

## Characteristics of gas-liquid pulsed discharge plasma reactor and dye decoloration efficiency

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### Abstract

The pulsed high-voltage discharge is a new advanced oxidation technology for water treatment. Methyl Orange (MO) dye wastewater was chosen as the target object. Some investigations were conducted on MO decoloration including the discharge characteristics of the multi-needle reactor, parameter optimization, and the degradation mechanism. The following results were obtained. The color group of the azo dye MO was effectively decomposed by water surface plasma. The decoloration rate was promoted with the increase of treatment time, peak voltage, and pulse frequency. When the initial conductivity was 1700  $\mu\text{S}/\text{cm}$ , the decoloration rate was the highest. The optimum distance between the needle electrodes and the water surface was 1 mm, the distance between the grounding electrode and the water surface was 28 mm, and the number of needle electrodes and spacing between needles were 24 and 7.5 mm, respectively. The decoloration rate of MO was affected by the gas in the reactor and varied in the order oxygen > air > argon > nitrogen, and the energy yield obtained in this investigation was 0.45 g/kWh.

**Key words:** multi-needle plasma reactor; water surface plasma; decoloration efficiency; Methyl Orange decoloration

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### Introduction

With the rapid development of the production of textile printing and dyeing, petrochemical, fine chemical, pharmaceutical and food industry, etc., large quantities of harmful substances were released into the environment. Consequently, the development of efficient and environmentally friendly elimination methods for refractory organic pollutants is a matter of great concern. Advanced oxidation technology effectively promotes the degradation or the mineralization of organic pollutants in water, which has received extensive attention. Recently, some advanced oxidation technologies, such as Fenton reaction (Fenton, 1894), ozonation (Lei and Wang, 2001), UV/O<sub>3</sub> oxidation (Olson and Barbier, 1994), H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> (Zhong et al., 1998), UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> (Kurbus, 2003), wet oxidation (Fu et al., 2007), electrochemical oxidation (Johnson, 2000), supercritical oxidation (Ding et al., 1995), photochemical oxidation (Nogueira and Guimaraes, 2000; Zhang et al., 2006), E-beam irradiation (Cooper et al., 2002) and high-voltage pulse discharge plasma have been considered to be promising alternatives for water treatment (Sun et al., 1999, 2000). High-voltage pulsed discharge plasma for the degradation of organic pollutants in water has characteristics such as a non-selective high degradation rate for organic pollutants, no secondary pollution, normal

temperature and pressure, and low power consumption, thus is a promising technology for wastewater treatment. Decoloration of dye solutions or decomposition of organic compounds using plasma on a water surface has been reported (Sato et al., 2008; Lukes and Locke, 2005; Hoeben et al., 1999; Hayashi et al., 2000). Corona discharge plasma on the water surface by the application of dc, ac, or pulses produces active species which diffuse in the gas phase and dissolve in the water through the surface layer to react with the organic materials in water. It takes some time for the active species to diffuse from the plasma region to the water surface. In that time period, short-lived active species such as radicals would disappear before reaching the water surface. Therefore, filamentary streamer discharge that produces plasma near the water surface was tried to decolor the dye in water (Sato et al., 2008; Lukes and Locke, 2005). Sato et al. (2008) reported that the water surface plasma (WSP) with bright filamentary streamer discharge mode had a higher decoloration rate and a shorter treatment time than that with the corona mode. Lukes and Locke (2005) investigated the degradation of phenol in a hybrid gas-liquid electrical discharge reactor under different gas conditions (pure argon and oxygen atmospheres) and liquid conditions (different initial pH values). They found that phenol was removed more efficiently in oxygen than in argon atmosphere in alkaline solution.

In this study, a multi-needle plasma reactor was proposed for decolorizing organic dye solution using a pulsed

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high voltage discharge directly on the water surface with a filamentary streamer discharge mode. Some factors influencing the dye elimination were studied, including the pulse parameters, such as peak voltage and pulse frequency, conductivity of the solution, spacing among needles, and the electrode distance between the needle tip and the water surface.

## 1 Materials and methods

A multi-needle to water surface discharge plasma reactor was used as previously reported (Sun et al., 2007). The schematic diagram of the experimental apparatus is shown in Fig. 1. The reactor is made of a Plexiglas cylinder containing a needle to water surface geometry electrode system. The inner diameter and the height of the discharge reactor are 90 and 150 mm, respectively. The needle electrodes for producing plasma are composed of 2 to 24 stainless steel syringe needles attached to a 50 mm diameter stainless steel disc. The ground plate electrode is a stainless steel disc of 50 mm diameter which is submerged in the water phase. A pulsed power supply with a rotating spark-gap switch was used to generate high voltage pulses. The pulse voltage, the frequency, and the capacity of the storage capacitor were 0–60 kV, 0–300 Hz and 3 nF, respectively.

During the experiment, the pulse peak voltage was set at 22, 26, and 30 kV; the pulse frequencies was varied from 20 to 100 Hz; the treatment time was varied from 3 to 15 min. The distance between needle electrodes and the water surface ( $d_s$ ) was varied from 1 to 10 mm and the distance between grounding electrode and water surface ( $d_g$ ) was varied from 13 to 28 mm. The number of needle electrodes was varied from 2 to 24. The needle electrode spacing ( $d_n$ ) was varied from 7.5 to 30 mm.

In each reaction, 450 mL of Methyl Orange dye (MO) solution with a initial concentration of 10 mg/L (pH = 6.6) was circulated by a peristaltic pump at a flow rate of 130 mL/min. The electrical conductivity of the MO

solution was adjusted from 500 to 3000  $\mu\text{S}/\text{cm}$  by addition of potassium chloride. A UV-Visible Spectrophotometer (JASCO V-550, Japan) was used to check the decoloration of MO before and after the treatment processing. The decoloration rate ( $R$ , %) of MO was calculated by the following Eq. (1):

$$R = \frac{(A_0 - A)}{A_0} \times 100\% \quad (1)$$

where,  $A_0$  is the initial absorbance before reaction;  $A$  is the absorbance after reaction.

## 2 Results and discussion

### 2.1 Plasma formation on water surface

The water surface plasma that was generated between the needle tips and water surface was seen as a bright streamer discharge, as shown in Fig. 2. It was a uniform corona discharge from each needle tip. Between each needle tip and the water surface, an umbrella discharge zone can be formed. Thus a reasonable needle-to-needle distance can form a uniform discharge zone on the water surface.

### 2.2 Effects of pulse peak voltage and liquid conductivity

The effect of pulse peak voltage on MO decoloration efficiency is shown in Fig. 3a. During the experiment, the pulse peak voltage was varied at levels of 22, 26, and 30 kV. The pulse frequency was set at 50 Hz, the conductivity of the MO solution was 1700  $\mu\text{S}/\text{cm}$ , and the treatment time was 3, 6, 9, 12 and 15 min. As shown in Fig. 3a, the effect of pulse peak voltage on the decoloration of MO is evident, that is, the decoloration rate of MO was increased with increasing pulse peak voltage. The reason is that when the pulse peak voltage increased, the average electric field strength and the number of plasma channels between the electrodes also increased, which led to generating a stronger discharge, more active species (i.e.  $\cdot\text{OH}$ , ozone, and hydrogen peroxide) and stronger ultraviolet light. In particular, the ozone concentration in the gas phase increased when the pulse peak voltage increased. The ozone in the gas phase transferred into the water, and part of the dissolved ozone in the liquid phase formed hydrogen peroxide ( $2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{OH}\cdot + \text{O}_2 + \text{HO}_2\cdot$ ), therefore,

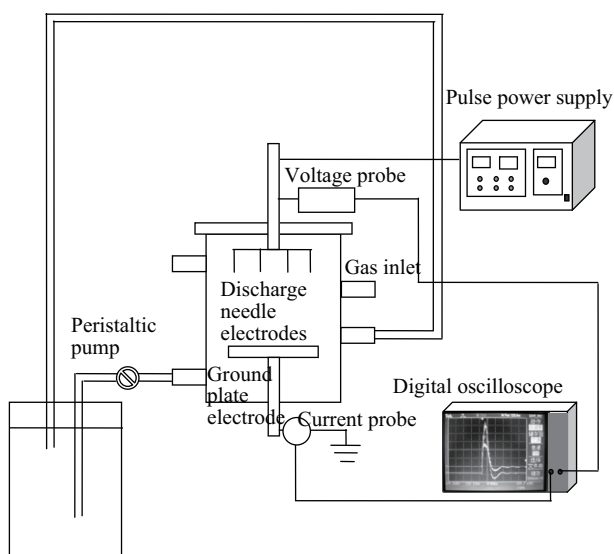


Fig. 1 Schematic diagram of experimental apparatus.

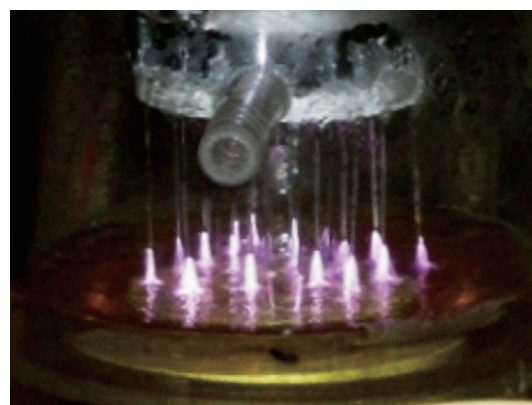
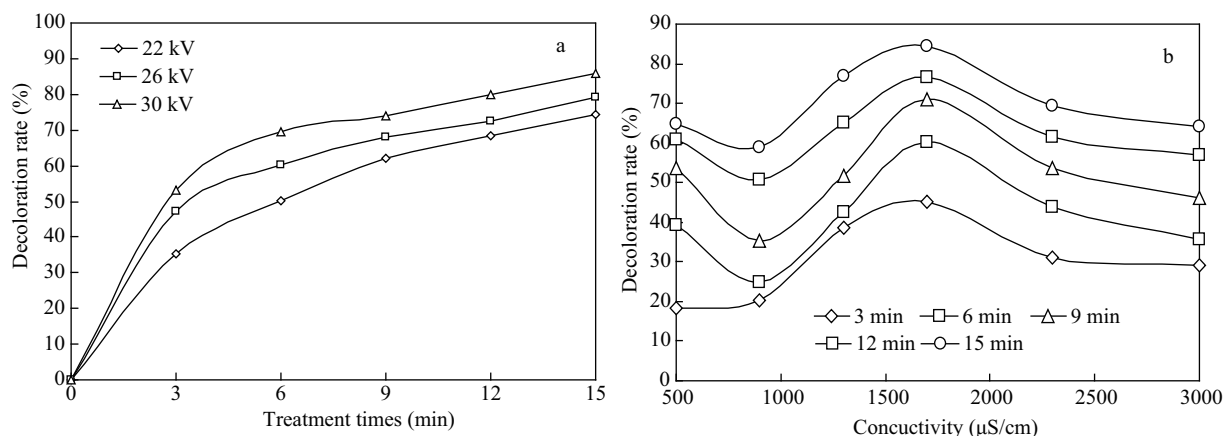


Fig. 2 Reactor photo when plasma was present (22 kV, 50 Hz,  $d_s$  1 mm, 1700  $\mu\text{S}/\text{cm}$ , introducing air).



**Fig. 3** Effect of peak voltage (a) and liquid conductivity (b) on decoloration rate of MO 50 Hz, 1700 μS/cm.

the concentrations of ozone and hydrogen peroxide in the liquid phase increased with increasing pulse peak voltage. Figure 3a also shows that the treatment time has an important effect on the MO decoloration rate. The MO decoloration rate increased with increasing treatment time, especially in the initial 3 min, when the decoloration rate increased rapidly, then increased slowly after 3 min. Actually, the residence time of the solution in the reactor increases with increasing treatment time, and the treatment effect changes with treatment time with an exponential dependence, approximately (Sun et al., 2000).

The effect of initial liquid conductivity on MO decoloration rate is shown in Fig. 3b. The liquid conductivity was varied from 500 to 3000 μS/cm. The highest decoloration rate of MO was obtained at the initial conductivity of 1700 μS/cm.

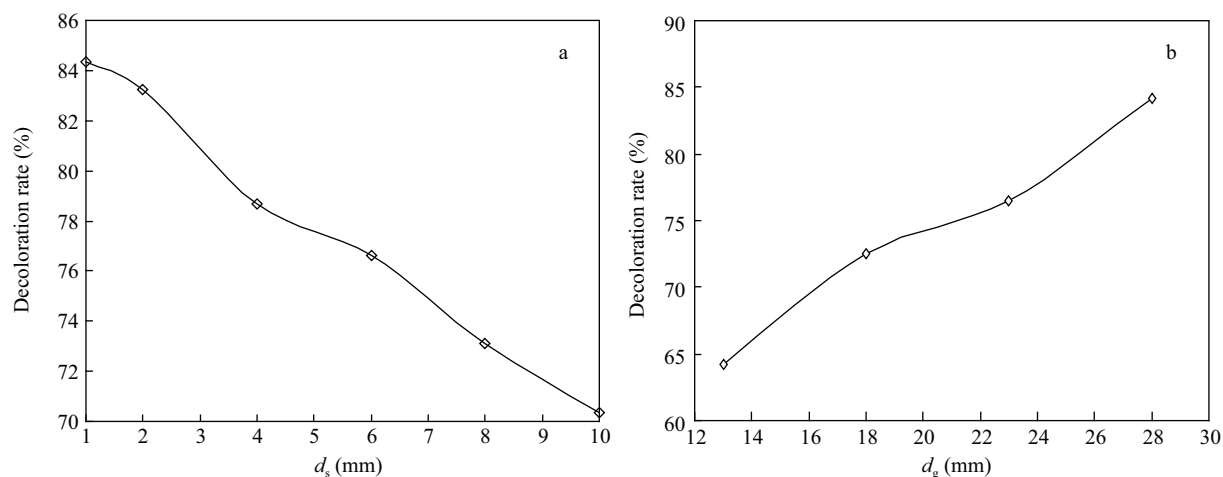
The gas-liquid hybrid discharge system, which consists of the plasma channel and bulk solution, is considered to be a series connection of resistors (including a small capacitance effect). The increase of the solution conductivity decreases the impedance of the circuit, leading to a larger current flow in the circuit. Stronger plasma can be formed due to the larger current, but the total electric energy is the same because of the use of a capacitor discharge type of pulse generator. As shown in Fig. 2, uniform filamentary discharges from every needle tip were formed on the water

surface at the liquid conductivity of 1700 μS/cm. As the liquid conductivity increased, the discharge spots gradually decreased. In the case of high conductivity such as 3000 μS/cm, the discharge spots moved among the needles due to the fluctuation of the water surface, which resulted in a lower decoloration rate. The maximum decoloration rate was obtained when the initial conductivity of the MO dye solution was 1700 μS/cm, which could be due to achieving an optimum matching condition in the discharge circuit. Experimentally, it was found that the energy injected into the reactor was different under the conditions of different conductivities. The highest energy was injected into the reactor at 1700 μS/cm, and the energy injected into the reactor decreased for higher conductivity due to oscillation of the circuit current.

## 2.3 Optimization of electrode configuration for water surface plasma

### 2.3.1 Distance between needle electrodes and water surface ( $d_s$ )

As shown in Fig. 4a, the  $d_s$  clearly influenced the decoloration rate of the MO solution. As  $d_s$  varied from 1 to 10 mm, the decoloration rate of the MO solution decreased from 84.3% to 70.3%. The amount of the active species generated in the plasma channels including  $\cdot\text{OH}$ ,  $\cdot\text{H}$ ,  $\cdot\text{O}$ ,  $\cdot\text{HO}_2$  and  $\text{O}_3$  was greatly influenced by the electric field in-



**Fig. 4** Effect of distance between needle-electrodes and water surface ( $d_s$ ) (a) and ground electrode and water surface ( $d_g$ ) (b) on decoloration rate of MO (22 kV, 50 Hz, 1700 μS/cm, and treatment time 15 min).

tensity between the needle electrodes and the solution. The increase of the electric field resulted in the enhancement of the discharge on the water surface and a large amount of active species being injected into the liquid. Therefore, the decoloration rate was increased by the decrease of  $d_s$  in the oxidation of the MO solution.

### 2.3.2 Distance between ground electrode and water surface ( $d_g$ )

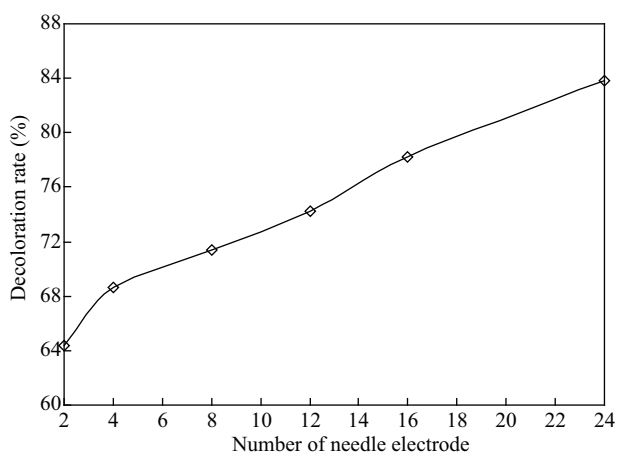
The effect of  $d_g$  on the decoloration rate of MO at 22 kV, 50 Hz, conductivity of MO solution 1700  $\mu\text{S}/\text{cm}$  and  $d_s$  of 1 mm is shown in Fig. 4b. The decoloration rate of MO became higher when  $d_g$  increased. This was probably due to the fact that the effective volume in the electric field increased with the increase of  $d_g$ , which thus increased the overall removal rate. When  $d_g$  increased, more discharge current flow passed through the MO solution in the electric field, which led to an increase of the reaction probability of the MO solution acted on by the electric field. The decoloration rate of MO was almost proportional to the increase of the distance  $d_g$ .

### 2.3.3 Number of needle electrodes and spacing between needles

Figure 5 shows the effect of the number of needle electrodes on the decoloration rate of the MO solution. When the number of needle electrodes increased, the decoloration rate of the MO solution was effectively increased.

With the increase of the number of needle electrodes, the spacing between needles decreased. When the number of needle electrodes was 24 and the spacing was 7.5 mm, the decoloration rate was the highest. When the number of needle electrodes was reduced or the spacing increased, the decoloration rate declined.

Under the same conditions of electrode distance ( $d_s + d_g$ ) and applied voltage, the growth in needle electrode number increased the plasma channels between the needle tips and the water surface, which resulted in the generation of more active species and a higher MO decoloration rate. It was shown that the reactor system had a suitable configuration when the number of needle electrodes was 24 and the spacing was 7.5 mm.



**Fig. 5** Effect of the number of needle-electrodes on decoloration of MO (22 kV, 50 Hz, 1700  $\mu\text{S}/\text{cm}$ , treatment time 15 min,  $d_s$  1 mm,  $d_g$  28 mm).

## 2.4 Introducing four kinds of gases

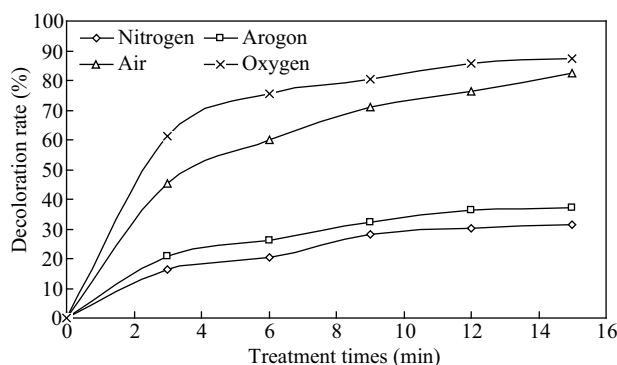
When different gases were introduced into the reactor system, different decoloration processes were observed. As shown in Fig. 6, the order of the decoloration efficiency was: oxygen > air > argon > nitrogen. The decoloration rate of the MO dye solution was highest when oxygen gas was introduced. The gas phase discharge generated not only  $\cdot\text{OH}$  but also other active species, such as ozone ( $\text{O}_3$ ), peroxide ( $\text{O}_2^-$ ) and singlet oxygen ( $^1\text{O}_2$ ).

The ionization energy of argon was lower than that of nitrogen, so it was more easily ionized. High energy electrons could be generated by the gas phase pulsed discharge when argon gas was used. In addition, argon is a noble gas so it has a lower ability to capture electrons compared to nitrogen. Therefore, the high energy electrons generated in the plasma can collide with water molecules to produce more hydroxyl radicals and hydrogen atoms. Under this condition, the decoloration rate was higher with argon than with nitrogen. The MO decoloration rate was the lowest in nitrogen as there are small amounts of strong chemically active substances, such as ozone. When oxygen gas or air was used, a high concentration of ozone was generated and dissolved into the water to produce more hydroxyl radicals and additional active substances (Al-Qaradawi and Salman, 2002). Therefore, the decoloration rate of MO was the highest when oxygen was used, and the value of the reaction rate constant  $k$  ( $1.38 \times 10^{-1} \text{ min}^{-1}$ ) was higher when using oxygen than with other gases (air =  $1.14 \times 10^{-1} \text{ min}^{-1}$ , argon =  $3.09 \times 10^{-2} \text{ min}^{-1}$  and nitrogen =  $2.51 \times 10^{-2} \text{ min}^{-1}$ ).

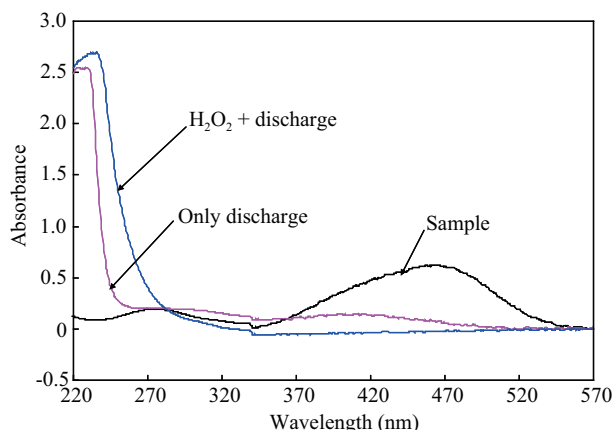
The active species generated by discharge in the gas phase include ozone ( $\text{O}_3$ ), OH radical, peroxide ( $\text{O}_2^-$ ) and atomic oxygen ( $\text{O}$ ). Some of them, such as  $\text{O}_3$  and OH radical, can dissolve into the water solution and form hydrogen peroxide in the solution. It was found that the concentration of hydrogen peroxide in the solution increased when the  $\text{O}_3$  concentration in the gas phase increased. Consequently, these active species generated at the gas-liquid interface helped the rapid decoloration of the organic dye.

## 2.5 UV-Visible spectrum

UV-Visible absorption spectra for the MO solution before and after the treatment are shown in Fig. 7.



**Fig. 6** Effect of different source gases on MO decoloration (22 kV, 50 Hz, 1700  $\mu\text{S}/\text{cm}$ , treatment time 15 min,  $d_s$  1 mm,  $d_g$  28 mm).



**Fig. 7** UV-Vis spectra of MO before and after pulsed discharge (22 kV, 50 Hz, 1700  $\mu$ S/cm, and treatment time 15 min).

The characteristic MO absorption peak for the  $n \rightarrow \pi^*$  transition is at 464 nm. This absorption peak arises from the strong chromophore azo double bond ( $-N=N-$ ) which is present in the entire group of dye molecules. The absorption peak at 280 nm occurs in a number of aromatic or polycyclic aromatic hydrocarbons and the chromophore group interaction peaks around 220 nm can be attributed to the absorption of aromatic or polycyclic aromatic hydrocarbons in the intrinsic absorption (Kulikovsky, 1997). After pulse discharge treatment, the visible region of the absorption peaks was weakened. This is because the azo group ( $-N=N-$ ) in the MO molecule which was linked with an amino benzene ring was an active site and susceptible to attack. During discharge, a large number of strong oxidizing species, especially  $\cdot OH$ , was produced and attacked the dye molecules. The  $\cdot OH$  radical decomposed the  $-N=N-$  bond conjugated with the benzene ring resulting in the bleaching of the solution. The absorption of the methyl orange solution at 300 nm was also reduced, indicating that the aromatic ring structure was damaged with the destruction of double bonds, producing small organic acid molecules.

## 2.6 Energy yield for decoloration

The energy yield is an important parameter for appraising the treatment method. The energy yield of the water surface pulsed discharge reactor was calculated by Eq. (2):

$$G_{50} = \frac{1}{2} \frac{C_0 V_0}{P t_{50}} \quad (2)$$

where,  $G_{50}$  (g/kWh) is the energy yield,  $C_0$  (mol/L) is the molar concentration of the pollutant at  $t = 0$ ,  $V_0$  (L) is volume of treated solution in liters,  $P$  (W) is power of the reactor, and  $t_{50}$  is the time in seconds required for 50% conversion.

The energy yield obtained in the present work was 0.45 g/kWh, which is higher than that in the other authors' works, i.e., the energy yield was 0.44 with pulse diaphragm discharges with air bubbling (Zhang et al., 2009); 0.09 g/kWh with pulsed streamer and spark discharges in water (Sugiarto et al., 2003). It is known from the above results that the discharge type affects the energy yield of the reactor system. In order to promote the energy yield, the

selection of discharge type must be considered first; then the space homogenization of electric discharge for a multi-needle reactor must be considered. The umbrella shape corona streamer discharge for each needle electrode is better than a column shaped spark discharge.

## 3 Conclusions

In this study, water surface discharge plasma was proposed for the discoloration of MO dye, and the following conclusions were reached. (1) When the pulse peak voltage, frequency and the treatment time increased, the decoloration rate also increased. (2) When the initial conductivity of the MO dye solution was 1700  $\mu$ S/cm, the highest energy was injected into the reactor and the maximum decoloration rate was obtained. (3) The highest decoloration rate was obtained when the distance between needle electrodes and the water surface ( $d_s$ ) was 1 mm, the distance between the ground electrode and the water surface ( $d_g$ ) was 28 mm, and the number of needle electrodes was 24 (spacing between needles was 7.5 mm). (4) The decoloration rate of MO was changed when introducing different gases (oxygen, air, argon and nitrogen) into the reactor system, and the decoloration rate varied in the order oxygen > air > argon > nitrogen. (5) The energy yield obtained in this investigation was 0.45 g/kWh, which was higher than in other reports.

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