

**DEGRADATION OF ORGANIC DYES VERSUS H<sub>2</sub>O<sub>2</sub> GENERATION DURING THE DC DIAPHRAGM DISCHARGE TREATMENT IN WATER SOLUTIONS<sup>1</sup>****Z. Stará<sup>2</sup>, F. Krčma***Faculty of Chemistry, Brno University of Technology Purkyňova 118, 61200 Brno, Czech Republic*

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The paper is focused on investigation and comparison of two chemical processes occurring in water solutions treated by DC diaphragm discharge - hydrogen peroxide generation and degradation of organic compounds dissolved in water. Concentration of hydrogen peroxide produced by the discharge depends on the discharge conditions (polarity and magnitude of the applied voltage etc.) and it is determined by photometry using a specific titanium reagent. Organic dyes in solid phase and dissolved in water are chosen as model compounds for the degradation processes. Their concentration is determined by photometry, too.

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**1 Introduction**

The discharges generated in liquids have a special position among the plasma sources. Various active chemical species such as hydroxyl radicals, hydrogen and oxygen radicals, hydrogen peroxide etc. are produced in water by this kind of the discharge [1]. These active species initiate many further chemical reactions. Therefore the processes taking place in such discharges can be applied in fields of water treatment, surface treatment etc. Especially the destruction of various organic pollutants or organic dyes dissolved in water and specific reactions in liquid phase are the main research fields of discharges in liquids [1, 2].

This work focuses on the diaphragm discharge created using the non-pulsed DC high voltage with the tension of about 2 kV. Such discharge is also called "electrode-less" [3, 4], because it is created in a small pinhole in the centre of the dielectric diaphragm in a relatively great distance from the high voltage electrodes (2 cm). The dielectric diaphragm is placed between two planar electrodes [5]. When the DC voltage is applied, different plasma channels (so-called streamers) are created in both parts of the reactor (see Fig. 1). These streamers have converse polarity and they differ both in their shape, velocity of propagation and energy of electrons [3].

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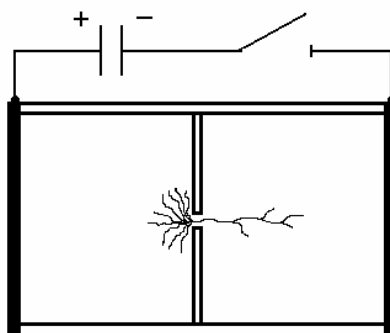
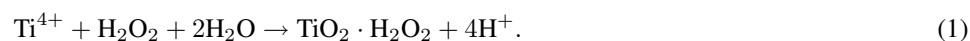


Fig. 1. Scheme of the diaphragm discharge principle with different plasma channels in the parts of the reactor.

## 2 Experimental and methods

A batch discharge reactor was used in experiments [6]. It consisted of two parts - a negative part with a cathode (positive discharge creation) and a positive part with an anode (negative discharge creation). The planar electrodes were made of stainless steel. The simplified scheme of the discharge reactor is shown in Fig. 2. The dielectric diaphragm (PET, 0.25 mm) with a pinhole in the centre was placed symmetrically between the electrodes. To generate the high voltage and to create the discharge, a non-pulsed DC HV source was used. Tension of the applied voltage can be varied from 1.4 to 2.8 kV. Due to the considerable heating of the reactor by the discharge and to minimize hydrogen peroxide thermal destruction, two cooling boxes were installed in both parts of the reactor. A mixing system was used to ensure homogenous conditions in the whole volume of the liquid.

As most of the organic dyes were not electrolytes, it was necessary to add extra electrolyte of a defined amount to the solution. Demineralised water containing NaCl electrolyte was used to obtain the defined liquid conductivity (optimally  $300 - 700 \mu\text{S}\cdot\text{cm}^{-1}$ ). Various organic solid dyes dissolved in water were used for the experiments. The organic dyes differed in structure, colour, origin and purpose of use (for textile dyeing, in food industry etc.). The concentration of the used dyes varied from 6 to  $20 \text{ mg}\cdot\text{l}^{-1}$ . The concentration of hydrogen peroxide produced by the discharge was determined by colorimetric method using a specific reaction between  $\text{H}_2\text{O}_2$  and titanium reagent [7]:



The yellow-coloured peroxotitanyl complex was determined by the UV-VIS spectroscopy at 407 nm, hydrogen peroxide concentration in this complex was directly proportional to its absorption intensity. Concentration of organic dyes in the solution was also determined by photometry.

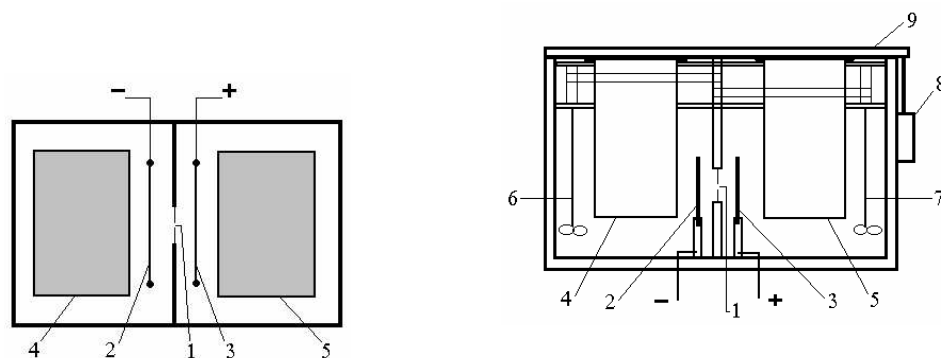


Fig. 2. Simplified scheme of the discharge reactor - a platform (left) and a side view (right): 1 - diaphragm with pinhole, 2 - cathode, 3 - anode, 4, 5 - cooling boxes, 6, 7 - stirrers, 8 - security pin, 9 - security top.

### 3 Results

The investigation of hydrogen peroxide generation by the DC diaphragm discharge in water solutions already was an object of our study in some previous works [5, 6]. Generally, hydrogen peroxide was produced by the discharge in water solution and its amount was dependent on the discharge conditions, such as applied high voltage (magnitude and polarity), material of electrodes, initial solution conductivity etc. [5].

The evaluation of  $\text{H}_2\text{O}_2$  concentration during the discharge treatment is given by Fig. 3 (right). Production of hydrogen peroxide was almost linear in time and it was highly dependent on the discharge polarity. In the case of the one-hour positive discharge treatment (i.e. in part of the reactor with the cathode!), the final concentration of  $\text{H}_2\text{O}_2$  was approximately  $1.8 \text{ mmol}\cdot\text{l}^{-1}$  (about  $60 \text{ mg}\cdot\text{l}^{-1}$ ), in the opposite polarity, the amount of hydrogen peroxide was only about  $0.3 \text{ mmol}\cdot\text{l}^{-1}$  (about  $10 \text{ mg}\cdot\text{l}^{-1}$ ), so six times lower.

A typical evaluation of the dye concentration during the discharge treatment is shown in Fig. 3 (left). This figure demonstrates the relative concentration decrease of the Evans Blue dye. The degradation was also dependent on the discharge polarity and the decolorisation process was faster in the negative discharge. The concentration of Evans Blue became less than 10% after 100 minutes in the negative discharge. In the positive discharge, the concentration decrease was only about 70%.

### 4 Discussion

The relation between two processes occurred in water solution treated by the electric discharge was examined. The comparison is shown in Fig. 3 and it gives very interesting results. In the case of the positive discharge treatment, the production of  $\text{H}_2\text{O}_2$  was higher than in the negative one and therefore we had expected more significant decolorisation in the positive discharge. But the experiments gave opposite results. This phenomenon is still an object of our contemporary study.

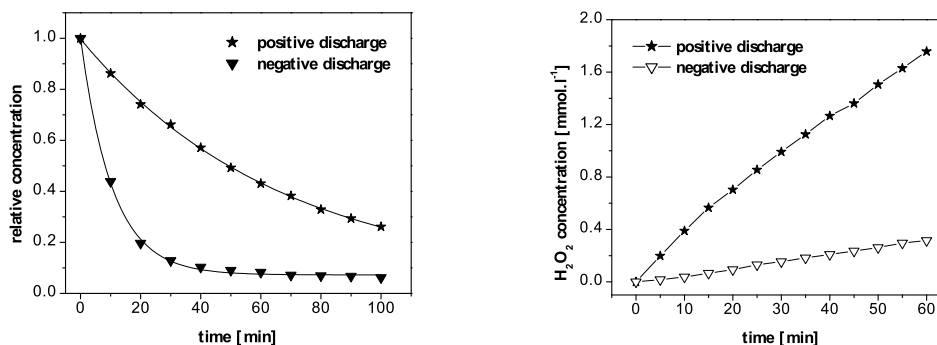


Fig. 3. Evans Blue dye decolorisation (left) and hydrogen peroxide generation (right) in time as a function of applied voltage polarity (2.45 kV, 5 mM NaCl, 500  $\mu\text{S}\cdot\text{cm}^{-1}$ ).

The results of the processes represented in Fig. 3 were studied during two different experiments but with the same discharge conditions and set parameters. But although they were observed simultaneously in the same water solution and at the same time, the evaluation of the dye and H<sub>2</sub>O<sub>2</sub> concentration did not change.

The possible reason of the dye decomposition could be also in an electrochemical oxidation, especially in anodic oxidation [7]. To confirm this explanation of the "contrary" polarities, another experiment was realised. It was important to avoid the discharge influence in the process and keep only electrolysis in the system. Therefore a relatively great pinhole in the dielectric diaphragm (about 3 mm) and a very low applied voltage (0.875 kV) were used. The result of this experiment with the solution of Saturn Red dye is given by Fig. 4 (right). The fact that the discharge was totally excluded, was confirmed by the determination of hydrogen peroxide – at these conditions, no hydrogen peroxide was generated. But although there were no reactive species in the solution the dye was decomposed in the both discharge polarities. So we can consider the electrolysis as an additional factor in the process of the degradation of organic compounds dissolved in water. The influence of electrolysis was probably so significant due to the non-pulsed DC high voltage used in experiments.

Figure 4 compares the degradation process caused the discharge (left) and by the electrolysis (right). It can be clearly seen that the process was more significant in the presence of the discharge. In this case, the decomposed amount of the dye was more than 80% while in the case of pure electrolysis, the relative dye concentration reached only about 50%.

## 5 Conclusions

Two chemical processes occurring in water solutions during the diaphragm discharge treatment are compared in this contribution, namely hydrogen peroxide generation and decomposition of organic dyes dissolved in water. The influence of the discharge conditions on these processes is investigated.

Concentration of hydrogen peroxide produced by the discharge in water solutions increased

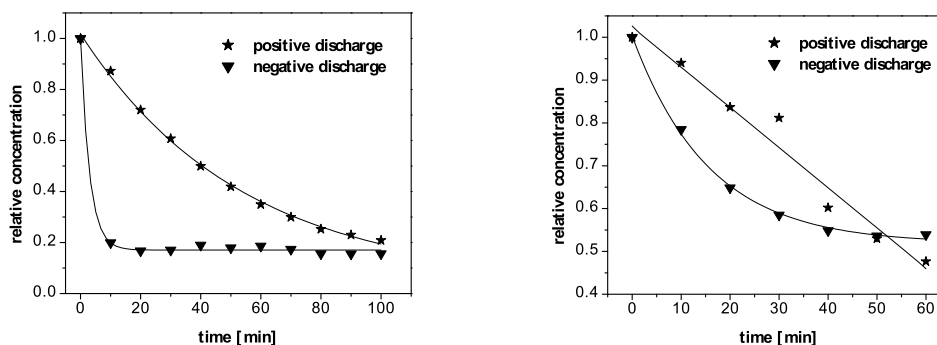


Fig. 4. Concentration decrease of Saturn Red dye during the discharge (left: 2.45 kV, 140 mA, 343 W) and electrolysis (right: 0.875 kV, 50 mA, 44 W) - 5 mM NaCl,  $500 \mu\text{S}\cdot\text{cm}^{-1}$ .

in time. Its generation was almost linear and was influenced by the applied voltage. The production of hydrogen peroxide was more significant in the positive discharge polarity. Its concentration became about  $60 \text{ mg}\cdot\text{l}^{-1}$  after an one-hour experiment.

The degradation of organic compounds by the diaphragm discharge was studied in water solutions of selected organic dyes. The decrease of the dye concentration was observed in both of the discharge polarities but in the negative discharge, the decolorisation was more significant. This was the opposite phenomenon compared with the production of hydrogen peroxide and its possible reason, especially the influence of the electrolysis, is discussed in the text. In the majority of experiments, the dye decomposition went to the final concentration less than 20% of the initial dye concentration after 100 minutes of the discharge treatment.

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