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Degradation of methyl orange by pulsed corona discharge process in water

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ABSTRACT

Properties of methyl orange (MO) degradation and their dependence on experimental parameters such as electrical polarity, pulse frequency, the material, and thickness of the discharge electrode, as well as electrode gap distance were investigated in a laboratory scale pulsed corona discharge system. The MO degradation and H_2O_2 generation were significantly enhanced by positive polarity than negative polarity because of the numerous micro-discharges that were generated by the space charge effect induced by positive polarity. The increase of pulse frequency reduced the MO degradation even though it enhanced the number of streamers produced. An electrode material having low electrical and thermal conductivities resulted in more MO degradation. The smaller the curvature radius of the discharge electrode, the more efficient the MO degradation was. The number of electrode needles and the electrode gap distance also affected MO degradation during the discharge process.

Keywords: Pulsed corona discharges; Dye treatment; Methyl orange degradation; Experimental parameters

1. Introduction

A variety of new synthetic complex dyes are used by modern textile industries. Therefore, the degradation of these dyes from effluents has become a major environmental concern because it can lead to potential toxicity and unpleasant color in the wastewater. Toxic organic compounds are not effectively degraded by conventional technology, such as biological treatment processes. In this regard, various technologies such as adsorption, coagulation, photocatalysis, electrochemical oxidation, electron beam, and electrical discharges have been applied to decolorize and decompose dyes [1–4].

Recently, pulsed corona discharges have attracted increasing attention as a novel alternative to conventional processes for the effective degradation of refractory pollutants in wastewater, especially toxic organic

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compounds including dyes. This technology utilizes a high voltage power source equipped with a pulse forming network, to supply narrow width and fast rising pulse voltages between two electrodes, namely, a high voltage electrode and a flat plate ground electrode. When the applied voltage exceeds a critical onset value, a corona or a streamer discharge is formed. The pulsed corona discharges propagate across the aqueous solution, accelerate free electrons which collide, ionize, dissociate, or excite the molecules present in aqueous solution. It has been demonstrated that high voltage pulsed corona discharges generate a plasma state that initiates a variety of physical and chemical phenomena in water. The target pollutants are decomposed by these phenomena, such as an intense electric field, ultraviolet radiation, overpressure shock wave, and the formation of various chemically reactive species including radicals (such as high energy electron, OH·, H·, and O·) and molecules (such as ozone and hydrogen peroxide, excited neutral molecules, and ionic species) [5]. These chemically reactive species and physically active conditions have effectively degraded a variety of organic compounds and inactivating micro-organisms in aqueous solutions [6,7]. Among them, the major reactive species involved in the degradation of organic pollutants are hydroxyl radicals and hydrogen peroxide. Hydroxyl radicals, which are strong and non-selective oxidants, directly attack and mineralize organic compounds. Corona discharges have been used to degrade colored wastewater containing organic dyes including azo dyes [8,9]. In this study, the effects of various experimental parameters on methyl orange (MO) degradation in a pulsed corona discharge system are evaluated.

2. Experimental methods

The electrical circuit of the pulse forming network was similar to that of our previous work (Fig. 1) [10,11]. The main components of the circuit were a rotating spark gap switch and a capacitor, which are used to supply high voltage pulses to a reactor from a DC power supply (Glassman, Germany). The operating parameters of the pulse voltage were 0–50 kV peak voltage and 0–100 pps (pulse per second) pulse repetition rate, which were adjustable. The discharge reactor had a water-jacketed structure with acrylic tubes (inner diameter; 80 mm, outer diameter; 120 mm, and height; 190 mm). Cooling water was circulated through the space between the inner and outer acrylic tubes to maintain the MO solution at a constant temperature. A needle-to-plate type electrode geometry was used to induce a strong electric field between the electrodes. The needle electrode on which voltage pulses were applied was located at the bottom of the reactor. A silicon compound was used as the insulator for the Teflon fitting, and a thin wire was inserted in a stainless steel tube (0.7 mm). Approximately 2 mm of the wire protruded from the high voltage needle electrode. Various kinds of metal wires (stainless steel, nickel chromium, molybdenum, and tungsten) of 0.5 mm diameter were used as needle electrodes to demonstrate the effect of electrode material on MO degradation. A round stainless steel plate having 30 mm diameter was used as the ground electrode. The distance between the high voltage and ground electrodes was maintained at about 5 cm. The test solution was circulated at 100 mL/min by a peristaltic pump and sampled under the discharging condition. Aqueous samples of 5 mL were collected at predetermined time intervals in 1-hour experiments. Deionized water of less than 1 μS/cm conductivity was used to make all the solutions. In all experiments, the initial MO concentration and pH were 20 mg/L and 5.6, respectively. Solution conductivity was adjusted to 100 μS/cm by adding potassium chloride.

The pulse voltage and current were measured by using a high voltage probe (Taeyang 1000:1 probe)

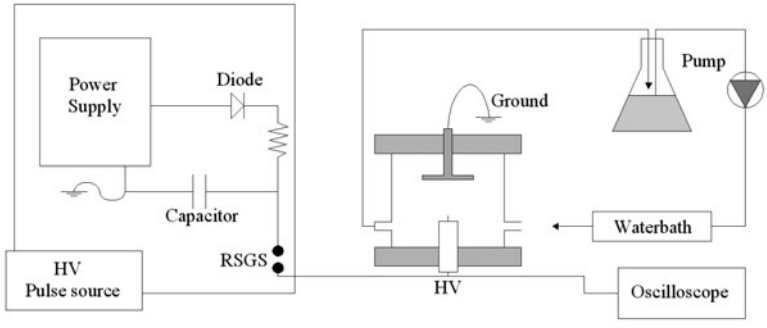

Fig. 1. Schematic diagram of the experimental setup.

and a wide band current transformer (Pearson Electronics M411), respectively, which were monitored with a digital oscilloscope (Lecroy LT354). The MO concentration was measured at 480 nm wavelength using a UV/VIS spectrophotometer (Agilent Technologies 8453). Hydrogen peroxide was determined colorimetrically from the reaction of H_2O_2 with titanyl ions [12]. Absorbance of the yellow peroxotitanium (IV) complex was measured at the wavelength of 410 nm. Initial and final pHs and conductivities were measured using a solution meter (Trans Instruments TI900). Three or more trials were performed for most sets of experimental conditions, and the average value was selected as the representative value.

3. Results and discussion

The initial MO concentration and conductivity were adjusted to 20 mg/L and 100 S/cm in the experiment, respectively. Typical voltage and current waveforms obtained from a liquid phase discharge are shown in Fig. 2. The pulse voltage and current fastly rise to peak values and then exponentially decay. The pulse width and pulse rise time which are defined as the pulse duration time and the time required for reaching peak value, respectively, are approximately 20 and 0.1 μS. The dissipated energy is 1.21 J/pulse, which was obtained by integrating the product of the voltage and current waveforms with time when the peak voltage was 40 kV at the pulse frequency of 60 Hz. Fig. 3 shows the intense plasma channels that formed between the high voltage electrode and the ground electrode in the solution. The solution showed no color after the treatment. Although not presented herein, the increase of the applied voltage increased the dissipated energy and promoted MO degradation. The increase of voltage created a strong electric field and thus generated more OH radicals which are responsible for MO degradation [10,11].

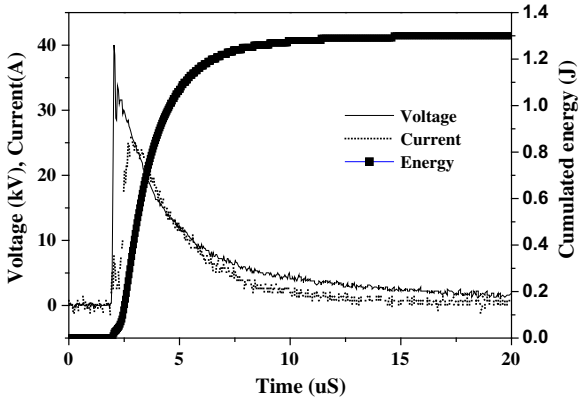

Fig. 2. Typical voltage and current waveforms obtained in the experiment.

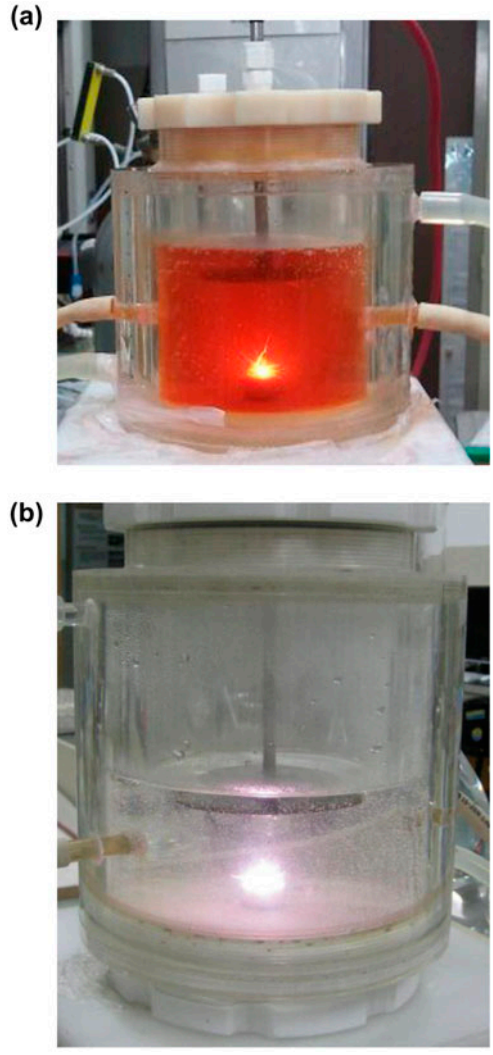

Fig. 3. Photographs of discharge phenomena in the pulsed corona discharge (initial state (a) and final state (b)).

Effects of the electrical polarity on MO degradation and H_2O_2 generation at the peak voltage of 45 kV are given in Figs. 4 and 5. MO degradation increased greatly under positive polarity than negative polarity. The MO conversion rates were 57 and 97% at 30 and 60 min, respectively, under positive polarity while 4 and 12% under negative polarity. This result is probably related to the difference in the physical properties of the discharges between the two electrical polarities. It has been reported that positive polarity generates numerous long micro-discharges, which are called "streamers" in a wider space while negative polarity produces short discharge channels in a limited space [13]. The development of corona discharge is usually

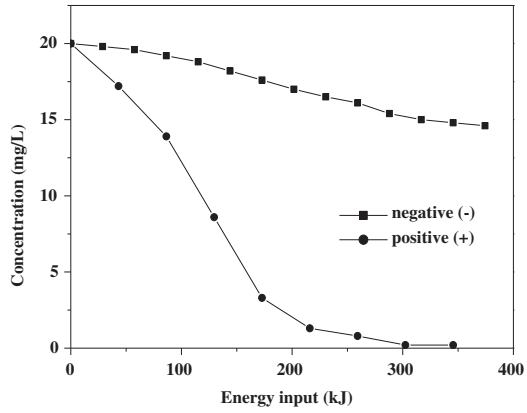

Fig. 4. Effect of electrical polarity on MO degradation.

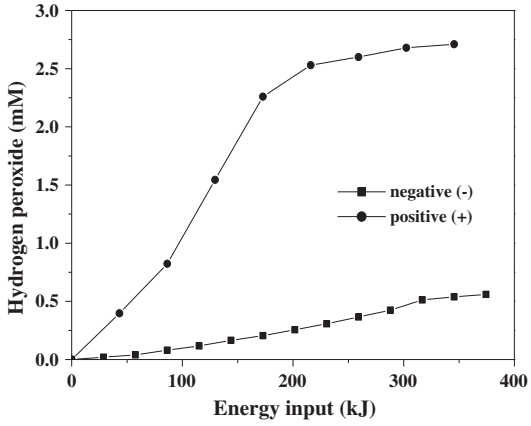

Fig. 5. Effect of electrical polarity on H_2O_2 generation.

space-charge limited, since positive ions accumulate in the space near the discharge electrode due to the difference of mobility between electrons and ions. Electric field strength is enhanced by the space charge effect for the positive polarity configuration, but is reduced for the negative polarity configuration. Therefore, the positive polarity configuration tends to produce more radicals than the negative polarity configuration as more energetic electrons are produced. Furthermore, the discharges generated by positive polarity propagate much faster than those generated by negative polarity due to the space charge effect [14,15]. As a result, positive streamers propagate much faster than negative streamers. The enhancement of H_2O_2 generation under positive polarity is also due to the space charge effect. More than 2.5 mM and approximately 0.5 mM of H_2O_2 were produced under positive and negative polarity configurations, respectively. A similar result was reported by Sun et al. [16], who observed an increased production rate of H_2O_2 under positive polarity than under negative polarity in pulsed corona discharges. Therefore, the positive polarity configuration was used in the subsequent experiments.

Fig. 6 shows the effect of pulse frequency on MO degradation with discharge time at peak voltage of 45 kV. MO degradation increased with the increase of pulse frequency. This result, however, could not demonstrate the pulse frequency effect on MO degradation because the variation of pulse frequency also affected the dissipated energy. In other words, the increase of pulse frequency increased the dissipated energy. Therefore, whether the enhancement of MO degradation was due to the increase of pulse frequency or that of input energy cannot be clearly determined.

The input energy is represented in Fig. 7 by the abscissa to reveal the net effect of pulse frequency on MO degradation. The result clearly indicated that the increase of pulse frequency reduced the MO degradation. This behavior can be explained by the fact that the discharging capacitor, at higher pulse repetition rates, does not have sufficient time to fully recharge [17]. Even though the increase of pulse frequency enhanced the number of streamers, it could not generate streamers having sufficient energy to efficiently degrade MO.

Fig. 8 shows the dependence of MO degradation on the material of the high voltage electrode. Used as the discharge electrode, the stainless steel (sus) wire gave the most efficient MO degradation, especially at higher energy inputs, while the nichrome (Nicr) wire gave similar MO degradation at lower energy inputs. The similar MO degradation was observed when tungsten (W) and molybdenum (Mo) wires were used as discharge electrodes. Although the exact reason is unknown, the difference in MO degradation according to electrode

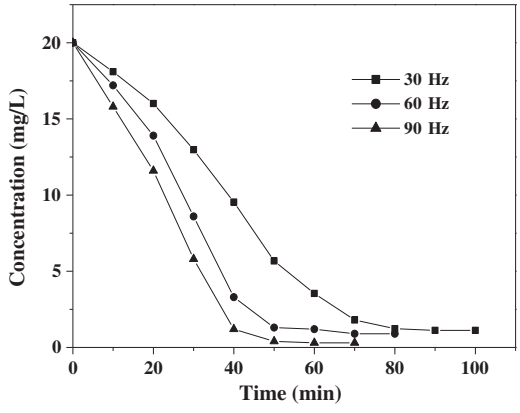

Fig. 6. Effect of pulse frequency on MO degradation according to discharge time.

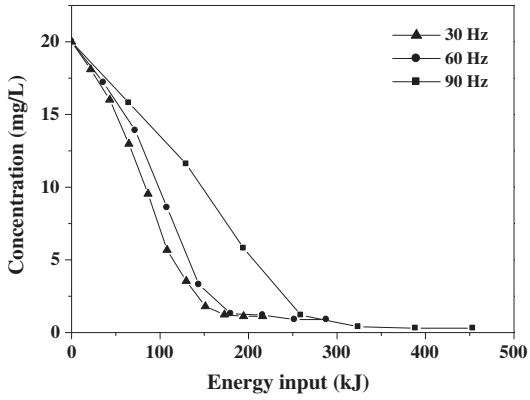

Fig. 7. Effect of pulse frequency on MO degradation according to dissipated energy.

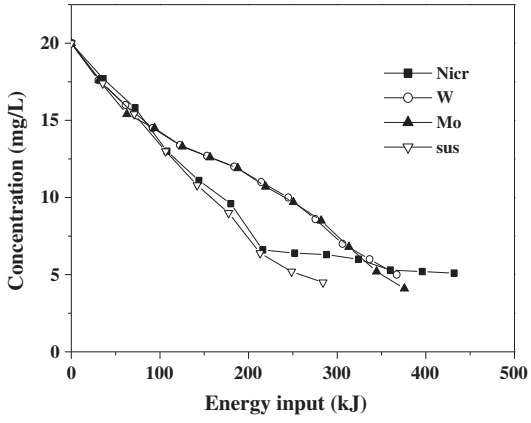

Fig. 8. Effect of electrode material on MO degradation.

material is closely related to material conductivity. The electrical and thermal conductivities of stainless steel are $0.0966 \times 10^6/\text{cm}\,\Omega$ and 80.2 W/m K, respectively, which are the lowest values among those of other electrode materials. The conductivities of molybdenum and tungsten have similar values ($0.187 \times 10^6/\text{cm}\,\Omega$ and 138 W/m K for Mo, $0.189 \times 10^6/\text{cm}\,\Omega$ and 140 W/m K for W) and those of nichrome are $0.1102 \times 10^6/\text{cm}\,\Omega$ and 90 W/m K. The lower conductivities could have induced a relatively higher resistance to electrical and thermal conduction, resulting in a stronger electric field [18]. Consequently, more radicals, including the hydroxyl radical which is responsible for MO degradation may be generated by using electrode materials of low electrical and thermal conductivities [19].

Fig. 9 shows the effect of electrode diameter and type on MO degradation. MO degradation was enhanced, regardless of the electrode material when the diameter of the wire electrode was reduced. The highest degradation was obtained when the hypodermic stainless steel tube was used as a discharge electrode. The increase of MO degradation with the decrease of wire diameter is due to the electric field strengthening from the small curvature electrode. In the case of the hypodermic electrode, the edge of the tube which has the smallest curvature radius formed the highest electric field strength, therefore, promoting the highest MO degradation. A high non-uniform electric field is needed to generate electrical discharges. In practice, this can be realized by applying high voltage pulses to a sharp electrode having a small curvature to generate more energetic electrons and chemically active species [10,20].

The effect of the number of needles of multiple discharge electrodes on MO degradation is shown in Fig. 10. The highest MO degradation was obtained for 3 needle, followed by 1 and 5 needles. The increase of discharge points enlarged the discharge region to promote the chemical reactions. However, a further increase of discharge points over the optimum number under a limited applied voltage reduced the strength of the discharges. Increasing the number of needles from 1 to 3 promoted the physical and chemical processes involved in the degradation of MO by enlarging the discharge region [21]. However, MO degradation was reduced when the number of needles was increased from 3 to 5 because of the reduction of the discharge strength. In fact, sparks formed intermittently, particularly in the region of high energy input, when five needles were used, and consequently, unstable discharges occurred.

The effects of electrode gap distance on MO degradation and H_2O_2 production are shown in Figs. 11 and 12, respectively. For gap distance of 5 cm, MO degraded and H_2O_2 generated more rapidly than for gap distance of 4 cm. This result may be due to the

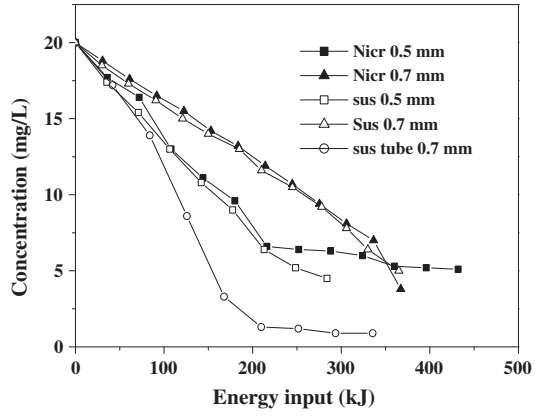

Fig. 9. Effect of electrode thickness on MO degradation.

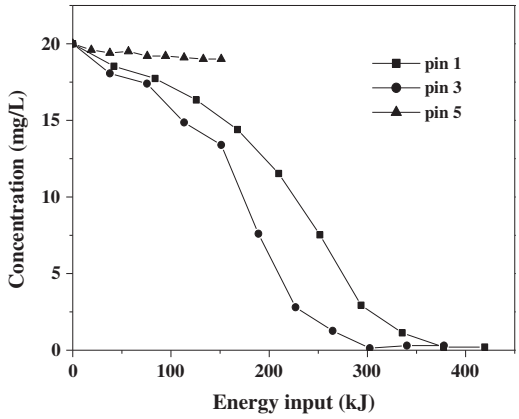

Fig. 10. Effect of the number of discharge needles on MO degradation.

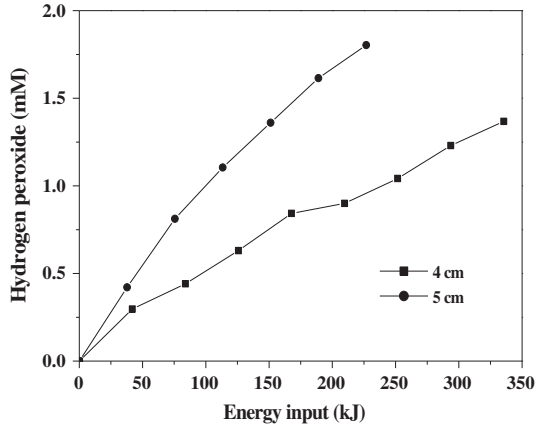

Fig. 12. Effect of electrode gap distance on H_2O_2 generation.

changes of discharge phenomena with the gap distance. Active species were distributed mainly around plasma channels, and a large number of plasma channels with strong energy would be very effective in generating a large number of active species [9,22]. For gap distance of 4 cm, a single and intensive plasma channel was formed but for gap distance of 5 cm, many plasma channels were formed. Although the strength of a plasma channel weakened, the discharge region was significantly enlarged with a 5-cm gap distance, therefore promoting the chemical reactions [23,24]. Although not presented herein, the experimental result for the case of a 3-cm gap distance showed intermittent and unstable spark discharges, which made continuous operating impossible.

The breakdown time determined by the statistical delay time depends on the electrode gap distance and the voltage. It becomes much shorter as the electrical field increases. The velocity of streamer propagation (υ) in an aqueous solution is a function of streamer formation time (t_f) and electrode gap distance.

$$\upsilon = d/t_f$$

The mean streamer velocity (υ) increases with the increase of electric field strength (E_0). Sparks are less likely to form if the pulse width is less than the breakdown time. The increase of electrode gap distance reduced the electric field strength, therefore a streamer was less likely to transform into a spark discharge.

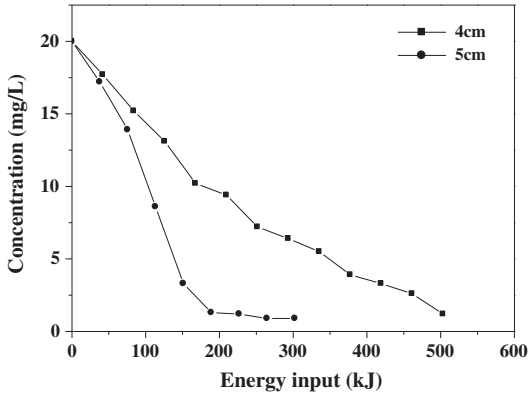

Fig. 11. Effect of electrode gap distance on MO degradation.

4. Conclusions

The degradation process of organic substances in a pulsed corona discharge process is complex and likely to occur through the oxidation by hydroxyl radicals. We investigated the effects of various experimental parameters on MO degradation in an aqueous solution by the pulsed corona discharge process. Positive polarity was more effective for the MO degradation and H_2O_2 generation than negative polarity because it generated more micro-discharges from the space charge effect. Even though the increase of pulse frequency enhanced the number of streamers, it deteriorated MO degradation because the streamers had insufficient energy. The material and thickness of the discharge electrode affected MO degradation. The electrode material having lower electrical and thermal conductivities induced more efficient MO degradation. The smaller the curvature radius of the electrode, the more efficient the MO degradation. The number of electrode needles and the electrode gap distance influenced MO degradation. Pulsed corona discharges with optimized operating parameters can be an alternative technology for the degradation of dye wastewater.

Acknowledgments

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