

## Degradation of a textile azo dye by pulsed arc discharge to the surface of wastewater

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**Abstract**—The pulsed arc discharge to the surface of wastewater was applied to the degradation of a textile azo dye (Acid Red 27). A high-voltage electrode (discharging electrode) was vertically placed above the surface of the wastewater while the wastewater itself was grounded. The pulsed arc discharge occurred between the tip of the discharging electrode and the surface of the wastewater, producing various oxidative species. Oxygen was used as the working gas instead of air to prevent nitrogen oxides from forming. The effect of several parameters on the chromaticity and chemical oxygen demand (COD) removal was examined. The results obtained showed that the chromaticity of the wastewater was completely removed by this process and the COD also decreased significantly. It has been found that ozone formed in the gas phase mainly affects the removal of the dye. The contribution of other effects such as ultraviolet light emission and OH radical formation during the arc discharge to the degradation of the dye was found to be less than 15%. For the present reactor system, the optimum pH, pulse repetition rate and agitation speed were found to be 3.0, 110 Hz and 300 rpm, respectively.

Key words: Pulsed Arc Discharge, Azo Dye, Chromaticity, Chemical Oxygen Demand

### INTRODUCTION

The increasing demand for clear water and ever-strengthened environmental regulations has generated intense interest in more economical post-treatment processes capable of effectively dealing with wastewater. Textile-dyeing wastewater is known to contain a large amount of suspended solids and high chemical oxygen demand (COD) concentration [1,2]. Conventional approaches to the treatment of textile-dyeing wastewater consist of several combinations of physical, chemical and biological methods including coagulation, precipitation, adsorption, aerobic and anaerobic biological treatment, etc [1-3]. Because of the large variability of the textile-dyeing wastewater, however, most of these methods are becoming inadequate. Besides, many attempts have been made to apply electron-beam irradiation, photo-oxidation, supercritical water oxidation and electrochemical methods to the treatment of wastewater [4-7], but no reliable textile-dyeing wastewater treatment process has been established so far.

Recently, different types of electrical discharges utilizing high-voltage and ground electrodes submerged in water or high-voltage electrode placed above the water surface with the ground electrode placed in water have been studied as possible methods for the treatment of waste [5-12]. It has been shown that pulsed high-voltage discharges generated directly in water initiate a variety of physical and chemical processes such as the formation of chemically active species (O, H, OH radicals, H<sub>2</sub>O<sub>2</sub> molecules), the radiation of intense ultraviolet light and overpressure shock waves [8-13]. These physical and chemical processes can be used to destroy or degrade biological cells and organic chemical compounds dissolved in water. However, this kind of electrical discharge utilizing high-voltage and ground electrodes submerged in water (generating electrical discharge

directly in water) may not be applicable to the treatment of the textile-dyeing wastewater because the electrical conductivity of the textile-dyeing wastewater is too high to induce effective electrical discharge. In the case of textile-dyeing wastewater with high electrical conductivity, the electrical discharge to the surface of water (high-voltage electrode placed above the water surface with the ground electrode placed in water) may be a desirable method. The primary species produced by the electrical discharge to the water surface occurring in an air or oxygen environment is ozone. Ozone can diffuse into the water and degrade aqueous contaminants [12-14]. If the electrical discharge takes place in close proximity to the water surface, the strongly oxidative compounds such as OH and O radicals and their reaction products (O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>) formed in the gas phase or at the gas-liquid interface can dissolve into the water and degrade the organic compounds via oxidation processes.

The most significant problem related to the textile-dyeing wastewater is its chromaticity [1,7]. In a colored wastewater, sunlight cannot penetrate deep into the wastewater, which disturbs the aquatic metabolism, eventually leading to decreasing so-called self-purification capability of water. Thus, chromaticity removal has been a matter of concern in the textile industry. As mentioned above, since the electrical discharge produces various oxidative species, it may be a promising way to degrade organic dye molecules. In an electrical discharge process, the dye molecules may not be completely oxidized to carbon oxides, but the chromaticity removal itself is of great importance in the textile industry.

The purpose of this study is to apply the electrical discharge to the treatment of textile-dyeing wastewater. The electrical discharge method adopted in this study was pulsed arc discharge to the surface of the wastewater that high-voltage electrode was placed above the wastewater with the ground electrode submerged in it. In this electrode configuration, the arc discharge occurs in the space between the tip of the discharging electrode and the surface of the wastewater. The performance of this process was evaluated with a simu-

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lated textile-dyeing wastewater, which was formed with an azo dye (Acid Red 27) and distilled water. The effect of several parameters such as treatment time, pH, agitation speed and pulse repetition rate on the chromaticity and COD removal was examined, and the results were discussed.

## EXPERIMENTAL

The batch experimental apparatus for the treatment of the textile-dyeing wastewater using the pulsed arc discharge is shown in Fig. 1. The high-voltage electrode (discharging electrode) was a 3 mm stainless steel rod, and the ground electrode submerged in water was 6 mm stainless steel rod. The distance between the tip of the discharging electrode and the water surface was 7 mm. The reactor vessel (inner diameter: 10 cm) having four baffles was made of glass, which was water-jacketed to maintain the wastewater at a constant temperature. The cooling water flowed through the jacket and maintained the temperature of the reactor vessel at 20 °C. The top of the reactor vessel was closed by a silicon rubber cap containing ports for transfer of oxygen. The high-voltage electrode pierced the center of the silicon rubber cap.

Fig. 2 shows the pulsed voltage generator to produce the arc dis-

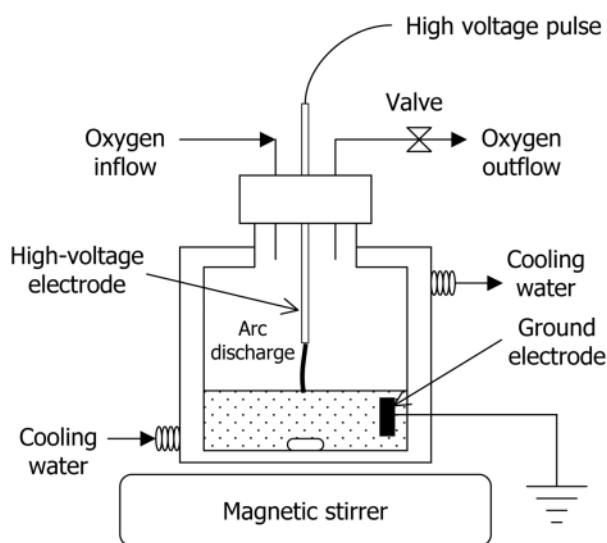


Fig. 1. Schematic of the batch reactor system.

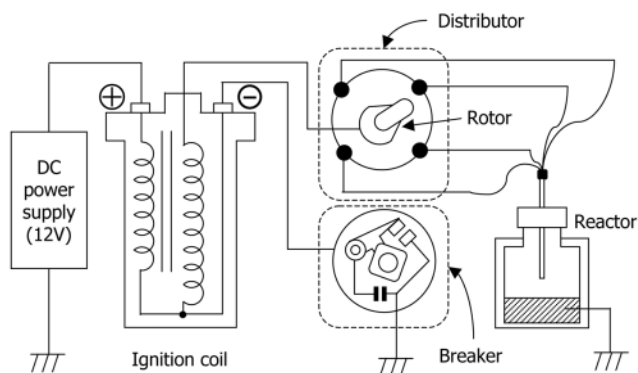


Fig. 2. Schematic of the pulse voltage generator.

charge. Made of some parts detached from the electrical ignition system of an internal combustion engine, it consists of a positive DC (12 V) power supply, an ignition coil, a breaker, a distributor, and four spark plugs. The spark plugs were put together and then connected to the discharging electrode of the reactor. Since this electrical ignition system is designed to deliver high voltage to four spark plugs by periods, one rotation of the rotor in the distributor produces four high voltage pulses. The rotor was operated by a motor, and the pulse repetition rate (frequency) was changed from 58 to 163 Hz (pulses/s). The electrical ignition system in Fig. 2 produced negative high voltage pulse. The voltage applied to the discharging electrode was about 13 kV.

The simulated wastewater was prepared by dissolving a given amount of an azo dye, Acid Red 27 ( $C_{20}H_{11}N_2Na_3O_{10}S_3$ ; Sigma-Aldrich Corp., USA) and sulfuric acid in distilled water. The volume of the simulated wastewater in the reactor vessel was 200 cm<sup>3</sup>, and the concentration of the dye was 20 mg/L. The space above the water surface was filled with oxygen. Before applying the pulsed high voltage to the discharging electrode, oxygen was flowed through the reactor vessel for 2 min, and then the valves for transfer of oxygen were closed to confine it in the reactor vessel. Air was not used as the working gas because it produces nitrogen oxides under the electrical discharge. The pH of the wastewater was changed from 2.0 to 6.0 by sulfuric acid. During the arc discharge, the wastewater was well mixed by a magnetic spin bar whose diameter and length are 8 mm and 25 mm, respectively. The agitation speed was changed up to 400 rpm. The experimental condition is summarized in Table 1.

The concentration of amaranth (chromaticity) was analyzed by an ultraviolet/visible spectrophotometer (Model UV-2500, Labomed, Inc., USA) at a wavelength of 521 nm. The COD concentration was measured by acidified potassium permanganate method using a COD meter (Model COD-60A, TKK-TOA Corp., Japan). For the measurement of the concentration of ozone in the gas phase, a 10 mL sample was taken from the gas phase and diluted 10 times. The concentration of ozone in the diluted sample was measured by a chemical detector (Product number 18 M, Gastec, Japan). For the measurement of the voltage applied to the discharging electrode, a 1000 : 1 high voltage probe (PVM-4, North Star Research, Corp., USA) and a digital oscilloscope (TDS 3032, Tektronix) were used.

## RESULTS AND DISCUSSION

### 1. Ultraviolet/Visible Spectra of the Wastewater

Fig. 3 shows the ultraviolet/visible spectra of the wastewater before and after the electrical discharge treatment. In these spectra, the abscissa is wavelength in nm, and the ordinate is absorbance.

Table 1. Experimental conditions

	Typical condition	Range
Initial concentration of the dye (mg/L)	20	-
Initial pH of the wastewater	3	2-6
Wastewater agitation speed (rpm)	300	0-400
Treatment time (min)	30	15-60
Pulse repetition rate (Hz)	136	58-163
Reaction temperature (°C)	20	-

As mentioned above, oxygen was confined in the upper region of the reactor vessel, where water vapor evaporated from the wastewater coexisted. The pulsed arc discharge toward the surface of the wastewater can produce various oxidative species such as oxygen radical, hydroxyl radical, hydrogen peroxide and ozone [15,16]:



These oxidative species can react with the dye molecules at the surface of the wastewater being stirred by a magnetic spin bar. In addition, ultraviolet (UV) light emission from the arc discharge can contribute to the degradation of the dye molecules. As observed in Fig. 3, the absorbance at 521 nm decreased to zero after 60 min treatment, indicating that the chromaticity was completely removed. The absorbance in the ultraviolet range (200–400 nm) also decreased considerably after the treatment. This result reveals that not only the chromaticity but also the concentration of the organic carbon was decreased by the pulsed arc discharge. The removal of the organic carbon will be discussed below in terms of the COD.

## 2. Parametric Study

Fig. 4(a) presents the chromaticity and COD removal efficiency

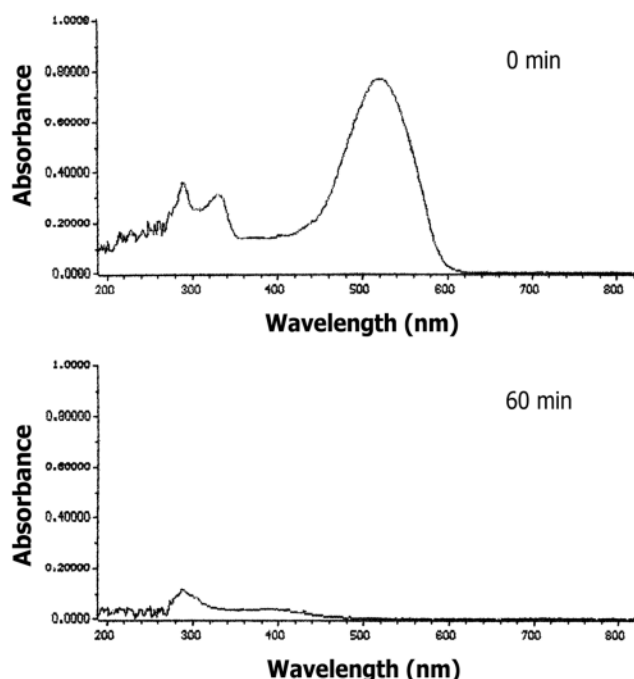


Fig. 3. Comparison of ultraviolet/visible spectrums before and after treatment (pH of the wastewater 3, pulse repetition rate: 136 Hz, agitation speed: 300 rpm, treatment time: 60 min).

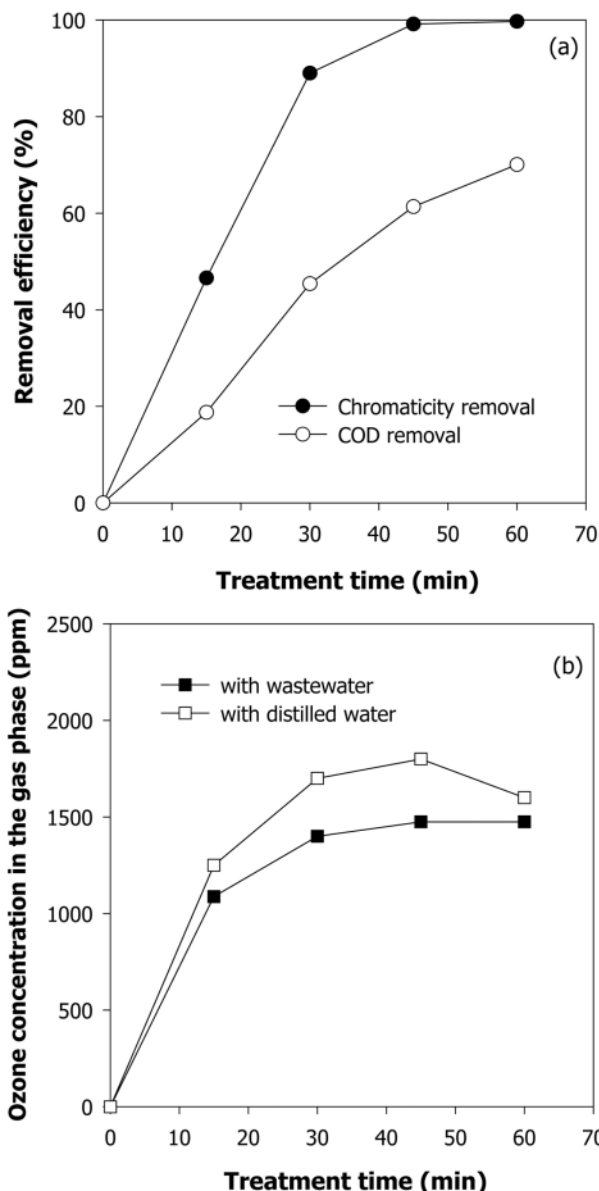


Fig. 4. Chromaticity and COD removal efficiencies as a function of time (a); Ozone concentrations in the gas phase with the simulated wastewater and with distilled water (b) (pH of the wastewater: 3, pulse repetition rate: 136 Hz, agitation speed: 300 rpm).

with the treatment time. As can be seen, the pulsed arc discharge method was very effective for the chromaticity removal. The chromaticity removal efficiency increased with the treatment time; the treatment time required to completely remove the chromaticity was about 60 min. The COD removal efficiency also increased with the treatment time, but it took longer time. The COD removal efficiency at 60 min was 70%, implying that the dye molecules destroyed were not completely oxidized to carbon oxides. Nevertheless, considering that the chromaticity removal from the textile-dyeing wastewater has been the main goal in the textile industry, the present pulsed arc discharge process capable of effectively treating the chromaticity may be a promising technology. Fig. 4(b) shows the ozone concentration in the gas phase with the treatment time. In this figure,

the concentration of ozone when the liquid phase was distilled water was compared with that when the liquid phase was the simulated wastewater. As observed, the concentration of ozone with the wastewater was lower than that with distilled water. This result indicates that ozone produced by the pulsed arc discharge was consumed for the oxidation of the dye. As mentioned above, the primary species produced by the electrical discharge in the gas phase is ozone. It has been reported that ozone can penetrate into the bulk wastewater and contribute to the oxidation of organic compounds [12,14]. But, it is believed that the reaction of the dye with ozone occurring at the interface between the gas and water phase is much more dominant than that in the water phase, because the solubility of ozone is extremely low. The Henry's Law constant of ozone is reported to be 5,284 atm [17]. This low solubility of ozone in water suggests that the penetration of ozone into the bulk wastewater cannot significantly contribute to the oxidation of the dye molecules.

Fig. 5 shows the effect of the initial pH on the chromaticity and COD removal. The treatment time was 30 min, and the agitation speed was 300 rpm. It was found that the chromaticity and COD removal efficiencies tended to increase with the decrease in pH. In this system, the electrical conductivity of the wastewater can play an important role in the degradation of the dye. It is certain that the increase in the conductivity as a result of decreasing pH increases the production of reactive species because of the increased electrical power, but it is believed that the effect of the conductivity on the production of reactive species disappears when the conductivity is sufficiently high. In Fig. 5, the highest chromaticity and COD removal efficiencies were observed at pH 3, but further decrease in pH did not affect them, which indicates that the conductivity in this pH range is sufficiently high to induce the pulsed arc discharge effectively. However that may be, the fact that lower pH is favorable for the removal of the dye can be a merit in terms of practical application, because the pH of real textile dyeing wastewater is generally low. For the rest of this work, all runs were conducted at pH 3.

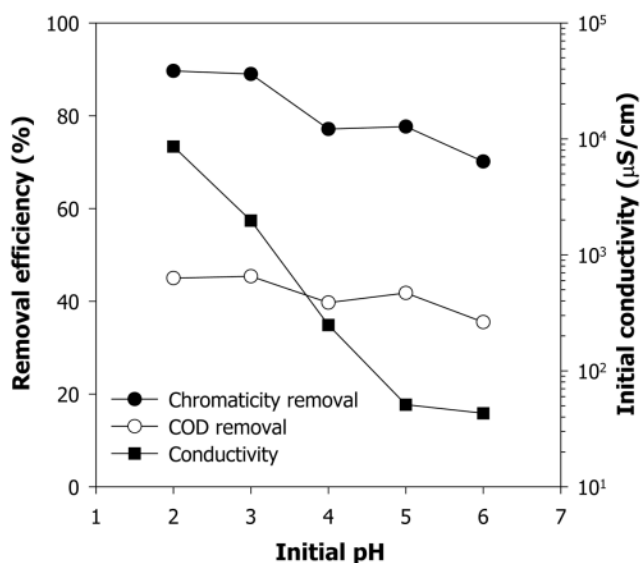


Fig. 5. Effect of the initial pH on the chromaticity and COD removal efficiencies, and the initial electrical conductivity of the wastewater (pulse repetition rate: 136 Hz; agitation speed: 300 rpm; treatment time: 30 min).

The effect of the agitation speed on the chromaticity removal is shown in Fig. 6. The mixing speed was varied up to 400 rpm, keeping other parameters constant. The results clearly show that there was a definite improvement in the chromaticity removal efficiency with the increase in the agitation speed from 0 to 300 rpm, and above 300 rpm the removal efficiency became insensitive to the agitation speed. The increase in the removal efficiency with the agitation speed implies that reactions occurring at the interface between the gas and liquid phases or in the vicinity of the interface dominated the removal of the dye. The optimum agitation speed of other reactor sys-

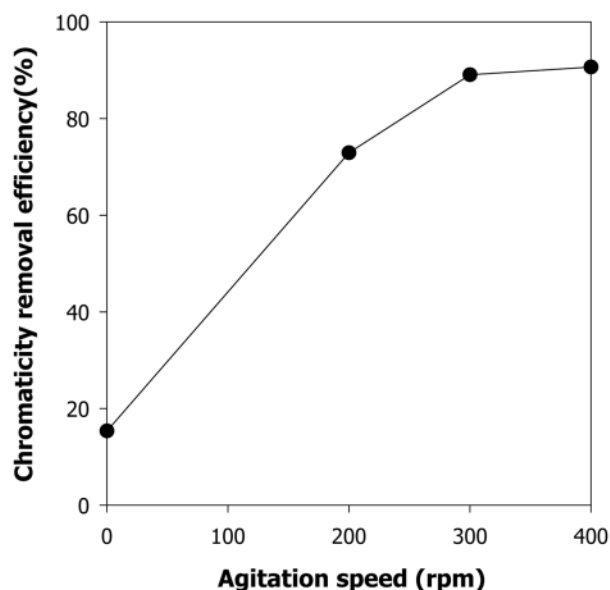


Fig. 6. Effect of the agitation speed on the chromaticity removal efficiency (pH of the wastewater: 3; pulse repetition rate: 136 Hz; treatment time: 30 min).

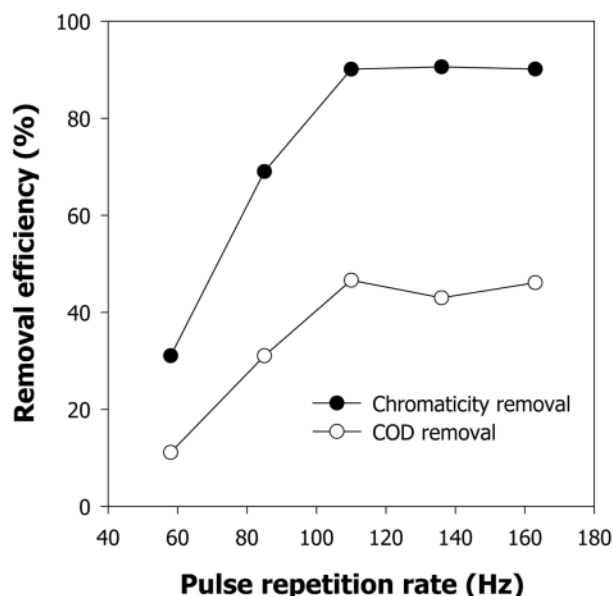


Fig. 7. Effect of the pulse repetition rate on the chromaticity and COD removal efficiencies (pH of the wastewater: 3; agitation speed: 400 rpm; treatment time: 30 min).

tems will differ from the result obtained in this study, but it is certain that satisfactory homogeneity in the bulk wastewater should be assured for effective treatment of the wastewater.

Fig. 7 presents the effect of the pulse repetition rate (pulse frequency) on the chromaticity and COD removal. The pulse repetition rate was changed up to 163 Hz (pulses/s). The increase in the pulse repetition rate provides the reactor system with more frequent reactive species production and ultraviolet light emission, and thus the degradation of the dye should depend on the pulse repetition rate. As expected, the chromaticity and COD removal efficiencies increased with the pulse repetition rate from 58 to 110 Hz. But, at pulse repetition rates higher than 110 Hz, similar results for the chromaticity and COD removal were obtained, which indicates that the rate of the degradation of the dye molecules is slower than the rate of reactive species production, i.e., excess amounts of reactive species were produced at pulse repetition rates higher than 110 Hz. When the rate of the degradation is slower, all the reactive species formed cannot be consumed for the reaction with the dye molecules. That is why the chromaticity and COD removal efficiencies were similar when the pulse repetition rate was higher than 110 Hz.

For the present system, the reactive species are generated in the gas phase above the surface of the wastewater. Thus, the working gas should play a key role in the degradation of the dye molecules. In Fig. 8, the chromaticity removal efficiency obtained in the presence of oxygen as the working gas is compared with the case of using nitrogen. When nitrogen was used, the chromaticity removal efficiency was very low. At 60 min treatment, only 14% chromaticity removal efficiency was obtained with nitrogen. On the other hand, the chromaticity was almost completely removed when oxygen was used. As mentioned above, several mechanisms including the oxidation by ozone and OH radical and the destruction by ultraviolet light emission can give rise to the degradation of the dye. The degradation of the dye in the absence of oxygen may be explained by the OH radical formed from water vapor and the ultraviolet light

emission during the pulsed arc discharge, but the contribution of these mechanisms to the chromaticity removal was only 14%. Consequently, it can be said that the reactive species produced from oxygen, especially ozone, mainly contributes the degradation of the dye.

## CONCLUSIONS

The pulsed arc discharge to the surface of wastewater has been employed for the treatment of the simulated dyeing wastewater. The results have shown that the present pulsed arc discharge method can effectively degrade the azo dye molecules (Acid Red 27). Almost complete removal of the chromaticity was achieved by this method, and the chemical oxygen demand level also significantly decreased. It has been found that the reactive species formed from oxygen, especially ozone, mainly affects the degradation of the dye molecules, and other mechanisms such as OH radical formation and ultraviolet light emission are minor. For the chromaticity removal, 45 min treatment time was required, but for chemical oxygen demand removal, it took longer time. For the present reactor system, the optimum pH, pulse repetition rate and agitation speed were found to be 3.0, 110 Hz and 300 rpm, respectively.

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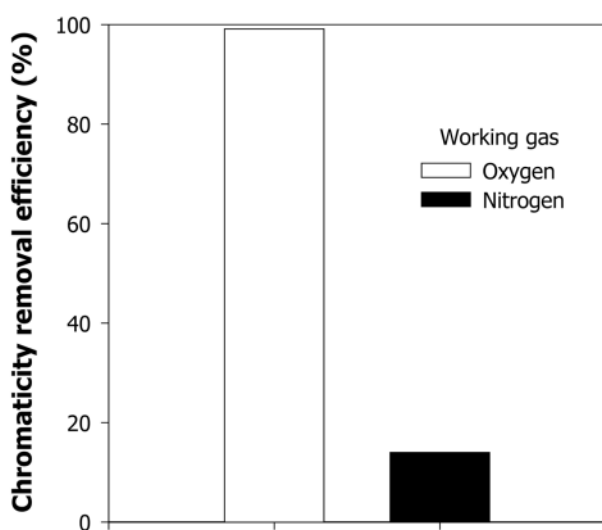


Fig. 8. Comparison of the chromaticity removal efficiency between oxygen and nitrogen as the working gas (pH of the wastewater: 3; pulse repetition rate: 136 Hz; agitation speed: 300 rpm; treatment time: 60 min).