems, DG535) was used to control the trigger.

The visualization was performed by shadowgraph and Schlieren, and the principles were introduced in previous works [5].

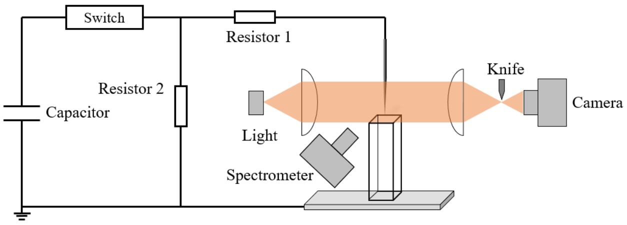

Fig. 1. Experimental setup.

2.2 Degradation evaluation

The sodium chloroacetate (99.0%, Sigma-Aldrich) was used to make solutions with different concentrations. The fluorescent agent PACKTEST (Kyoritsu Chemical-Check Lab., Corp.) was conducted to detect the concentration of chloride ions as an indicator to evaluate the degradation. A microplate absorbance reader for 96 well plates was used to detect the relative absorbance at different wavelengths to check the concentration of chloride ions.

3. Results and discussion

To test the performance of the indicator, different concentrations of chloride ions were achieved by using saline and diluting to desired concentration in the range of 0-300 mg/L. Then the relative absorptance of different wells in the plate was checked at different wavelengths. The relationship between relative absorptance and the concentration of chloride ions is shown in Fig. 2. It can be found that the absorptance profile shows a linear relationship in the whole detected range at 405 nm and 620 nm. It suggests that both wavelengths can be used for the concentration evaluation. Considering the values in relative absorptance have larger differences at 405 nm, it is easier to achieve a higher signal-noise ratio, 405 nm was selected for detection in our protocol.

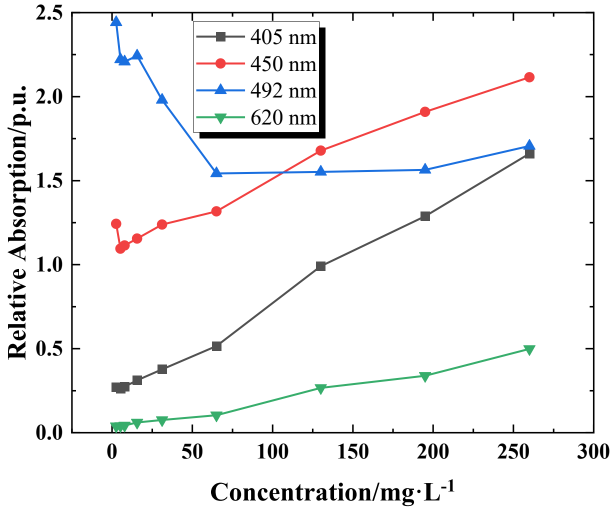

Fig. 2. Relationship between relative absorptance and the concentration of chloride ions.

Fig. 3 shows the time-resolved spectra of the plasma in the typical experimental condition. The figure was accumulated by 10000 individual tests with a repetitive frequency of 1 kHz. The duration of one pulse is 1 ms while the duty is 30%, which makes the accumulation of images representative and distinguishable. The spectra at the needle tip were recorded in the 365 – 708 nm in Fig. 3 with a resolution of 5.3 nm. Two main bands of light emission can be recognized, which correspond to the instants of the voltage application and reverse. The contents of wavelengths for the two bands show no difference, however, the total intensity, as well as the width, changes significantly. In this setup, the reverse voltage causes only half of the light emission compared with the applied voltage. Also, there are mainly two regions in which the wavelengths can be recognized, mainly located in 350-450 nm. The emission line for Hα can be also clearly distinguished in Fig. 3. The results reveal the dominant species generated in this process might be from nitrogen gas as well as water vapor.

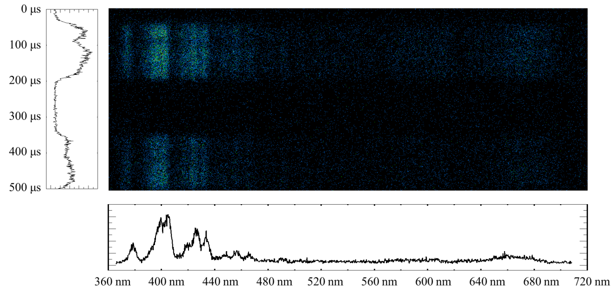

Fig. 3. Time-resolved spectra.

The concentration of chloride ions with respect to the treatment time by plasma was recorded in this study. The results found that the mass concentration of chloride ions, which remained in the target solution, increases exponentially when the treatment time increase. These results confirm the potential for enhancement of degradation of chlorinated compounds by using plasma. We believe that the strong reduction potential of reactive species can be one of the key reasons for dichlorination. The determination of the dominant species in this process will be discussed in detail based on the results of the time-resolved spectra in the future.

4. Conclusion

The degradation of chlorinated compounds has been experimentally explored by repetitive plasma. The release of the chloride ions from the monochloroacetic acid solution was regarded as an indicator and the effect was recorded and compared with different working conditions, regarding the treatment time. The results suggest that repetitive plasma effectively releases the chloride ions from chlorinated compounds by breaking the C-Cl bond. The time-resolved spectral emission of plasma was also adopted to examine the reductant species which can be used to interpret degradation mechanisms. Further study is required to understand the pathways of dechlorination in this study.

5. Acknowledgements

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6. References

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