

# Kinetics of decolorization of azo dye by bipolar pulsed barrier discharge in a three-phase discharge plasma reactor

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## Abstract

Removal of amaranth, a commercial synthetic azo dye widely used in the dye and food industry, was examined as a possible remediation technology for treating dye-contaminated water. Effects of various parameters such as gas flow rate, solution conductivity, pulse repetition frequency, etc., on decolorization kinetics were investigated. Experimental results show that an aqueous solution of 24 mg/l dye is 81.24% decolorized following 30 min plasma treatment for a 50 kV voltage and 0.75 m<sup>3</sup>/h gas flow rate. Decolorization reaction of amaranth in the plasma reactor is a pseudo first order reaction. Rate constant ( $k$ ) of decolorization increases quickly with increasing the applied voltage, pulse repetition frequency and the gas flow rate. However, when the applied voltage is beyond 50 kV and increases further, increase rate of  $k$  decreases. In addition,  $k$  decreases quickly when the solution conductivity increases from 200 to 1481  $\mu\text{S}/\text{cm}$ . The decolorization reaction has a high rate constant ( $k = 0.0269 \text{ min}^{-1}$ ) when the solution pH is beyond 10. Rate constant  $k$  decreases with the decrease of pH and reaches minimum at a pH of about 5 ( $k_{\text{min}} = 0.01603 \text{ min}^{-1}$ ), then increases to  $0.02105 \text{ min}^{-1}$  when pH decreases to 3.07. About 15% of the initial TOC can be degraded only in about 120 min non-thermal plasma treatment.

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## 1. Introduction

Azo dyes, the largest class of synthetic dyes used in the food industries, are characterized by the presence of one or more azo bonds ( $-\text{N}=\text{N}-$ ) in association with one or more aromatic systems. Many studies indicate that these dyes are toxic or carcinogenic. However, these dyes are not normally removed by conventional wastewater treatment systems. Decontamination of azo dye wastewater is major health issue due to heightened public awareness. In the past few years, several advanced oxidation processes (AOPs), such as non-thermal plasma technology [1,2], photo catalysis [3–5], supercritical water oxidation [6,7],

etc., had been investigated to degrade dye pollutants. Aqueous phase non-thermal plasma-based technology for water purification is an AOPs, characterized by the production of high oxidation potential species such as  $\text{OH}^\bullet$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and  $^\bullet\text{O}$  [1,2]. Recently, plasma chemical processes have attracted much attention due to their high efficiency in promoting oxidation, enhancing molecular dissociation, and producing free radicals to stimulate chemical reactions. Plasma treatment of contaminated water appears to be a promising alternative for the oxidation of aqueous organic pollutants [8].

Non-thermal plasma can be created by several discharge modes (such as under water corona discharge, glow discharge, dielectric barrier discharge, etc.), using reactors of different electrode geometries (such as point to plane electrode, wire to cylinder, etc.). All these methods, however, possess their own distinctive drawbacks, like low energy efficiency, short life time of the electrode, limit mass transfer area, etc. To eliminate those drawbacks mentioned above, it is necessary to develop more capable reactors to scale up the practical utilization of this technique.

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Electrical discharges in water and water–air mixture have been extensively studied in the past several years [1,2,9–12]. Most of these studies used a unipolar pulsed power supply. However, few studies focused on the discharge in the water–air–solid particle three-phase mixture [13], especially none of these studies attempted to investigate the discharge in the water–air–solid particle three-phase mixture powered by a bipolar pulsed power supply. In our previous study [14], the combination of a three-phase discharge reactor and the bipolar pulsed power supply was accomplished and enhancement of the plasma chemistry process in the reactor had been investigated. Effect of several solid packing on the chemical performance of the reactor was tested.

Based on our previous studies, simple glass beads are selected as the packing and a water–air–solid particle three-phase discharge plasma reactor was constructed. In the present investigations, experimental studies of decolorization kinetics of azo dye (amaranth or acid red 27) solution by bipolar pulsed barrier discharge in the three-phase discharge plasma reactor were carried out. Effects of several parameters on decolorization kinetics of the solution were systemly studied.

## 2. Experimental

### 2.1. Experimental setup

Fig. 1 shows the experimental system used in the present investigation. The structure of the plasma reactor and measurement equipments are the same as described in our previous study [14]. Simple glass beads (3–4 mm in diameter) were randomly packed into the annular space between the two electrodes. Height of the packing bed layer is 180 mm and effective electric field height is 220 mm.

A bipolar pulsed power supply was used to provide pulsed energization of the high voltage discharge electrode with peak-

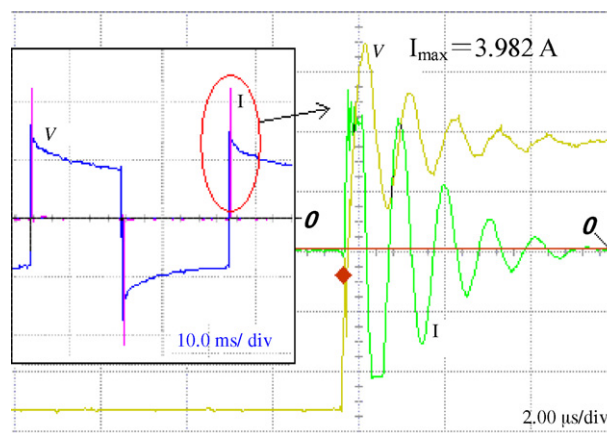


Fig. 2. Typical waveforms of the applied voltage and discharge current.

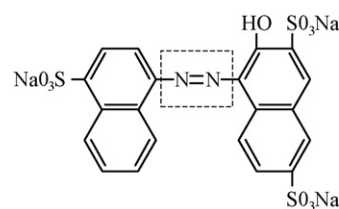


Fig. 3. Molecular formula of amaranth (AR27, CI 16185).

to-peak voltage ( $V_{pp}$ ) in the range of 0–100 kV, pulse width of 500–1000 ns, pulse rise time of 40–100 ns, and a repetition frequency of 1–100 Hz. The applied voltage and discharge current were measured by HV-P60 pulse high voltage probe (IWATSU Electric Co. Ltd.), TM6303 pulse current probe (Tektronix Co. Ltd.), and a digitizing oscillograph (HP 54820A). Typical waveforms of the applied voltage and the discharge current are shown in Fig. 2.

### 2.2. Experimental method and analysis

The dye, reagent grade amaranth (AR 27, CI 16185, Fig. 3) was used as received. Analytical grade KCl was used to give different initial solution conductivity. Dye solution was prepared in batch to avoid possible error.

Dye solution was added to the reactor before each run and then air was bubbled into the reactor through the aerator fixed at the bottom of the reactor. Air flow rate was measured by the gas flow rate meter.

All experiments were conducted in a batch mode. Typically, 5 ml samples were taken from the reactor vessel at 1 min intervals during each run. Dynamic UV–vis spectrum of the solution was scanned using a Jasco V-550 UV–vis spectrometer. Dye concentration was measured at its maximum absorbance (522 nm) with deionized water as blank. The total organic carbon was analyzed using Shimadzu TOC-Vcph analyzer.

Three trials were made for each experimental condition and resulted in errors of less than 5%. Actually, all experiments gave a high reproducibility during the experimental process.

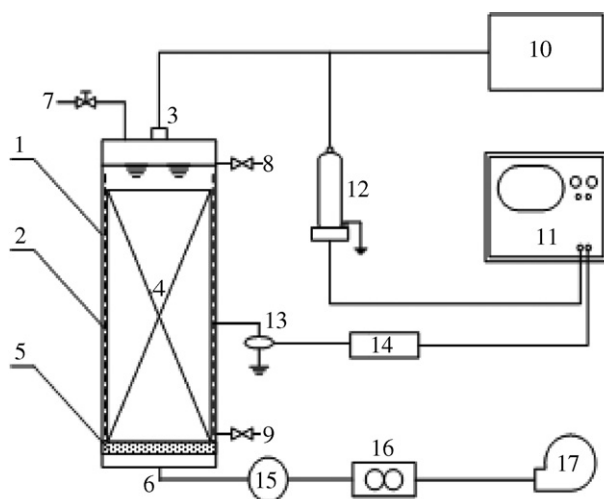


Fig. 1. Diagram of the experimental setup system. (1) Reactor; (2) ground electrode; (3) high voltage electrode; (4) packed bed layer; (5) gas aerator; (6) gas outlet; (7) gas inlet; (8) water inlet; (9) water outlet; (10) bipolar pulsed power; (11) oscilloscope; (12) high voltage probe; (13) pulse current probe; (14) amplifier; (15) buffer tank; (16) gas flow meter; (17) gas pump.

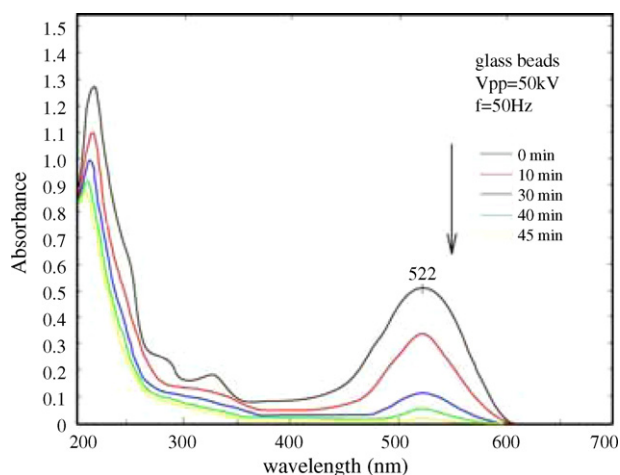


Fig. 4. Absorption spectra of the amaranth solution before and after treatment.

### 3. Results and discussion

#### 3.1. Decolorization of amaranth solution

Fig. 4 shows the absorption spectra of the amaranth sample. The absorption spectra of the sample is characterized by a strong absorption band in the visible range ( $\lambda_{\max} = 522$  nm) responsible for the red color.

As can be seen from Fig. 4, the absorption peaks corresponding to the red color disappear completely following the discharge plasma treatment. Even more surprising is the relative speed with which the dye decolorization can be achieved. An aqueous solution of 24 mg/l dye is 81.24% decolorized following 30 min plasma treatment. The rapid disappearance of the 522 nm absorption band in Fig. 4 suggests that the chromophore responsible for the characteristic color of the dye is broken down. However, decolorization was not observed at all without discharge plasma, suggesting that the plasma chemistry process results in the decolorization of the amaranth solution.

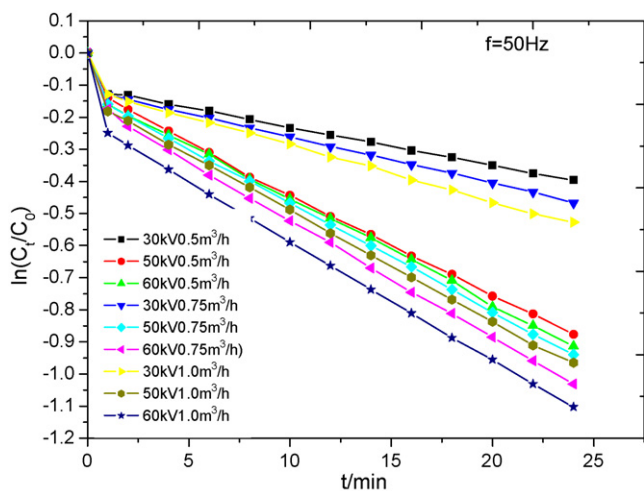


Fig. 5. Decolorization kinetics of the amaranth solution for different air flow rate and applied voltage.

Experimental results show that the concentration of amaranth in the solution decays exponentially and, at the same time,  $\ln(C_t/C_0)$  varies linearly with the treatment time  $t$  (Fig. 5), indicating that decolorization of the dye in the solution is a first ordered reaction.

In the plasma water treatment reactor, energy is electrically introduced into an aqueous solution through plasma channels. Active species such as high energy electrons, hydroxyl radicals, ozone, etc., are contained in the plasma generated. Those active species distribute and diffuse with the propagation of the plasma channel, and then selectively react with the azo groups in amaranth molecules, which results in broken-down of the N=N double bonds. Hence, the absorption band at 522 nm decreases quickly. Decolorization kinetics of the solution differ greatly for different experimental conditions such as initial solution conductivity, applied voltage, gas flow rate and pulse repetitive frequency.

#### 3.2. Effect of peak to peak voltage

Applied voltage has significant effect on the plasma generated as well as the active species formed, which finally results in different decolorization kinetics of the solution in the plasma reactor. Rate constant ( $k$ ) of the decolorization reaction increases with the increase of  $V_{pp}$ , however, when the applied voltage is beyond 50 kV, the increase rate of  $K$  decreases with the increase of applied voltage, as is shown in Fig. 6. That is because electrical discharges occur only when external applied voltage is beyond the breakdown voltage of the system. As the voltage increases, electrons will gain much more energy in the electric field and induce strong ionization of oxygen and water molecules by collision. Accordingly the discharge inside the air bubbles and around the contact point between the two contacted glass beads becomes much more intense, and more active species will be formed. Thus, rate constant ( $k$ ) increases quickly.

On the other hand, applied voltage also affects the temperature of the plasma channels and the discharge mode of the three-phase mixture. As the applied voltage further increases beyond 50 kV, temperature of the plasma channels also increases, which

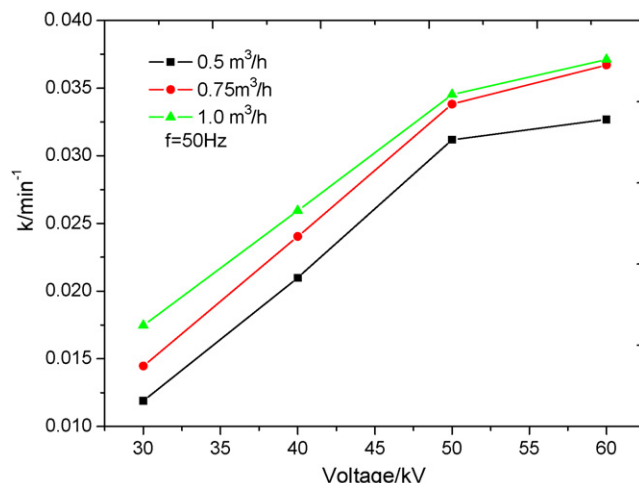


Fig. 6. Effect of applied voltage and gas flow rate on the rate constant  $k$ .

may induce the part decomposition of the ozone formed in the plasma channel. Therefore, increase rate of the ozone concentration decreases. The increase rate of the reaction constant  $k$  decreases.

### 3.3. Effect of gas flow rate

Gas bubbles play an important role during the discharge plasma water treatment process. Gas bubbling not only facilitates the breakdown of the system, but enhances the removal efficiency of pollutants by the oxidation of ozone when oxygen contained gases used [9]. As the most conventional and cheap gas sources, air was used here. Effect of air flow rate on the decolorization kinetics of amaranth was studied, as is shown in Fig. 6.

Gas flow rate greatly affects the number of air bubbles presenting in the reactor, thereby affects the number of broken down bubbles and the quantities of active species formed. In addition, gas flow rate determines the resident time of the gas in the reactor and also the reaction time of the gas phase active species (such as  $O_3$ ) with pollutant molecules, which finally determines the utilization ratio of the active species. As the gas flow rate increases, the number of air bubbles presented in the reactor increases. The broken down possibilities of air bubbles will thereby increase and more active species will be generated during the discharge process. Once generated, active species diffuse into the liquid phase and react with the organics. However, increase of the gas flow rate, in turn reduces the resident and reaction time of the active species with the pollutants. Consequently there may be a gas flow rate at which the balance between the formation and diffusion rate and reaction rate of the active species can be reached. Detailed work may be done to find this optimized gas flow rate in the future work.

### 3.4. Effect of initial solution conductivity

Initial solution conductivity is another important factor that affects the reaction kinetics of the plasma reactor (Fig. 7). As the initial conductivity of water increases, rate constant  $k$  decreases greatly.

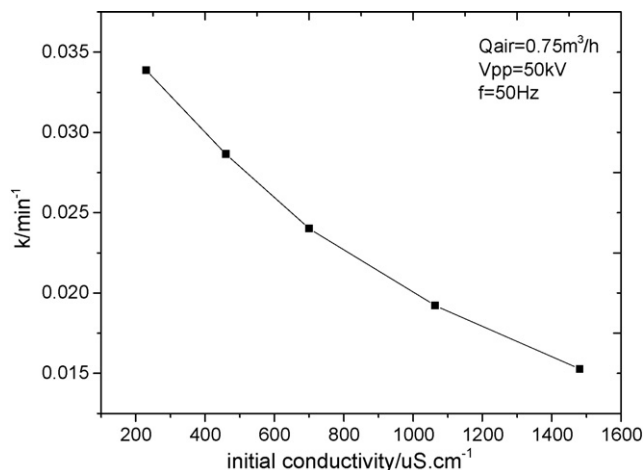


Fig. 7. Effect of initial conductivity on rate constant  $k$ .

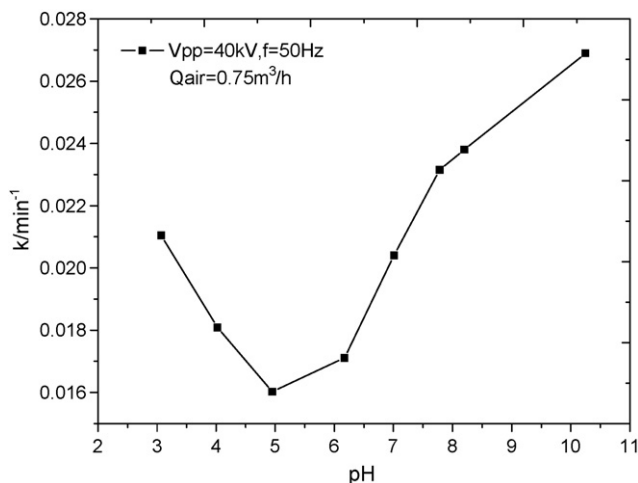


Fig. 8. Effect of pH on rate constant  $k$ .

More ions present in the solution when the solution has a higher conductivity. These charged ions greatly lower the influence of the space charge on the electric field distribution. The direct result is that the establishment of the high partial electric field is much more difficult and the number of breakdown micro-channels decreases. In addition, the quantities of ions present in the solution can strongly alter the propagation of the streamer by quickly compensating the space charge electric field on the streamer head of the plasma channel, and that lead to the decrease in the generation of chemically active species [15].

### 3.5. Effect of solution pH

Fig. 8 shows the dependence of the rate constant  $k$  on pH of the solution. As can be seen from the figure, decolorization kinetics of the solution varies greatly for different solution pH. The pH of the solution not only affects the characteristics of the dye micelle, but affects the generation and reaction of some active species (OH) contained in the plasma.

The solution pH changes the chemical composition of the ozone; for instance OH radicals were formed by decomposing ozone at high pH [16,17], whereas the molecular ozone content remained unchanged at a low pH. Ozone has an oxidation potential of 2.07 V, and the OH radical has an oxidation potential of 2.80 V; thus, the direct oxidation by ozone is slower than radical oxidation. Hence, the  $k$  values of the dyes increased with the pH under the alkaline solution condition.

### 3.6. Effect of pulse repetition frequency

Rate constant  $k$  increases with the increase of pulse repetition frequency, as is shown in Fig. 9. At higher pulse repetition frequency, much more energy is injected into water per unit time and a higher energy density per unit volume of water-air mixture obtained. Under the same experimental conditions ( $V_{pp}$ , initial solution characteristics and gas flow rate), the number of micro-discharges during every unit of time increases, broken down bubbles and the quantities of chemically active species would greatly increase, which finally leads to the increase in the colli-



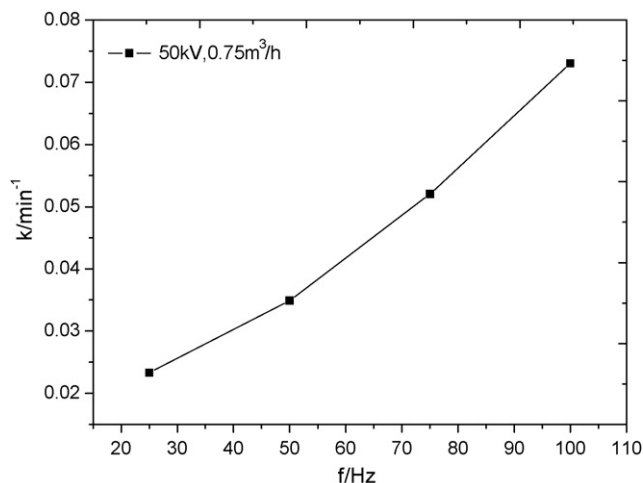


Fig. 9. Effect of pulse repetition frequency on rate constant  $k$ .

sion and even reacting probabilities of the generated species with the pollutants. The absolute quantities of reacting active species increase and higher color removal efficiency is obtained.

### 3.7. Variation of TOC

It is evident that the plasma chemistry process is not involved only the decolorization of the dyes, i.e., the cleavage of azo groups. The aromatic fragments are also degraded, but at a slower rate than that of decolorization. Consequently, the non-thermal plasma treatments of dyeing wastewater not only provide decolorization, but also an appreciable degree of aromatic ring destruction in the dye molecules. Fig. 10 shows the degradation of the TOC of the solution during the treatment process. Unlike the color removal process which can occur at a very fast speed, mineralization of the dye solution may take a relative longer time. This implies that more energy will be needed for a complete degradation of organics. In addition, like our previous investigation with another dye, increase of COD and BOD<sub>5</sub>/COD of the dye solution were found [9], indicating that part of the complex dye molecules has been broken.

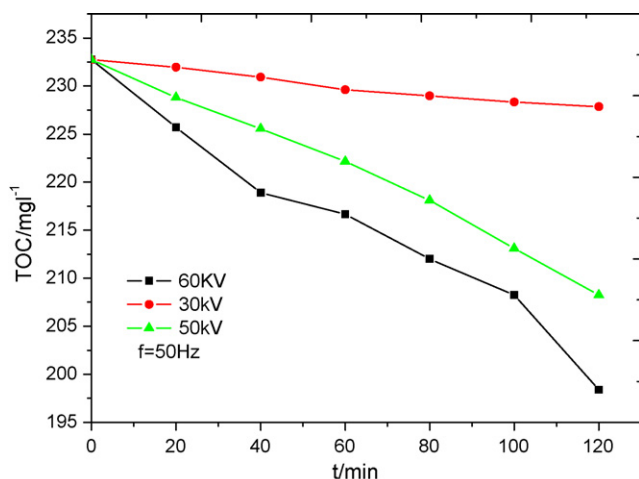


Fig. 10. Variation of the TOC.

Similar results have been reported by other researchers [18,19]. However, detailed study need to be carried out such as on the identification of the intermediates and clarification of possible reaction mechanisms. Nevertheless, experimental finding in this investigation reveals this technology can be used for quick decolorization of the dyeing wastewater, as well as pretreatment unit integrated into other water treatment process, i.e., used as a pretreatment process to increase the biodegradability of the water, followed by a conventional bio-treatment process.

## 4. Conclusions

Degradation of the azo dye in the plasma chemical reactor was studied following the disappearance of the parent molecules (decolorization) and the degree of mineralization, as measured by the reduction of the TOC in the sample. As the experimental results shows, decolorization is a fast process, whereas mineralization is attained after a long period of time. Although electric discharges is capable of mineralizing many recalcitrant pollutants, it requires considerable amounts of energy to attain the complete mineralization, whereas only the initial attack on pollutants with partial decolorization proved to be of the highest cost efficiency.

In addition, there are some problems remained unresolved for this technology, including the identification of possible intermediates produced during the treatment processes, reacting pathways of the oxidation species with pollutants, etc. Detailed understanding of these processes will help clarify the mechanisms of the plasma-based chemical reactions as well as guide the optimization of the reactor designation. Nevertheless, this technology will become more and more appealing to researchers.

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