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Characteristics and applications of diffuse discharge of water electrode in air

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Abstract

Plasma water treatment technology, which aims to produce strong oxidizing reactive particles that act on the gas–liquid interface by way of discharging, is used to treat the organic pollutants that do not degrade easily in water. This paper presents a diffuse-discharge plasma water treatment method, which is realized by constructing a conical air gap through an uneven medium layer. The proposed method uses water as one electrode, and a dielectric barrier discharge electrode is constructed by using an uneven dielectric. The electric field distribution in the discharge space will be uneven, wherein the long gap electric field will have a smaller intensity, while the short one will have a larger intensity. A diffuse glow discharge is formed in the cavity. With this type of plasma water treatment equipment, a methyl orange solution with a concentration of 10 mg l^{-1} was treated, and the removal rate was found to reach 88.96%.

Keywords: diffuse discharge, water electrode, water treatment, organic pollutants, electric field

(Some figures may appear in colour only in the online journal)

1. Introduction

With the continuous improvements in industrial production and living standards, the types and quantities of wastewater are increasing, and water pollution is becoming more and more serious, and can cause great harm to human wellbeing and safety. Some methods of wastewater treatment commonly used now are physical adsorption, chemical oxidation, biological treatment, and so on [1–5]. However, these methods have difficulties in completely degrading organic pollutants, and some intermediate pollutants may be generated in addition. Moreover, these water treatment technologies are constrained by the cost of equipment and the operating environment; therefore, their further developments are limited.

Glaze *et al* proposed a few advanced oxidation processes (AOPs) in 1987 [6]. AOPs based on high chemical activity, with no selective oxidation properties of the hydroxyl group, oxygenolyses the poisonous and harmful biological refractory organic matter, eventually achieving innocent treatment [7, 8]. Plasma water treatment is a type of wastewater treatment involving high-energy electrons, ozone oxidation, and ultraviolet radiation [9, 10]. Moreover, compared to other AOPs, its claim to the reaction system environment is lower, and it has good treatment effects even at normal temperature and pressure. Furthermore, it has no selective processing, and hence, it can be suitable for almost all refractory organic pollutants. Most of the existing plasma water treatment methods require aeration or atomization devices, or high discharge voltages, which brings large investment and high energy consumption [11–14]. The discharge forms are usually corona discharge or filament discharge, both of which have a definite effect on liquid handling; however, in order to improve the efficiency of wastewater handling further, the density and diffusibility of plasma need to be increased.

This paper presents a plasma water treatment method. The liquid to be processed serves as one side of the electrode, and the other side uses the uneven thickness of the medium to form an uneven air gap structure on the water surface. Diffuse discharge is produced in the gap to deal with organic compounds, which are refractory in water. This paper discusses the discharge characteristics for different angles between the medium and water, from the aspect of electric field distribution. Based on the actual treatment, the conductivity of the liquid to be treated will be different, and the regulation that the conductivity of the water electrode gives effect to

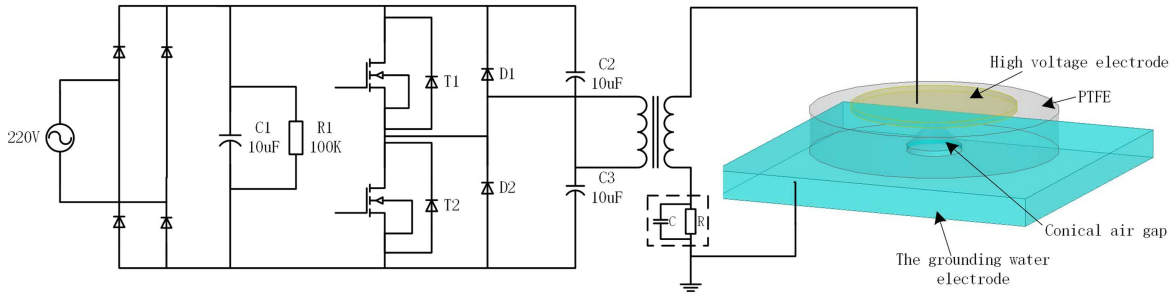


Figure 1. Main circuit and structure of electrodes.

discharge is studied. Compared to the traditional low-temperature plasma treatment methods, the plasma produced by this method has better dispersion, which can form a large contact area with the liquid to be treated, and a high utilization rate. Moreover, the reactor has a simple structure that enables it to achieve high efficiency. This method can be expected to achieve a certain treatment effect on organic matter, which is refractory in water.

2. Experimental system

In our work, a high-frequency AC power supply with a discharge frequency of 20 kHz and an adjustable output voltage of 0–10 kV is adopted. One end of the power supply is grounded and is connected with the water electrode. The other end is connected to the high-voltage electrode, as shown in figure 1. The discharge voltage is obtained through Tektronix high-voltage probe P6015A measurement. The discharge current is obtained by measuring the resistance between the transformer output and the ground electrode with a resistance value of 100 Ω. The discharge voltage and current waveforms are recorded and stored by Tektronix TDS1012B-SC. The resistance R change of capacitance C in dotted the line in figure 1, the discharge power can be obtained from the Lissajous figure.

In our study, the Maxwell 3D software is adopted for electric field simulations. The material used in the insulation medium is polytetrafluoroethylene (PTFE). The high-voltage electrode is made of copper metal. The discharge phenomenon is captured by a model Coolpix P100 SLR camera. The methyl orange used in the preparation of the simulated wastewater is produced by the Tianjin Fuchen chemical reagent factory. The organic wastewater is simulated using a methyl orange solution of concentration 10 mg l^{-1}. The decolorizing effect of the methyl orange solution is determined by the absorbance measured by a UV spectrophotometer [15]. The formula for the rate of decoloration of the solution is:

$$\text{decoloration rate} = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

(A_0: maximum absorption wavelength in the initial solution; A_t: maximum absorption wavelength in the treatment solution).

The discoloration rate of the solution is calculated using the absorbances of the solution, before and after treatment, measured by an UV spectrophotometer. The decoloration rate is the parameter used to evaluate the removal rate of methyl orange in the solution.

3. Study of discharge characteristics of water electrode

Because the solution to be treated generally has conductivity, it can be used as a discharge electrode directly [16]. Charged particles in water have the ability to move freely, and their discharge characteristics are different from those of unilateral and bilateral DBDs. Both the water electrode and the metal electrode have free particles that are free to move, and the insulating medium does not have charged particles. There are also some differences between the water electrode and the metal electrode. There is a large amount of free electrons in the metal that can move. However, the water mainly depends on the movement of positive ions and negative ions to transfer the charge [17]. Therefore, during the discharge process, the metal electrode can release secondary electrons by the effect of ion impinging on the metal plates, which is the γ function. The water electrode does not have many free electrons inside; therefore, it cannot release secondary electrons.

In this chapter, the discharge characteristics of water, as the electrode on one side, are discussed, and the influence of the conductivity parameters of the water electrode, on the discharge, is studied.

3.1. Generation of discharge plasma in conical air gap

The reason for the difficulty in forming a diffuse discharge in air is that the air breakdown field is too high. Once the breakdown field is strong, the electron collapse is too intense, and easy to contract into filamentary discharge.

In this case, in order to avoid the filamentary discharge, the existing methods are used to shorten the length of the discharge gap, reduce the intensity of the discharge field, and adopt a nanosecond-pulse power supply. For the discharge water treatment, because hydroelectricity is the fluid, if the air gap is too small, the liquid surface can easily be absorbed directly to the surface of the electrode once the discharge occurs. In other words, it is difficult to ensure that the air gap

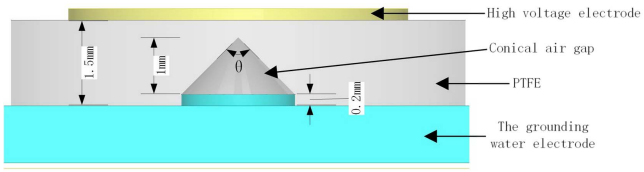


Figure 2. Conical air gap.

between the electrode and water is stable; thus, it is difficult to achieve stable discharge to treat wastewater.

In this study, the discharge area is designed as a conical air gap, in order to reduce the length of the discharge gap and reduce the electric field strength. The electrode structure designed is shown in figure 2. The water electrode is grounded. The insulating medium on the high-voltage electrode side is PTFE, with a thickness of 1.5 mm. A conical space with a depth of 1.2 mm is formed in the insulating medium. In order to stabilize the discharge process, the groove is divided into two parts. The upper part is a conical air gap with a height of 1 mm, which acts as the discharge area. The lower part is a cylinder with a height of 0.2 mm, into which a part of the water will be pushed under pressure. The design of a cylindrical groove is used to fix the air in the air gap better.

In general, the breakdown field strength of air is $3 \times 10^6\,\mathrm{V\,m^{-1}}$, which is much larger than the breakdown field strength of the creepage discharge [18]. In the conical air gap, the maximum intensity of the electric field is at the three-junction position of solid–liquid–gas, as shown in figure 3(a). Then, it can be determined that the discharge will be generated there first, and it will then develop along the surface of the medium. Charged particles diffused simultaneously by the discharge along the surface can provide more seed electrons. Thus, the entire discharge is generated at a lower electric field strength. The discharge is generated under a strong electric field initially, which will subsequently provide seed electrons to the adjacent areas with relatively weak electric fields. That is, discharge will be generated from the surface of the medium to the middle area, in order. In the discharge space, there will be an uneven electric field distribution in which the long-gap electric field will have a smaller intensity and the short one will have a larger intensity. This can effectively inhibit the development of an electron avalanche, reducing the possibility of the discharge transforming to the filament discharge. It is thus easy to achieve a more even diffuse discharge [19, 20].

When the apex angle θ of the air gap changes, the distribution of electric field in the space will change. By varying θ, a suitable field strength distribution can be obtained. During the discharge along the surface, a diffuse discharge is formed in the whole air gap.

The discharge voltages of three types of air gaps are all set to 4 kV. When θ is 60°, 90°, or 120°, the distributions of the electric field intensity component along the conical surface are shown in figure 3(b), and the electric field intensity distributions on the water surface are shown in figure 3(c). The distribution of the electric field intensity component along the conical surface is calculated by the electric field strength E and the units vector along the surface direction multiplication, that is Dot [(E_x, E_y, E_z), line tangent].

According to the results of the electric field simulations, as θ increases, the electric field intensity increases. The larger the θ is, the larger the field strength in the junction of the three is. The reason is that the electric fluxline will be deflected at the interface of the medium and air. The larger the incident angle of the electric field line is, the bigger the refraction angle will be. Therefore, the larger θ is, the denser the electric field strength in the junction of the three will be, and the maximum field strength will be larger. The smaller θ is, the bigger the distribution of the field strength component along the conical surface will be.

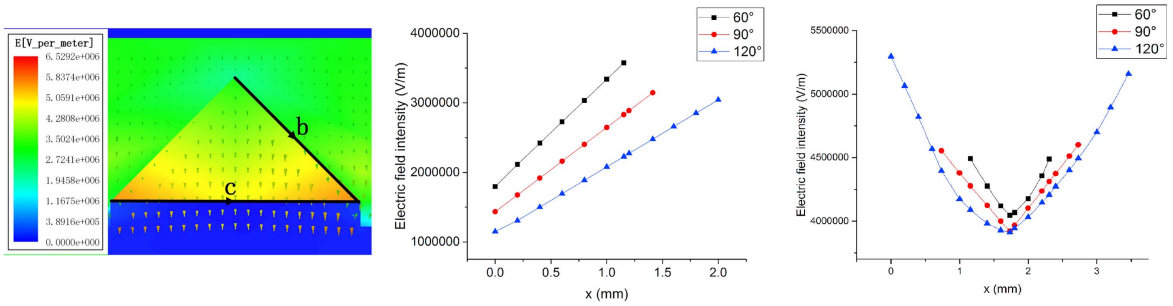
Figure 4 shows the discharges of three types of air gaps. It is observed that a discharge is generated in the entire conical air gap. Each discharge cycle has one or two pulses of conduction current. In the case where the angle $\theta = 60°$, the wall is clearly bright and the central area is darker. It shows that discharge along the surface of the medium is so severe that it contracts, which defuses out less seed electrons. Therefore, the discharge in the inner space of the air gap will be weaker. In the case where the angle $\theta = 120°$, it is observed that the discharge is generated over the entire electric field; however, there are some obvious discharge filaments in the partial space.

Combined with electric field simulation in figure 3(c), it can be determined that, when the apex angle of the air gap is too large, due to the long distance between the weak electric field and the strong electric field, the maximum electric field intensity will be much higher than that of the other two, in order to generate enough seed electrons in the weak electric field to produce a discharge. Therefore, in the area where the field strength is too large, it is easy to cause the discharge to develop too drastically and cause shrinkage. In the case where the angle $\theta = 90°$, the discharge evenly fills the entire air gap.

Therefore, the study on the discharge characteristics and wastewater treatment described below is conducted for the case where the angle $\theta = 90°$.

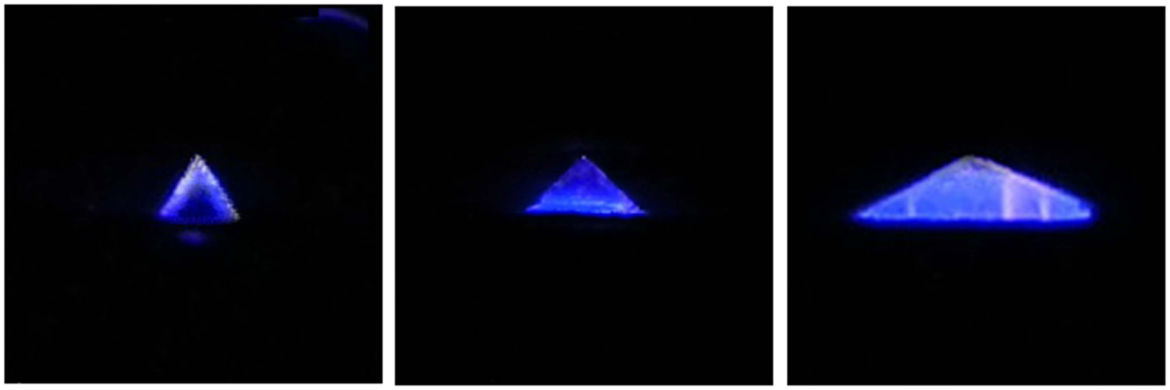
3.2. Influence of different conductivities of water electrode on discharge characteristics

In actual industrial wastewater, the conductivities of the liquids produced in different environments are different. While in water, the migration of charges is facilitated by the movement of anions and cations; the valence of ions are directly related to the concentration of the solution's conductivity. Therefore, the conductivity of the water electrode will have some effects on the discharge, which are discussed in this section. The water electrodes are NaCl solutions with concentrations of 0.1, 0.05, and $0.025\,\mathrm{mol\,l^{-1}}$, and the corresponding conductivities are 0.966, 0.374, and $0.193\,\mathrm{s\,m^{-1}}$. The control group is deionized water. The discharge characteristics of these four cases are analyzed.



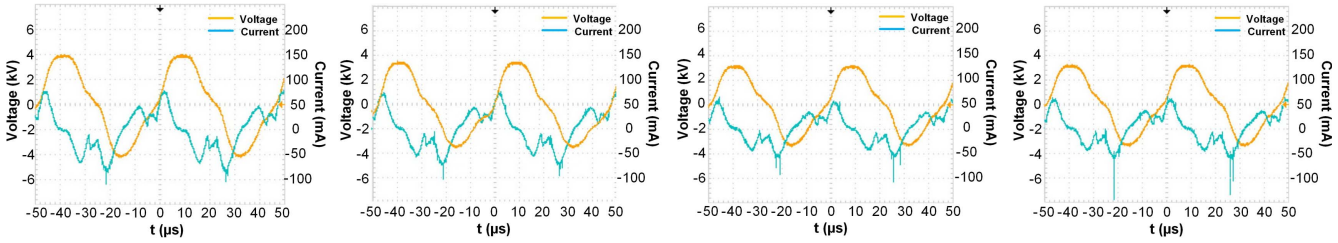
(a) Electric field distribution (b) Component along the conical surface (c) Water surface

Figure 3. Distribution of electric field intensity in conical air gap.



(a) $\theta = 60°$ (b) $\theta = 90°$ (c) $\theta = 120°$

Figure 4. Discharge phenomena in a conical air gap.



(a) deionized water (b) 0.966 s/m (c) 0.374 s/m (d) 0.193 s/m

Figure 5. Voltage and current waveforms for different conductivities.

Table 1. Discharge voltage and maximum conduction current corresponding to different conductivities.

Conductivity (s m^{-1})	Discharge voltage (kV)	Maximum conduction current (mA)
0	4.08	3
0.193	3.56	3.5
0.374	3.08	6
0.966	2.96	10

As shown by the discharge phenomenon, with the increase in the conductivity of the water electrode, the discharge uniformity deteriorates and filamentous discharge appears. It can be concluded, from the waveforms of discharge, that the discharge current is positively correlated with the electrode conductivity, and that the discharge voltage is negatively correlated with the electrode conductivity, as shown in figure 5 and table 1. For the same solute solution, the greater the conductivity, the greater the concentrations of positive ions and negative ions in the water will be. In the process of discharge on the surface of water, when charged particles in the discharge region are forced by an alternating electric field to move directionally, the positive and negative ions in the solution will follow them in the same direction. The aggregation of ions in the solution will react with the charged particles in the discharge region, which will increase the force between the charged particles in the same direction of the electric field force. Thus, the electron avalanche will be prone to contraction. Therefore,

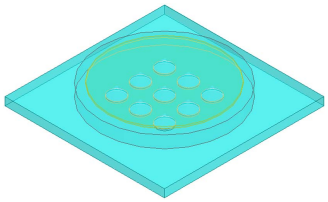


Figure 6. Array structure diagram.

with the increase in the conductivity of the water electrode, the discharge conduction current will increase and the discharge uniformity will deteriorate.

4. Large-area discharge characteristics and plasma treatment effect

4.1. Large-area conical air gap discharge characteristics

In the actual water treatment applications, the liquid to be processed needs treatment for large-area discharge, because of its considerable amount. Therefore, the conical air gap array designed in this paper can be arranged on the surface of the PTFE medium, as shown in figure 6. The discharge characteristics of the array layout are different from that of a single air gap. This section analyzes the characteristics from the perspective of the DBD equivalent circuit.

The phenomenon of array discharge is shown in figure 7(a). According to the calculation formula [21]

$$P = fC_m \int V_y \mathrm{d}V_x. \tag{2}$$

The array discharge power can be obtained from the Lissajous pattern in figure 7(c), and is found to be 5.27 W; the power density is 0.42 W mm^{-2}. Comparing with the single-point discharge, the voltage amplitude of the array discharge stays basically unchanged. However, the number of pulses of conduction current in each cycle increase significantly, while the pulse amplitude decreases and the width increases, as shown in figure 7(b). The equivalent circuit of the DBD process is shown in figure 8. The dielectric capacitance C_d is in series with the gap capacitance C_g. The equivalent discharge path is parallel to the gap capacitor C_g. Since the discharge electrode designed by the institute is non-uniform, the value of the C_g and C_g equivalent to each branch is different.

Since the discharge point increases at the array discharge, and the discharge time is different, the number of pulses increases. Since the time of one discharge process is very short, the power supply can be seen as a dc voltage source, and the discharge branch can be regarded as a current source whose excitation is

$$i_\mathrm{g} = \frac{\mathrm{d}q}{\mathrm{d}t}. \tag{3}$$

The circuit can be considered to be the superimposition of a voltage source and a current source, and using the superposition principle, the conduction current part of the discharge current can be deemed to be caused by a current source, voltage source can be regarded as short circuit. The equivalent circuit is shown in figure 9.

The total capacitance of each branch path is C_i,

$$C_i = \frac{C_\mathrm{d} C_\mathrm{g}}{C_\mathrm{d} + C_\mathrm{g}}. \tag{4}$$

The current in the main circuit is:

$$i_\mathrm{conduct} = i_\mathrm{g} - \sum_{i=1}^{n} C_i \frac{\mathrm{d}U}{\mathrm{d}t} = \frac{\mathrm{d}q}{\mathrm{d}t} - \sum_{i=1}^{n} C_i \frac{\mathrm{d}U}{\mathrm{d}t}. \tag{5}$$

U is also the voltage between the inductance and the resistor in the dry circuit:

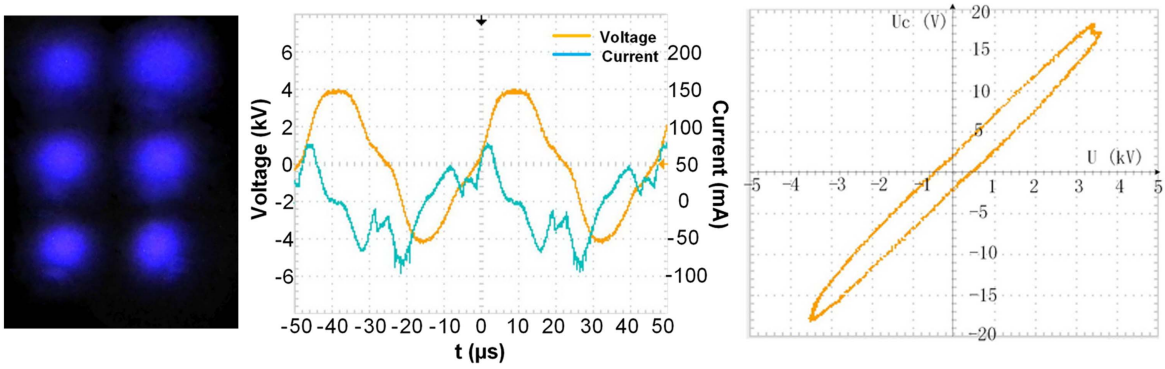
$$U = i_\mathrm{conduct} R + L \frac{\mathrm{d}i_\mathrm{conduct}}{\mathrm{d}t}. \tag{6}$$

From (5) and (6), it can be concluded that, if only one branch discharges, i_conduct will decrease when n increases. Generally, the two discharge pulses of different discharge points may overlap or appear separately. In an ideal state, each unit has the same electric field distribution when arrayed, and the discharge should develop at the same time. In fact, due to the error in structure processing, or the difference in the bubble shape produced by the electrode when it enters water, the discharge time will not be synchronized. Therefore, the overall conduction current of the multigroup electrode discharge decreases.

4.2. Treatment effect on methyl orange solution by dispersion-type discharge

The organic wastewater is simulated using a methyl orange solution of concentration 10 mg l^{-1}. The simulated wastewater discharge is treated with the electrode described in section 4.1. The absorption spectra of the solutions with different processing times are shown in figure 10.

A large stable plasma area is formed to deal with the organic matter in the solution by generating a discharge in the air gap between the electrode and the water surface. High-energy particles and high-oxidation free radicals (HO, HO_2, H_2O_2) in the plasma react with the methyl orange molecules, breaking down the benzene chain. The generated small molecules can interact with the active particles further. In the end, the organic compounds in the solution will be degraded into inorganic ions, water, and other compounds. In this plasma treatment process, the methyl orange molecules, which are in direct contact with the plasma, are degraded, and a concentration difference appears. The methyl orange molecules in the solution will soon spread to the discharge areas nearby and continue to be decomposed. Therefore, the concentration of organic molecules in the solution decreases with the increase in processing time. After 40 min of discharge treatment, the removal rate of the solution can reach 88.96%. It is proved that the plasma reactor designed in this



(a) Discharge phenomenon (b) Waveforms of voltage and current (c) Lissajous pattern

Figure 7. Array discharge characteristics.

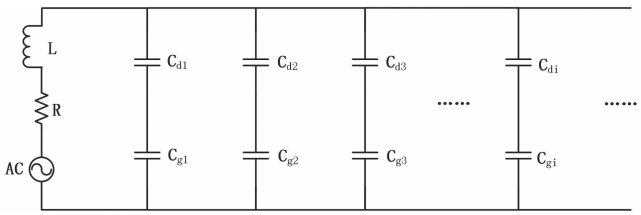


Figure 8. Equivalent circuit of the DBD.

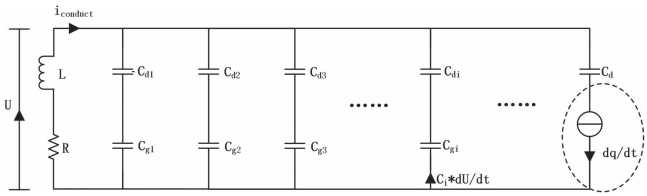


Figure 9. Equivalent circuit stimulated by current source.

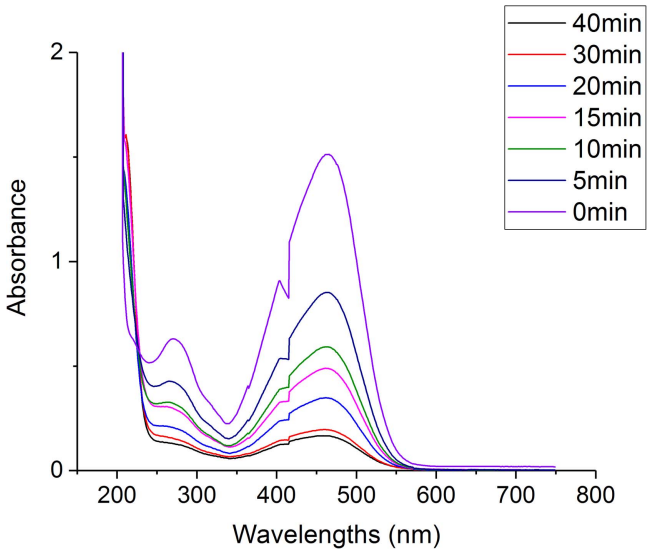


Figure 10. Absorption curves of methyl orange solution.

research can achieve high removal efficiency for organic components in solution.

5. Conclusion

This paper was based on the design of a conical air gap, the characteristic research on the water electrode discharge, realizing diffuse discharge on the untreated liquid surface, and the testing of the treatment effect. The specific conclusions are as follows:

(a) With respect to the conical air gap structure, if the air gap is too small, the discharge will be too severe to form a dispersive discharge in the air gap. When the air gap is too large, the field density will be so large that the discharge will easily contract and form a filamentary discharge. Eventually, a reasonable air gap apex angle parameter is determined to be 90°. Under this condition, a diffuse discharge will be formed throughout the air gap.

(b) If water serves as one side of the electrode, when the conductivity of the water electrode increases, the discharge voltage will decrease and the discharge conduction current will increase. Meanwhile, the discharge uniformity will become worse. In practical applications, it is considered that a reactor with different parameters can be designed according to the conductivity of the actual treated liquid.

(c) When using the dispersion-type discharge plasma treatment device designed in our work, to deal with a methyl orange solution of concentration 10 mg l^{-1}, the removal rate reaches 88.96% after 40 min.

Acknowledgments

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References

[1] Crini G 2005 *Prog. Polym. Sci.* **30** 38
[2] Gogate P R and Pandit A B 2004 *Adv. Environ. Res.* **8** 553
[3] Polaert I, Wilhelm A M and Delmas H 2002 *Chem. Eng. Sci.* **57** 1585
[4] Saratale R G *et al* 2016 *J. Environ. Eng.—ASCE* **142** 04015064
[5] Le-Clech P, Chen V and Fane T A G 2006 *J. Membr. Sci.* **284** 17
[6] Glaze W H 1987 *Environ. Sci. Technol.* **21** 224
[7] Deng Y and Zhao R Z 2015 *Curr. Pollut. Rep.* **1** 167
[8] Stasinakis A S 2008 *Global Nest J.* **10** 376 (https://www.researchgate.net/publication/228474561_Use_of_Selected_Advanced_Oxidation_Processes_AOPs_for_Wastewater_Treatment_-_a_Mini_Review)
[9] Jiang B *et al* 2014 *Chem. Eng. J.* **236** 348
[10] Tijani J O *et al* 2014 *Water Air Soil Pollut.* **225** 2102
[11] Yamabe C *et al* 2005 *Plasma Process. Polym.* **2** 246
[12] Nose T *et al* 2014 *Kagaku Kogaku Ronbunshu* **40** 27
[13] García M C *et al* 2017 *Chemosphere* **180** 239
[14] Locke B R *et al* 2006 *Ind. Eng. Chem. Res.* **45** 882
[15] Abdullah F H, Rauf M A and Ashraf S S 2007 *Dyes Pigments* **72** 349
[16] Liu W Z *et al* 2016 *Plasma Chem. Plasma Process.* **36** 1011
[17] Mukerjee P and Mysels K J 1958 *J. Phys. Chem.* **62** 1400
[18] Liu J *et al* 2014 *IEEE Trans. Dielectr. Electr. Insul.* **20** 1887
[19] Liu W Z *et al* 2017 *Appl. Phys. Lett.* **110** 024102
[20] Liu W Z *et al* 2017 *Plasma Chem. Plasma Process.* **37** 465
[21] Kriegseis J *et al* 2011 *J. Electrostat.* **69** 302