Diagnosis of hydroxyl radicals and the treatment of Acid Orange Π in negative pulsed discharge

M Sun*, Y Zhang, L J Cai, H Y Wang
Institute of Electrostatics, Shanghai Maritime University, Shanghai, China
E-mail: mingsun@shmtu.edu.cn

Abstract. A kind of device supplied with negative pulsed high voltage was designed for water treatment. The nozzle discharge electrode was supplied with high voltage and the cylinder wall of the treatment chamber was grounded. Since the non-thermal plasma, especially, hydroxyl radicals played the dominant role in removing pollutants in the water by discharge plasma, hydroxyl radicals were measured in the negative pulsed discharge process by the optical emission spectroscopy (OES) effects of the repetition rate and the peak value of the pulsed discharge on the hydroxyl radicals’ production and the decomposition rate of the Acid Orange Π solution were studied.

1. Introduction
The application of pulsed discharge technology in the removal of pollutant in the air or in the water has been widely studied [1, 2]. It is well known active species, such as OH, HO₂, O and O₂* play a dominant role to remove the contamination during the discharge plasma technology. Especially, hydroxyl radicals are the most significant active species on decoloration or different kinds of pollutants’ removal for its very strong oxidation. So it is very useful for optimizing the device to measure the hydroxyl radicals’ production in different experiment conditions. In this paper, the structure of nozzle-cylinder electrode supplied with negative pulsed high voltage was adopted. The effects of the repetition rate of the pulsed discharge, the peak value of pulsed discharge voltage on the hydroxyl radicals’ production and the decomposition rate of the Acid Orange Π solution were studied.

2. Experimental set-up
The experiment system consists of power supplied system, treatment chamber, discharge voltage and discharge current monitor system etc. The structure of treatment chamber is shown in figure 1. Discharge electrode is a single nozzle supplied with negative pulsed high voltage. A steel cylinder treatment chamber is grounded. The space between the nozzle and the wall of the chamber grounded is 35 mm. Air is injected into chamber though the nozzle discharge electrode. Observation of the discharge phenomenon and the measurement of the hydroxyl radicals were completed through the window for observing in the wall of the chamber.

3. Results and discussion
In air discharge, high energy electrons are produced when free electrons gain energy from the strong electric field. A great number of collisions happen between different kinds of particles for particles

* To whom any correspondence should be addressed.
thermal movement. During the collisions between high-energy electrons and the air molecules such as O$_2$, N$_2$ and H$_2$O, high-energy electrons transfer the energy to the molecules. Chemical bonds of these molecules are broken. Ions, substance in metastable state, atoms and radicals with strong oxidation such as OH, HO$_2$, O and O$_2^*$ were produced. Some instable substance in excitated states, for an example, O (1D), continues the reactions with other species and transfers the energy [3-6]:

\[
e + O_2 \rightarrow O + O + e \tag{1}
\]

\[
e + O_2 \rightarrow O + O (1D) + e \tag{2}
\]

\[
e + H_2O \rightarrow OH + H + e \tag{3}
\]

\[
e + N_2 \rightarrow N + N + e \tag{4}
\]

\[
O (1D) + H_2O \rightarrow OH + OH \tag{5}
\]

\[
O (1D) + H_2O \rightarrow O + H_2O \tag{6}
\]

\[
O (1D) + O_2 \rightarrow O + O_2 \tag{7}
\]

\[
O (1D) + N_2 \rightarrow O + N_2 \tag{8}
\]

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During these reactions, reactions (3) and (5) describe the formation mechanism of hydroxyl radicals. In Reaction (3), hydroxyl radicals were produced by the collision between the electrons and water molecules. To the reaction (5), hydroxyl radials were produced by the propagation reaction of O (1D) radicals.

Figure 1. Schematic diagram of the treatment chamber.

In the paper, we want to learn about the effect of the different experiment conditions on the hydroxyl radicals’ production in order to optimize our experiment setup in the future. The point cared is when more hydroxyl radicals produced, not the acute quantity. So, in this work, we paid attention to the relative intensity of hydroxyl radicals’ OES, which is effected directly by the quantity of hydroxyl radicals.
3.1. The effect of peak value of the negative pulsed high voltage on the hydroxyl radicals’ production

Hydroxyl radicals’ OES was measured with the absolute peak value of the negative pulsed high voltage being from 18 kV to 34 kV, the outer diameter of nozzle electrode being 3 mm and the repetition rate of the pulsed discharge being 80 Hz. The OES of the hydroxyl radicals with different peak value of the pulsed high voltage is shown in figure 2.

![Figure 2](image)

**Figure 2.** OES of hydroxyl radicals with different absolute peak value of pulsed discharge high voltage.

From figure 2, we can see the relative intensity of hydroxyl radicals’ OES rises with the absolute peak value of the pulsed high voltage. The onset corona discharge should be near negative 26 kV, for the hydroxyl radicals can be detected at this peak value.

![Figure 3](image)

**Figure 3.** OES of hydroxyl radicals with different repetition rate of pulsed discharge.
3.2. The effect of the repetition rate of the pulsed discharge on the hydroxyl radicals’ production

OES of hydroxyl radicals with the repetition rate of pulsed discharge at the range of 20 Hz to 80 Hz is shown in figure 3. In the experiments, the outer diameter of nozzle electrode was 3 mm. And the absolute peak value of pulsed high voltage was -28 kV.

From the figure 3, the conclusion can be drawn that the relative intensity of hydroxyl radicals’ OES increases with the repetition rate of the pulsed high voltage. High energy electrons increase with the repetition rate of the pulsed high voltage supplied to the nozzle discharge electrode because the input energy increases.

3.3. The effect of the peak value of the pulsed discharge voltage on the decomposition rate of the Acid Orange II solution

The effect of the peak value of the pulsed discharge voltage on the decomposition rate of the Acid Orange II solution is shown in figure 4. The experimental conditions were the discharge time, initial concentration of the solution, the pulsed repetition rate, solution volume and the electrode diameter being 20 min, 10 mg L\(^{-1}\), 50 Hz, 460 mL and 3.5 mm, respectively.

The result indicated that the decomposition rate of Acid Orange II solution increased with the peak value of the pulsed discharge voltage. When the discharge voltage was -32 kV, the decomposition rate was about 25%. The input energy increases with the discharge voltage, the increased input energy improving the number of active species which reacted with Acid Orange II.

3.4. The effect of the pulsed repetition rate on the decomposition rate of Acid Orange II solution

The decomposition rate of the Acid Orange II solution as a function of the pulsed repetition rate (20 ~ 60 Hz) is shown in figure 5. The experimental conditions were the discharge time, the peak value of the pulsed discharge voltage, initial concentration of the solution, solution volume and the electrode diameter being 20 min, -32 kV, 10 mg L\(^{-1}\), 460 mL and 1.2 mm, respectively.

The result shows that the decomposition rate of Acid Orange II solution increased with the pulsed repetition rate. The decomposition rate improved from 12% to 28% with the pulsed repetition rate being 20 Hz and 60 Hz, respectively. The input energy increases with the pulsed repetition rate when the discharge voltage being constant. The increased input energy improves the number of active species which reacted with Acid Orange II.
4. Conclusions
Hydroxyl radicals were measured in air negative pulsed discharge with nozzle-cylinder electrodes by the OES. The effects of the repetition rate and the peak value of the pulsed discharge high voltage on the relative intensity of the hydroxyl radicals’ OES and the decomposition rate of the Acid Orange Π solution were studied. Conclusions drawn from the result of the experiments are hydroxyl radicals’ production and the decomposition rate of the Acid Orange Π solution increase with the absolute peak value and the repetition rate of the pulsed. The conclusions of this work will be helpful for the optimizing the experimental setup in the next step work of this project.

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