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PRACE

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exist for the publication of theoretical and experimental investigations of all aspects of the mechanics and thermodynamics of fluid-flow with special reference to fluid-flow machines

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poświęcone są publikacjom naukowym z zakresu teorii i badań doświadczalnych w dziedzinie mechaniki i termodynamiki przepływów, ze szczególnym uwzględnieniem problematyki maszyn przepływowych

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# Decoloration of dyes in aqueous solution by pulsed discharge plasma in water through the pinhole

Recently, it has been widely reported that some kinds of organic compounds can be degraded by high voltage pulsed discharge in water. The authors proposed a new method to generate plasma in water through the pinhole, which can also efficiently degrade organic materials (for example phenol) in water. In the present work, plasma discharge through the pinhole was applied to the decoloration of some kinds of dyes. The molecules of the dyes were decomposed and decolored within one or two hours (depending on the dye) due to the pulse treatment. Decoloration rate was accelerated by adding hydrogen peroxide. It was concluded that the decoloration was occurring as a result of the attack of high-speed electron and radical reaction in the plasma.

## 1. Introduction

Recently, the application of the high voltage pulsed discharge in water for decomposition of small amounts of organic substances was carried out by some researchers [1-6]. Many kinds of active species, such as OH and O radicals, hydrogen peroxide and others, are produced by the plasma in water phase. By means of the powerful active species (especially OH radical with high oxidation potential), the authors have shown that a small amount of phenol in aqueous solution was degraded and removed using the streamer corona, spark, and spark with streamer discharges [7]. This technique was applied in decomposition of o-nitrophenol, trichloroethylene, and perchloroethylene.

The pulsed discharge in water has some forms such as the streamer corona, spark, spark with streamer and the streamer through the pinhole. The authors reported that it was possible to produce the streamer discharge through a small hole opened in the insulating plate between plate electrodes due to concentrated electric field supplied to the pinhole [8,9].

The coloring of the wastewater from dying processes became a large problem.

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Oxidation by ozone and ultraviolet radiation, as well as adsorption to the active carbon, etc., were tried to remove them, but it could be difficult to find a method with high-energy efficiency and low cost. In this study, decoloration of dyes by means of high-speed electron and active species, which were generated by plasma in water, was tried. The effect of the additives on the increase of energy efficiency was also examined.

## 2. Experiment and method

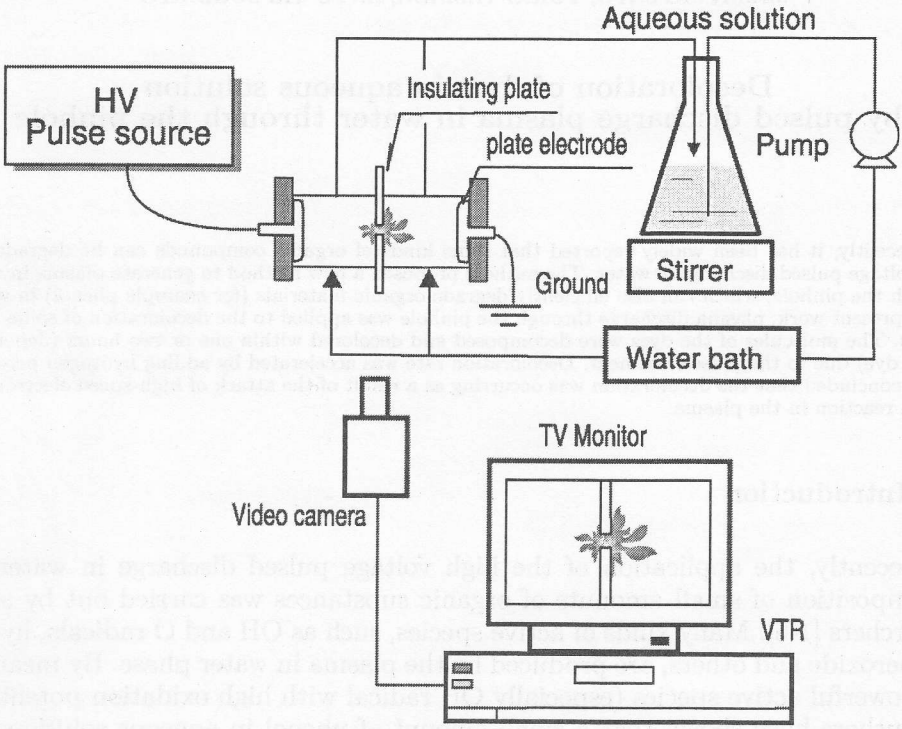


Fig. 1. Schematic diagram of experimental apparatus.

The schematic diagram of experimental apparatus is shown in Fig. 1. The round-edged plate electrodes (3 cm diameter) faced each other in the Plexiglas cylinder. Insulating plate made of polyvinyl chloride was set between the electrodes and the high voltage pulse was applied to the electrodes. The pulse voltage, pulse frequency and the capacitance of the pulse forming capacitor were 0 – 23 kV, 10 – 50 Hz and 6.000 pF, respectively. The electric field was concentrated in a pinhole having a diameter of 1 mm opened in the insulating plate. The electrical breakdown has occurred due to the high intensity field that caused the streamer discharge in water. The sample solution was circulated through the flask and tem-

perature controller by peristaltic pump (micro-tube pump), which flowed into the bottom of the reactor and out from the top. Rhodamine B, Evans blue, neutral red, acid orange 7, Chicago sky blue, methylene blue and blue black dyes were used as samples. Their concentrations were either 0.1 or 0.01 g/L and processing volume was 200 mL. The conductivity of the solution was changed by adding KCl, and it was adjusted to be $2 \times 10^{-2}$ S/m. Using the spectrophotometer (Shimadzu, UV-mini 1240), the decoloration effect of the dye was obtained from the ratio of the absorbency in the following equation.

$$\text{decoloration ratio} = \frac{\text{absorption (initial)} - \text{absorption (treated)}}{\text{absorption (initial)}} \tag{1}$$

## 3. Results and discussion

Streamer discharge was observed at the pinhole where the electric field was concentrated. However, no discharge occurred at the conductivity smaller than $5 \times 10^{-3}$ S/m. Streamer length at the negative electrode side was longer than that at the positive side, because the pinhole acts as a positive point as well as the case of point to plane electrode configuration. Using the point to plane electrode, it was reported that the streamer length in the case of the positive pulse applied is longer than that of negative. With the increase of the water flow rate through the pinhole, the streamer length decreased at both sides, which could be influenced by blowing out the ions or tiny bubbles due to the high-speed water flow.

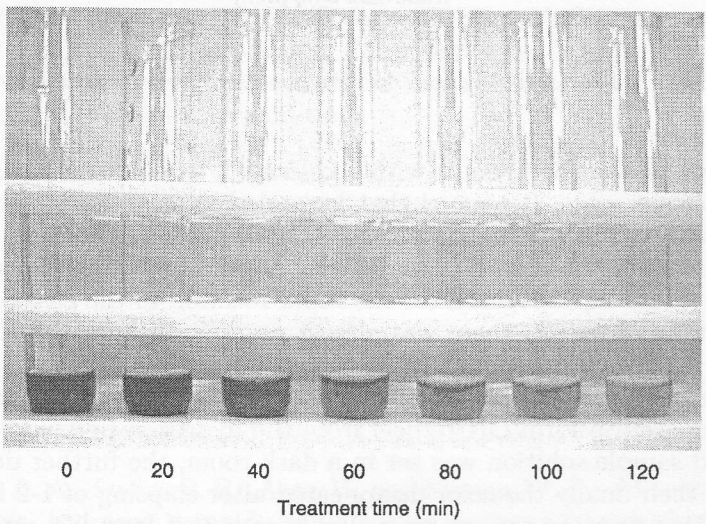


Fig. 2. Decoloration of Evans blue aqueous solution (0.1 g/l).

Fig. 2 shows decoloration of the Evans blue (0.1 g/l initial concentration) in test tubes, where each sample was taken with a time interval of 20 minutes. The dye was gradually decolored with increasing the processing time as shown in the photograph. Using the spectrophotometer, decoloration of several kinds of dyes was tested as shown in Fig. 3. By means of the plasma treatment the decoloration of about 80% was possible on either dye. It is considered that the decoloration occurred in the form of breakup of the bonds between chromophores due to attack of high-speed electrons or by means of the radical reaction in plasma region.

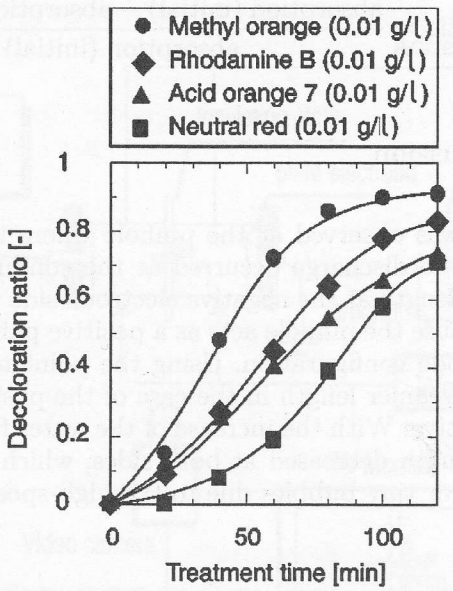


Fig. 3. Decoloration of aqueous dye solutions with plasma treatment.

Fig. 4 shows decoloration results with accelerated, by addition of a small amount of hydrogen peroxide. It seemed that large decoloration effect was obtained due to combined use of hydrogen peroxide. OH radical was formed by decomposition of hydrogen peroxide due to UV radiation and high-speed electron in plasma, which could be the reason for the rapid reaction in the case of hydrogen peroxide addition. However, there was almost no difference on the effect of the reaction rate between the amount of hydrogen peroxide addition of 0.1 and 1 g/l. This is due to the fact that the amount of the ultraviolet light becomes the rate-controlling step to form OH radical from the hydrogen peroxide. When the plasma treated sample solution was set in a dark room, the further decoloration was observed, then finally the color disappeared after elapsing of 1-2 h. This natural decoloration may be caused by a slow reaction of long life active species such as hydrogen peroxide.

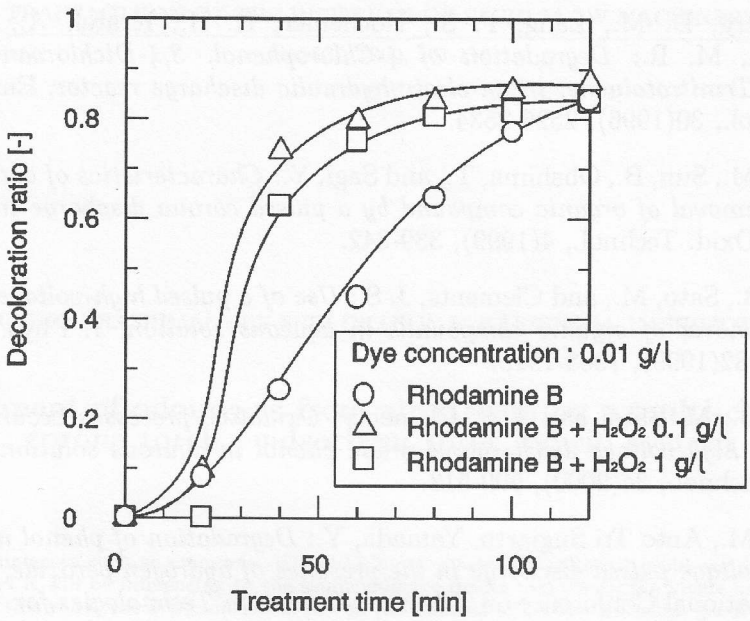


Fig. 4. The effect of hydrogen peroxide on decoloration.

## 4. Conclusion

Decoloration of dyes was tried using high voltage pulsed discharge in water through the pinhole. The streamer discharge was observed at the pinhole where the electric field was concentrated. The streamer length decreased with increasing water flow rate through the pinhole. The Evans blue or some kinds of dyes were decolored with increasing processing time. The addition of hydrogen peroxide was effective to accelerate the decoloration.

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## Odbarwianie roztworów wodnych za pomocą plazmy wyładowania impulsowego w dielektryku z otworami

**Streszczenie**

Znana jest możliwość zastosowania wysokonapięciowego impulsowego wyładowania elektrycznego w wodzie do eliminacji pewnych związków organicznych. Autorzy wykorzystali tego typu wyładowanie do odbarwiania roztworów wodnych z kilkoma typami barwników. Wyładowanie generowane było na otworach znajdujących się w płycie wykonanej z dielektryka i umieszczonej pomiędzy elektrodami wyładowczymi. Pod wpływem wyładowania impulsowego trwającego 1-2 h cząsteczki barwników ulegały rozkładowi, a roztwory wodne odbarwieniu. Za proces ten odpowiedzialne są elektrony i rodniki powstające w roztworze wodnym podczas impulsu wyładowania elektrycznego. Czas odbarwiania można skracać poprzez dodanie do roztworu nadtlenku wodoru.