Persistent Organic Pollutants Treatment in Wastewater Using Nanosecond Pulsed Non-Thermal Plasma

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Abstract—Persistent organic pollutants (POPs) are bioaccumulative and environmentally persistent substances. As POPs cannot be decomposed by conventional water treatments, a new treatment method is required. Several attempts to decompose organic compounds have been performed using various types of plasma reactors. Nano-second (ns) pulsed discharges enable higher energy efficiencies of plasma processing and have already demonstrated their advantages at such gas phase treatment processes as NOx treatment and ozone generation. However, few reports exist on water treatment using ns pulsed discharge plasmas. This study reports on efforts to decompose acetic acid solutions using ns pulsed discharge method by spraying solution into the gas phase plasma region; it also evaluates the influence of pH and gas flow rate on wastewater decomposition. The time course of pH and concentration of Total Organic Carbon (TOC) in the solution is evaluated under several treatments.

Keywords—Persistent organic pollutants (POPs), nano-seconds pulsed discharge, acetic acid, water treatment

I. INTRODUCTION

The global water environment continues to worsen mainly due to organic pollution caused by agricultural and domestic and industrial wastewater. Wastewater includes many kinds of pollutants. Among them, persistent organic pollutants (POPs) present serious problems due to their high environmental persistence and hormone-like activation. Further, they are resistant to environmental degradation and thus cannot be decomposed by conventional water treatments. The search for a highly efficient POP treatment method has brought attention to direct water treatment by discharge plasma [1], [2]. Discharge plasma can make reactive oxygen species (ROS) efficiently by high energy electrons, and thus offers promise as a method of wastewater treatment; for example, a nano-second (ns) pulse generator generating a pulsed high voltage with 5 ns of duration and 2.5 ns of rise and fall times was developed by Namihira et al. [3].

In pulsed discharges, it is known that the discharge propagation consists of a streamer discharge phase followed by a glow-like discharge phase. A temperature rise occurs during the glow-like discharge phase, causing energy loss; however, ns pulsed discharges enable higher energy efficiencies of plasma processing, as they inhibit change to the glow-like discharge phase [4].

While ns pulsed discharges have been previously demonstrated for gas phase treatment such as NOx treatment and ozone generation [5]–[7], no reports exist on their efficacy for water treatment. In this study, the application of ns pulsed discharge plasma on water treatment was performed. In the experiment, a method of spraying wastewater into a gas-phase plasma region was used. The discharge reactor had coaxial cylindrical geometry, and the treated wastewater was circulated and continuously treated in the reactor. A paper by Malik et al. indicated that this method is the most effective for wastewater treatment using discharge [8]. Minamitani et al. also have reported water treatment by pulsed discharge in sprayed water droplets [9]–[11].

In discharge plasma water treatments, it is known that water pH influences degradation characteristics of organic materials in water [12], [13]; furthermore, higher pH concentrations in solutions have been reported to improve discharge treatment efficiency. A number of plasma water treatments use oxygen atmosphere gas because it can generate ROS abundantly. In the present study, the evaluation of the influence of pH and pure oxygen gas flow rate on the decomposition of 1000ppmv acetic acid solution using ns discharge plasma. In many research institutes, acetic acid is used as a treatment model because it is difficult to decompose by ozone [14]–[17]. The acetic acid concentration used was higher than in other experiments since our objective is industrial waste water directly treatment.

II. EXPERIMENTAL SETUP

The acetic acid solution was composed of pure acetic acid (99.7%, Nakalai Tesque) dissolved in deionized water. The concentration was 1000ppmv, and liquid measure was 1 L. Sodium hydroxide was used for preparation of pH, which was measured by a pH meter (TOA-DKK, HM-25R). Total organic carbon (TOC) is the amount of as a carbon found in an organic compounds and is often used as a non-specific indicator of water quality or cleanliness. Concentration of acetic acids solution TOC was measured using a TOC meter (TOC-Vw, Shimadzu corporation) and compared before and after experiments. Initial states TOC of the acetic acid solution were measured averages of 340 mgTOC/L.

Fig. 1(a) is a schematic diagram of the ns pulse forming line, which is illustrated in Fig. 1(b). The generator consists of a coaxial high-pressure spark gap switch as a low induc-
tance self-closing switch, a triaxial Blumlein line as a pulse-forming line, and a voltage transmission line which transmit energy from the triaxial Blumlein line to the load. The triaxial Blumlein line and transmission line were filled with silicone oil (KF-96, Shin-etsu Chemical, Japan) as an insulation and dielectric medium.

The triaxial Blumlein line consists of an inner rod conductor, a middle cylinder conductor, and an outer cylinder conductor. The inner, the middle, and the outer conductors of the triaxial Blumlein line are concentric. The outer conductor of the triaxial Blumlein line was grounded, and the inner conductor connected to the charging inductor. For operation of the ns pulse generator, the middle conductor of the triaxial Blumlein line was charged through a charging port that was connected to a pulsed charging circuit.

Fig. 2 shows a schematic diagram of micro-second pulse generation circuit, which consists of a DC source (TDK-Lambda ALE152A Series-20kV), a charging resistance $R$ of 600 $\Omega$ (Enamelled, TAMA-OHM), charging capacitors $C_1$ and $C_2$ of 8.4 nF (High withstand voltage type capacitor, TDK FHV-15AN), self-making inductors $L_1$ of 15 $\mu$H, $L_2$ of 70 $\mu$H, $L_3$ of 5.5 mH, a thyratron switch (TGI-1000/25), and a self-making pulse transformer (PT). A thyratron switch controller was used to control charging time and output pulse repetition rate. The PT had a primary to secondary winding ratio of 5:15. The voltage polarity of ns pulse generator outputs to inverse polarity of charging voltage, which can control by PT polarity. A capacitive voltage divider was mounted on the transmission line between the triaxial Blumlein and load to measure output voltage of the ns pulse generator. Discharge current through the load was measured using a current transformer (MODEL CT-F1.0, Bergoz Instrumentation, France).

Fig. 3 shows the experimental setup for wastewater treatment. A concentric coaxial cylindrical reactor was employed as the discharge vessel. The central H.V. wire was made of tungsten, 0.3 mm in diameter placed coaxially in a stainless taper cylinder with respective upper and lower internal diameters of 76 mm and 60 mm and length of 1,000 mm. Solution
was sprayed into the reactor from a spray unit which was mounted in the upper inlet of the reactor. The spray passed downward through the plasma regions. The water flow rate was controlled by a pump (Iwaki magnet pump MD-70R with Inverter) at 2.5 L/min at standard flow rate and circulated to be continuously treated in the reactor. The reactor was filled with oxygen gas and flowed into the reactor through a PFA tube at a flow rate of adjusted by mass flow controller. Positive pulse polarity was chosen for the discharge in the reactor as nanosecond pulsed discharge has no significant difference in polarity [5]. The output voltage of the ns pulsed generator was controlled at 40 kV by adjusting the gas pressure of the SF6 in spark gap switch. A pulse repetition rate of 200 pulses per second (pps) was used. A digital oscilloscope (DPO71254C, Tektronix) recorded the signals from the capacitive voltage divider and the current transformer.

Fig. 4 shows typical waveforms of the applied voltage and the discharging current in the reactor during acetic acid treatment. The applied ns pulse had such as peak voltage of 40 kV, peak current of 400 A and the pulse duration about 5 ns determined by the full width at half maximum.

III. RESULTS AND DISCUSSION

A. Effect of oxygen flow rate

The acetic acid solution (1 L, 1000ppm, pH 3.2) was treated using ns pulse discharge plasma wastewater treatment system. Experimental conditions are as follows: treatment time was three hours, pump circulation rate was 2.5 L/min, pulse peak voltage was 40 kV, a pulse repetition rate was 200 pps and the gas was atmospheric pressure pure oxygen with the gas flow rates at 100 mL/min, 1 L/min or 3 L/min. After treatment, gas vented harmlessly. Fig. 5 shows time changes of TOC concentration removal ratio detected from treated acetic acid for different oxygen flow rates. Acetic acid was decomposed by OH dissolved in solution. Eqs. (1)–(3) shows that how to generate ‘OH by discharge. O(\textsuperscript{3}P) is the excited state of oxygen and the O(\textsuperscript{1}D) is ground state of oxygen.

\[
\begin{align*}
H_2O + e^- & \rightarrow 'OH + H + e^- \quad (1) \\
e^- + O_2 & \rightarrow O(\textsuperscript{3}P) + O(\textsuperscript{1}D) + e^- \quad (2) \\
O(\textsuperscript{1}D) + H_2O & \rightarrow 2'OH \quad (3)
\end{align*}
\]

When oxygen flow rate is decreased, ozone concentration...
increases because ozone retention time in the reactor become longer. When the reactor is under higher ozone concentration, the generation rate of oxygen radicals due to self-decomposition reactions of ozone and discharge increases. For this reason, a low oxygen flow rate increases treatment ratio. From the point of view of practical application, reducing oxygen usage also has the decided advantage of a lower cost.

Fig. 6 shows time changes in pH detected from treated acetic acid at different oxygen flow rates. At 1 L/min and 3 L/min, changes of pH are minimal after three hours of discharge treatment. However, pH decreased with treatment time in the case of 100 mL/min. This is attributed to the large amount to high acidity byproducts generated due to acetic acid decomposition as oxygen flow rate decrease.

B. Initial pH dependencies

The influence of pH was evaluated. In this case, acetic acid solution pH was prepared 3.2, 5.0, 7.0 or 11.6 by mixing of NaOH. Oxygen flow rate under all experimental conditions was fixed at 1 L/min, and other conditions were the same as section A. Fig. 7 shows the time course of TOC concentration removal ratio detected from treated acetic acid for different initial pH levels. For an initial pH of 3.2, TOC removal ratio increased with treatment time and reached up to 25% at 3 hours. At the initial pH 5.0, TOC removal rate becomes twice that of pH 3.2 by 2 hours treatment; after this, TOC removal rate rises dramatically, and reached up to 80% after 3 hours treatment. At the initial pH 7.0, TOC removal rate was nine times higher than pH 3.2 until two hours treatment. Removal ratio was saturated after two hours treatment because it already reached 93% at two hours. Finally, TOC removal ratio reached 98% at three hours. The case of pH 11.6 shows a similar trend as pH 7.0. These results indicate that pH has significant effect for acetic acid treatment by discharge. As such, it can be said that ns pulsed discharge with pH control can decompose efficiently acetic acid in water. The reason why TOC removal rate was affected by pH is because ‘OH is generated not only by discharge plasma but also by self-decomposition reactions of ozone. When solution pH over the acid dissociation constant ($pK_a$) of the acetic acid of 4.76 and decreases concentration of acetic acid, progress of acetic acid ionize and abundance ratio of $\text{CH}_3\text{COO}^-$ increases. In other words, progress of neutralize reaction by decomposition of acetic acid. When the acetic acid further decomposes and pH exceeds the neutralization point, a surplus of hydroxide ions occurs in the solution. The hydroxide ion concentration increases, and self-decompose reaction of ozone is increasingly activated. Eq. (4) shows that the self-decompose reaction of ozone is greater activated by pH increase. Under Eqs. (5)-(7), ‘$\text{O}_2^-$’ and $\text{HO}_2^-$ generates ‘OH.

\[
\begin{align*}
\text{O}_3 + \text{OH}^- & \rightarrow '\text{O}_2^- + \text{HO}_2'^- \quad (4) \\
\text{HO}_2'^- & \rightarrow \text{H}^+ + '\text{O}_2^-' \quad (5) \\
\text{O}_3 + '\text{O}_2^- & \rightarrow '\text{O}_3^- + \text{O}_2 \quad (6) \\
'\text{O}_3^- + \text{H}_2\text{O} & \rightarrow '\text{OH} + \text{O}_2 + \text{OH}^- \quad (7)
\end{align*}
\]

Fig. 8 shows time courses of pH for different initial pH levels. The initial pH of 3.2 shows almost no changes of pH during three hours of discharge treatment due to the buffer capacity of the acetic acid. pH of deionized water shows almost no change as it does not include the organic substances of reactive with ozone in it. For an initial pH of 5.0 which is near the $pK_a$ value of the acetic acid 4.76, pH slowly increases for two hours treatment due to the buffer capacity of the acetic acid. When the solution is over buffer capacity of pH 7.0, the balance of solution pH collapses and alkalize. As a result, TOC removal ratio shows a clear increase by increase of hydroxide ion concentration and activation of self-decomposition reaction of ozone.

At the initial pH 7.0, pH continues rising with treatment of acetic acid. Finally, pH reaches 9.3 after 3 hours of treatment. At the initial pH 11.6, pH drastically decreased after 1 hour...
Table I

<table>
<thead>
<tr>
<th>Treatment time [h]</th>
<th>TOC removal ratio [%]</th>
<th>TOC treatment efficiency [g_{TOC}/kWh]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58</td>
<td>7.7</td>
</tr>
<tr>
<td>2</td>
<td>93</td>
<td>6.5</td>
</tr>
<tr>
<td>3</td>
<td>98</td>
<td>4.3</td>
</tr>
</tbody>
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C. Energy efficiency

Fig. 9 shows output energy (E) from ns pulse generator into the reactor per pulse, calculated from Fig. 4. E was determined from the recorded signals of the voltage, current, and time using the following equation:

\[ E = \int V I \, dt \] (8)

where V and I are output voltage and current from ns pulse generator to the reactor. In this experiment, E was calculated 128 mJ.

Table I shows TOC treatment efficiency calculated from Eq. (9) under the experimental conditions pH 7.0 and gas flow rate 1 L/min. This is the best condition gaining the highest energy efficiency. The value of TOC removals in Eq. (9) was obtained by multiplying TOC removal ratio, initial TOC concentration and solution volume. The consumption energy was obtained by multiplying energy per pulse, pulse repetition rate and treatment time. Table I shows that, as treatment time elapses, treatment efficiency decreases due to increasing weakness of acetic acid concentration.

\[ \text{Treatment efficiency of TOC [mg/kWh]} = \frac{\text{TOC removal [mg]}}{\text{Consumption energy [kWh]}} \] (9)

The maximum treatment efficiency of acetic acid is calculated 7.7 g_{TOC}/kWh. This result is the highest efficiency of other acetic acid treatments by discharge [15]–[17]. However, it should be noted that we used a significantly higher concentration of acetic acid than other studies. From these results, higher concentration of acetic acid solution has been functioned for high energy efficiency treatment by ns pulse discharge system.

IV. Summary

Energy efficient treatment of acetic acid solution using ns pulse discharge with pH control was demonstrated. Oxygen flow rate can be reduced for the treatment and the reduction become the advantage of a lower cost. A solution pH of over 7.0 maximizes treatment efficiency due to synergy effects of discharge and self-decomposition reactions of ozone.

REFERENCES


