Refractory Organic Solute Decomposition in Water using Microwave Plasma

著者	Ishijima Tatsuo, Saito Ryota, Sugiura Hiroyasu, Toyoda Hirotaka
journal or publication title	Transactions of the Materials Research Society of Japan
volume	36
number	3
page range	475-478
year	2011-09-01
URL	http://hdl.handle.net/2297/36049

doi: 10.14723/tmrsj.36.475

Transactions of the Materials Research Society of Japan 36[3] 475-478(2011)

Refractory Organic Solute Decomposition in Water using Microwave Plasma

Tatsuo Ishijima, Ryota Saito*, Hiroyasu Sugihara*, and Hirotaka Toyoda*
Plasma Nanotechnology Research Center, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
Fax: 81-52-789-3152, e-mail: ishijima@nuee.nagoya-u.ac.jp
*Department of Electrical Engineering and Computer Science, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
Fax: 81-52-789-3152, e-mail: ishijima@nuee.nagoya-u.ac.jp

Microwave excited plasma source with slot antenna in water is a novel plasma applicable to materials processing in liquid. In order to apply this microwave plasma source to a practical use for solute decomposition, it is necessary to evaluate the decomposition efficiency for refractory organic solutes and understand the decomposition process of solution as well. In this paper, the microwave plasma treatment was demonstrated through decomposition of refractory organic solutes such as acetic acid, polyvinyl alcohol (PVA), and 4-chloro-2-methylphenoxy acetic acid (MCPA) in aqueous solutions. Total organic carbon concentration and high-performance liquid chromatography measurements revealed that the refractory organic substances such as acetic acid, PVA, and MCPA were decomposed by microwave plasma. Intermediate products of MCPA were investigated by gas chromatography coupled to a mass spectrometry and ion chromatograph during MCPA degradation using microwave excited plasma.

Key words: Microwave plasma, solute decomposition, refractory organic substance

1. INTRODUCTION

Recently, increasing environmental issues have motivated research into new technologies to purify polluted effluents from factories, hospitals and so on. So far, the most common water purification technology is ozone method where ozone dissolved in water effectively decomposes chemical species without causing damage to the environment. Recently, however, advanced water treatment technologies that can decompose refractory organic materials become important, and plasma production technique in liquid has been given attention because the plasma can produce various reactive species such as ozone or hydroxyl radical (OH). As these species have much higher chemical reactivity than ozone, almost all organic chemical compounds such as trichloroethylene, dyes, phenoxy-acetic acid herbicides, and so on [1] can be decomposed in a very efficient manner under synergetic effect of UV radiation or electrochemical reactions.

So far, electrical breakdown in liquid has been realized by extremely high voltage [2,3] applied to metal electrodes in liquid, or by microwaves injection into liquid through coaxial cables [4]. As an alternative technique to produce plasma in liquid, we have proposed slot-antenna excited microwave discharge, and have demonstrated decomposition of methylene blue (MB) as an example. In order to apply this technique to practical use, however, it is necessary to decompose not only simple organic substances but also various complex organic substances those are hardly decomposed by conventional purification techniques. As the first example, this technique has been successfully applied to purification of contaminated liquids [5,6]. In this paper, various organic substances those are difficult to be decomposed in conventional chemical techniques, i.e., acetic acid (CH_3COOH), polyvinyl alcohol (PVA) and 4-chloro-2-methylphenoxy acetic acid, $C_9H_9ClO_3$ (MCPA), are treated. Temporal evolution of total organic carbon (TOC) concentration for acetic acid and MCPA concentration were investigated during microwave plasmas treatments.

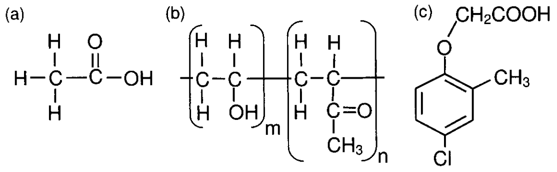

Fig.1 Structure formulas of (a) acetic acid, (b) polyvinyl alcohol (PVA), and (c) 4-chloro-2-methylphenoxy acetic acid (MCPA).

2. EXPERIMENTAL

Detailed experimental apparatus has been described in elsewhere [6] and is briefly explained. A cylindrical metal vessel (30 cm in diameter, 15.5 cm in length) was partly filled with organic solutions. The vessel was equipped with a scroll pump to control the pressure in the vessel at pressures of 4~6.6 kPa. Solution temperature, which is one of important parameters to determine the H_2O vapor pressure, was monitored by a thermocouple and was controlled at a constant temperature during the plasma treatment using a water-cooling system.

Pulsed 2.45 GHz microwave (power: < 3 kW, pulse repetition frequency: 10 kHz, on-time duty ratio: 35%) was guided along a rectangular waveguide and was injected into the solution through three slot antenna[6]. Optical emission spectra were monitored through an optical fiber with a compact multichannel CCD-array detector (wavelength: 200-1100 nm) and a quartz window located in front of the slot antenna. Commercial reagent acetic acid (99.7%), PVA (Kuraray Poval, PVA-CST, <94%), and MCPA (98%) were used as samples of refractory organic solute.

Aqueous sample solutions of acetic acid, PVA, and MCPA at concentrations of 10 ppm (1.6×10^{-4} mol/l), 10 mg/l, and 100 ppm (5.0×10^{-4} mol/l), respectively, were prepared by dissolving reagents in deionized water. The structure formulas of acetic acid, PVA, and MCPA are shown in Fig. 1(a), (b) and (c), respectively.

To evaluate rates of reagent decomposition by the plasma treatment, concentration of total organic carbon (TOC) were measured using a TOC analyzer (Sievers 900). Here, TOC was defined as concentration of any organic chemical compounds except for carbon dioxide (CO_2). The concentrations of MCPA and by-products were measured with a high-performance liquid chromatography (HPLC) with UV-VIS detector. Qualitative analysis of the sample solution after the plasma treatment was performed on a gas chromatography coupled to a mass spectrometry (GC-MS). Concentrations of acetic acid and formic acid were estimated from ion chromatograph (IC) measurement [7].

3. RESULTS AND DISCUSSION

At first, the microwave plasma production was examined using the deionized pure water to give an insight into chemically-reactive species in liquid. From optical emission spectroscopy, emission lines of H_α(656 nm), H_β (486 nm), O I (777 nm) and OH (~309 nm) were observed [5]. Like the cases of earlier plasma treatment studies in aqueous solutions, results of the optical emission spectroscopy suggests that several water molecules at plasma-liquid interfaces are activated by energetic electron and H, O and hydroxyl radicals (OH) from water (H_2O) vapor are produced [8-12].

These chemically reactive species produced from water molecules dissociation are considered to be useful for the decomposition of organic substances. It is known that the OH radical has higher oxidation potential (2.85 V) than those of O_3 (2.07 V), or H_2O_2 (1.78 V), and this fact implies that OH radicals have important role for the decomposition of organic materials.

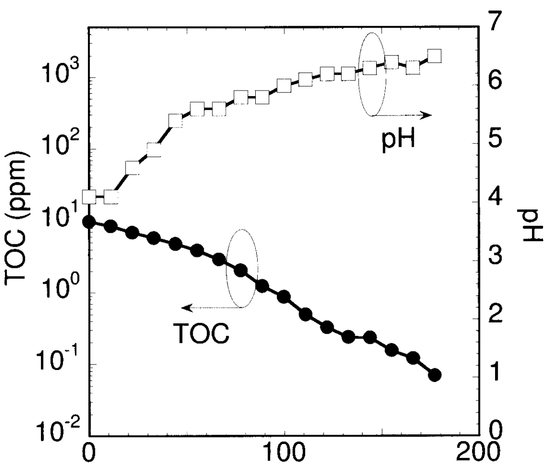

Fig.2 TOC and pH variations in acetic acid decomposition process as a function of cumulative energy input per unit solution volume.

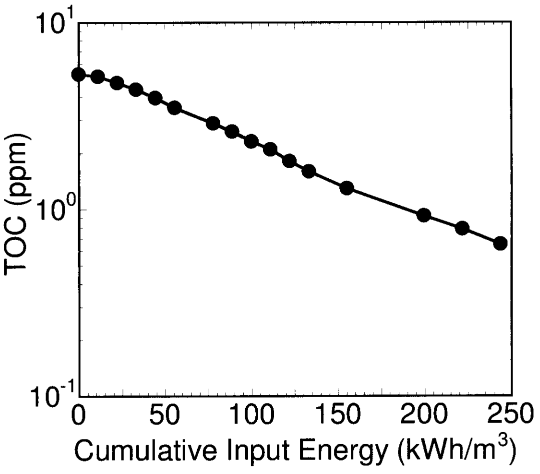

Fig.3 TOC concentration of PVA as a function of cumulative energy input per unit solution volume.

Compared to very low chemical reactivity for ozone, acetic acid has remarkably high chemical reactivity for OH as shown in Table I[13,14]. Therefore it is strongly expected that the acetic acid, one of typical refractory organic solutes, can be decomposed by the microwave-excited plasma. To demonstrate this, TOC in the acetic acid solution was measured by the TOC analyzer and the decomposition rate was evaluated. Figure 2 shows TOC and pH of the solution as a function of the cumulative energy. Microwave power and pressure were 570 W and ~6.6 kPa, respectively. Solution temperature was controlled at 308 K. During the microwave plasma treatment, TOC decreased exponentially with increasing the cumulative input energy, i.e., the treatment time. This result suggests that the microwave plasma can decompose refractory materials and reduce their TOC concentration below ~0.1 ppm. Furthermore, decrease in the TOC in Fig. 2 indicates that the acetic acid is finally decomposed into CO_2 or H_2CO_3 and is removed from the water as CO_2 evaporation into the gas phase. This can be also supported by the pH result. The initial pH value before the treatment is ~4.0 because the acetic acid is dissolved in the water. With increasing the plasma treatment time, i.e., the cumulative input energy, the pH value increases monotonically and reaches ~6.5. It is known that the pH value of deionized water is ~ 6.5 under atmospheric environment because CO_2 in the air is

Table I. Reaction rate coefficients for ozone and OH radical[13,14].

Substances	Molecular formula	K_{O3} / L mol^{-1} $^{-1}$	K_{OH} / L mol^{-1} $^{-1}$
Acetic acid	CH_3CO_2H	$< 3\times10^{-5}$	1.6×10^{7}
Acetone	CH_3COCH_3	3.2×10^{-2}	1.1×10^{8}
Carbonic acid ion	CO_3^{2-}	$< 1\times10^{-1}$	3.9×10
Formic acid	HCO_2H	5	1.3×10^{8}
Benzene	$C_6 H_6$	2	7.8×10^{9}

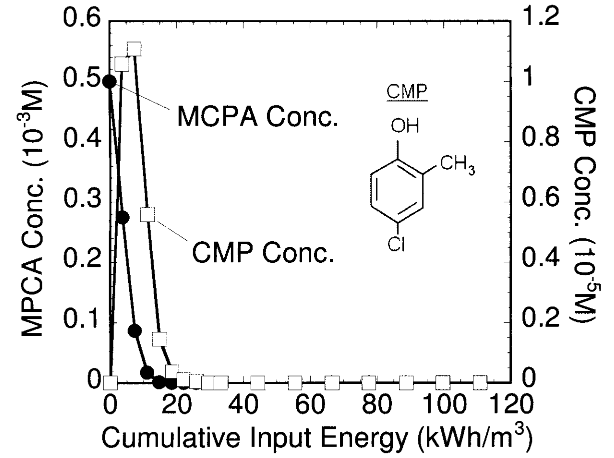

Fig.4 MCPA and CMP concentration as a function of cumulative energy input per unit solution volume.

dissolved in the water, and the result indicates that the acetic acid is decomposed by the plasma treatment.

In a previous work of phenol decomposition [15], it has been pointed out that there is a synergistic effect between the pH value and the decomposition reaction and that the decomposition reaction is enhanced when the pH is shifted to acidic. The present experiment, however, shows that the decomposition rate of the acetic acid is slightly low at low pH value (~4) and increases with increasing the pH value, suggesting that the synergistic effect is not the case in this experiment. Little influence of the pH value on the decomposition process may be attributed to the difference in the plasma production mechanism between the microwave plasma and other plasma production methods such as DC or RF plasma. The latter discharge processes utilize high electric field between two electrodes to initiate bubble production by Joule heating followed by the electric breakdown. In the case of the microwave plasma production, however, bubbles production is caused by the microwave heating and electric conductivity of the liquid has little influence on the bubble formation.

As the next example of the refractory organic substance, PVA decomposition was demonstrated. 9 liter PVA solution was treated by the microwave excited plasma at a power of 570 W and a pressure of ~ 4 kPa. In this experiment, the solution temperature was kept at 300 K during the microwave plasma treatment to ensure that the PVA decomposition is not caused by thermal chemical reaction. Figure 3 shows the TOC concentration of PVA solution as a function of the cumulative energy. Monotonic decrease in the TOC was observed with increasing the cumulative energy, suggesting that C-C bonds of the PVA is continuously cracked by the plasma treatment and that the PVA is converted into CO_2. Present result indicates that the microwave plasma can decompose stable polymer with large molecular weight even at the room temperature.

Finally, as toxic and refractory organic substance, MCPA decomposition was demonstrated. Microwave power and pressure were 570 W and ~6.6 kPa, respectively. Solution temperature was controlled at 308 K. In the decomposition process of the MCPA, weak bonds are preferentially attacked and 4-chloro-2-methyl phenol (CMP), CH_3COO^-, and $HCOO^-$ are produced as intermediate substances. Such substances can be detected by GC-MS and IC and their concentrations are shown in Figs. 4 and 5 as a function of the cumulative input energy. By the microwave plasma treatment, MCPA concentration monotonically decreases with increasing the cumulative energy and is less than 1×10^{-6} M at a cumulative input energy of 15 kWh/m^3 shown in Fig.4. In contrast to the monotonic decrease in the MCPA, CMP concentration shows a maximum at a cumulative input energy of 11 kWh/m^3 and then decreases. This means that the CMP is produced in the course of the MCPA decomposition and that the CMP is also decomposed by the plasma treatment. The observed maximum CMP concentration was $\sim1\times10^{-5}$ M, which corresponding to the 2% of initial MCPA concentration. This result suggests that cracking of oxygen-carbon bonds connected with acetic acid is not occurred selectively without breaking other chains in MCPA.

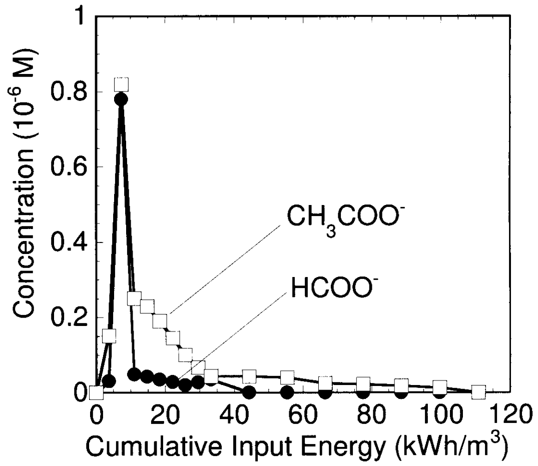

Fig.5 CH_3COO^- and $HCOO^-$ concentration measured by ion chromatograph for MCPA decomposition process as a function of cumulative energy input per unit solution volume.

Concentrations of carboxylic acid ions (CH_3COO^- and $HCOO^-$) show their maximum at a cumulative input energy of 11 kWh/m^3, and then decrease as shown in Fig. 5. This result indicates that not only oxygen-carbon bonds connected with acetic acid but also carbon-carbon bonds in acetic acid are cracked simultaneously in the early stage of MCPA degradation. The concentrations of both CH_3COO^- and $HCOO^-$ are about 10 times less than that of CMP, indicating that CMP is preferentially produced compared with carboxylic acid ions (CH_3COO^-, $HCOO^-$) produced as intermediate organic substances from MCPA. After giving a maximum concentration, the decrease in $HCOO^-$ concentration is faster than that of CH_3COO^- concentration. This may be explained by the difference in the reaction rate coefficient between the formic acid and the acetic acid with OH radical reaction (Table I).

To investigate further decomposition process, TOC

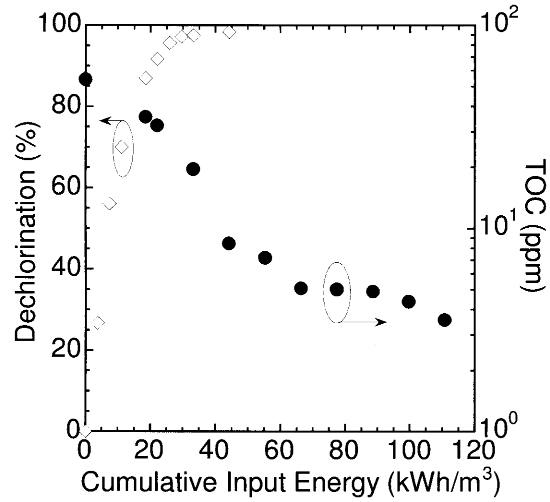

Fig.6 Dechlorination and TOC concentration as a function of cumulative energy input per unit solution volume.

and Cl$^-$ measurements are performed. Figure 6 shows TOC and dechlorination as a function of the cumulative input energy. Here, dechlorination is defined as a degree of degradation of chlorinated organic compounds with release of inorganic chloride ions to detoxify a substance. As increasing cumulative input energy, dechlorination increases rapidly and exceeds ~90% at a cumulative input energy of ~20 kWh/m^3. These results show that microwave plasma attacks chlorine bonds as well as other bonds (c.f. Figs. 4 and 5) simultaneously with high-decomposition rate in the early stage, indicating that the capability of large amount of toxic organic solutes decomposition by microwave plasma treatment.

The results of TOC measurements show that TOC monotonically decreases with increasing the cumulative input energy. It is interesting that there is an inflection of the TOC decrease at a cumulative input energy of ~35 kWh/m^3. This point corresponds to the disappearance of the benzene ring structure in the microwave plasma treated MCPA solution (c.f. Fig. 4), suggesting that benzene ring decomposition contributes to the TOC decrease in the initial stage of the MCPA treatment.

4. CONCLUSION

Microwave plasma was applied to decomposition process for 9 liter aqueous solutions containing refractory organic solutes to realize a practical use. As examples of refractory organic substances, acetic acid, PVA and MCPA decomposition were investigated. TOC analyzer was used to realize the decomposition capability. Furthermore HPLC, GC-MS and IC measurements were performed to investigate decomposition process and intermediate products by microwave plasma treatment.

It was revealed that the acetic acid, which had remarkably low chemical reactivity for ozone, was decomposed exponentially by microwave plasma below 0.1 ppm TOC. The result of acetic acid decomposition was also supported by the pH measurement. In the case of PVA decomposition, TOC decreased monotonically with increasing the cumulative input energy, suggesting that C-C bonds in the long chained polymer was continuously cracked by the microwave plasma treatment. From TOC measurements, carbons containing the decomposed refractory organic compounds were finally evaporated through CO_2 into the gas phase.

HPLC, GC-MS and IC revealed that CMP, CH_3COO^- and $HCOO^-$ were detected as intermediate substances during MCPA degradation process by microwave plasma, and that the concentration of those intermediate substances were much smaller (<2%) than that of MCPA. It was realized that intermediate substances were produced in the course of MCPA decomposition and those were also decomposed simultaneously. Furthermore IC measurement revealed that microwave plasma could detoxify MCPA through reductive dechlorination. It was pointed out that the initial stage of TOC reduction was owing to the benzene ring decomposition. These results showed that large amount of refractory and toxic organic solution can be treated with the slot antenna excited microwave plasma.

Acknowledgement

The authors would like to thank Prof. H. Matsuda and Dr. M. Kubota, Department of Energy Engineering and Science, Nagoya University for HPLC, GC-MS, and IC measurements.

References

[1] B.R. Locke, M. Sato, P. Sunka, M.R. Hoffmann, J.S. Chang, Ind. Eng. Chem. Res. **45**, 882-905 (2006).
[2] J.S. Clements, M. Sato and R.H. Davis, IEEE Trans. Ind. Appl. IA-**23**, 224 (1987).
[3] K. Kitano, H. Aoki and S. Hamaguchi, Jpn. J. Appl. Phys. **45**, 10B 8294 (2006).
[4] S. Nomura, H. Toyota, S. Musaka, H. Yamashita, T. Maehara and M. Kuramoto: Appl. Phys. Lett. **88**, 211503 (2006).
[5] T. Ishijima, H. Hotta, M. Sato and H. Sugai, Appl. Phys. Lett. **91**, 121501 (2007).
[6] T.Ishijima, H. Sugiura, H. Toyoda, and H. Sugai, Plasma Sources Sci. Technol. **19**, 015010 (2010).
[7] Y. Kojima, T. Fujita, E.P. Ona, H. Matsuda, S. Koda, N. Tanahashi and T. Asakura, Ultrason. Sonochem. **12**, 359 (2005).
[8] K.S. Susanta, S. Rajeshwar and K.S. Ashok, J. Electrochem. Soc. **145**, 2209 (1998).
[9] J.Z. Gao, Y. J. Liu, W. Yang, L.M. Pu, J. Yu, Q.F. Lu, Plasma Sources. Sci. Technol. **12**, 533 (2003).
[10] P. Sunka, V. Babicky, M. Clupek, P. Lukes, M. Si-mek, J. Schmidt and M. Cernak, Plasma Sources. Sci. Technol., **8**, 258 (1999).
[11] A. Sugitaro, T. Ohshima and M. Sato, Thin. Solid. Films, **407**, 174 (2002).
[12] L.R. Grabowski, E.M. van Vlednuizen, A.J.M Pemen, and W.R. Rutgers, Plasma Sources. Sci. Technol. **16**, 226 (2007).
[13] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data, **17**, 513-886 (1988).
[14] P. Neta, R.E. Huie, A.B. Ross, J. Phys. Chem. Ref. Data, **17**, 1027-1284 (1988).
[15] Y.J. Liu and X.Z. Jiang, Environ. Sci. Technol. **39**, 8512 (2005).

(Received February 14, 2011; Accepted March 28, 2011)