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On degradation mechanisms of organic dye molecule in DC diaphragm discharge in water solutions

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Introduction

Generation of electrical discharge in water initiates several physical and chemical processes which more or less participate on the subsequent decomposition reactions of organic compounds dissolved in water. The main processes are UV radiation, shock waves formation, production of chemical reactive species (hydroxyl, hydrogen and oxygen radicals, hydrogen peroxide), electrolysis (if constant electric current flows through the system) or ozone production if oxygen is introduced into the solution [1]. These processes could cause further decomposition of organic molecules presented in the solution. However, contribution of each mechanism is different. This paper presents results obtained by the investigation of DC diaphragm discharge in water solutions of selected textile dyes and compares contributions of several degradation processes on the dye removal.

Due to the application of DC voltage, two kinds of plasma streamers were formed on each side of the diaphragm. In the cathode space, longer channels with few branches propagated towards the electrode. On the other side, dense net of shorter plasma streamers filled the spherical volume around the pin-hole. Both kinds of plasma streamers differed not only in their shape but at most in the electron energy responsible for further initiated processes [2].

Experimental

Diaphragm discharge was generated in a batch reactor divided into two electrode spaces by the dielectric barrier with the pin-hole in its centre (PET diaphragm, thickness of 0.25 mm, initial pin-hole diameter of 0.4 mm) [3]. High voltage source giving the mean power up to 300 W was used for the discharge generation in the pin-hole. Effect of electrolysis was studied in the same batch reactor as the discharge experiments. HV source was adjusted on the level providing only low discharge power to keep only electrochemical processes and no discharge in the reactor. Effect of pure UV light was investigated in a separate experiment. Testing cell with a sample solution was placed into an optical desk. The desk consisted of UV light source (deuterium lamp), mirror and a cell holder.

Water solutions of textile organic dyes (Direct Red 79, Direct Blue 106) were prepared in total volume of 4 litres and completed by an electrolyte (NaCl) to adjust proper solution conductivity in the range of 300–600 μS·cm^{-1}. Solution pH was not extra modified (initial value was approximately 6.5). Discharge and electrolytic experiments were carried out for 40 minutes with 5 minute sampling. Testing cells containing 3 ml of the dye solution were exposed by UV light for 1.5 hour. Decoloration of the dye solution was determined by the absorption spectroscopy (spectrometer Helios Omega, wavelength range from 350 to 700 nm) with respect to the electrode space polarity.

Results and discussion

Utilization of the DC diaphragm discharge for organic dye decomposition in water solutions was already proved and published [4]. Decrease of the dye concentration was observed in both electrode spaces of the discharge reactor. However, more effective decoloration was determined in the part with the positive electrode than with the negative one [4].

Decomposition rate of both Direct Red 79 and Direct Blue 106 dyes reached more than 60 % after 40 minutes of the discharge treatment in the anode space. The absorption spectra of the blue dye obtained from the samples treated in the anode space are shown in Fig. 1. It is clear that the dye absorbance decreased during the discharge. Moreover, a significant shift of the dye absorption maximum wavelength was observed. This effect was probably related to the creation of various by-products of the dye degradation by the discharge.

The comparison of absorption spectra of both tested dyes gave an interesting result. While in the case of the blue dye DB106 the maximal absorption shifted to the longer wavelength, in the case of the red dye DR79 it moved to the shorter wavelength. This phenomenon was probably connected to the different decomposition by-products as well.

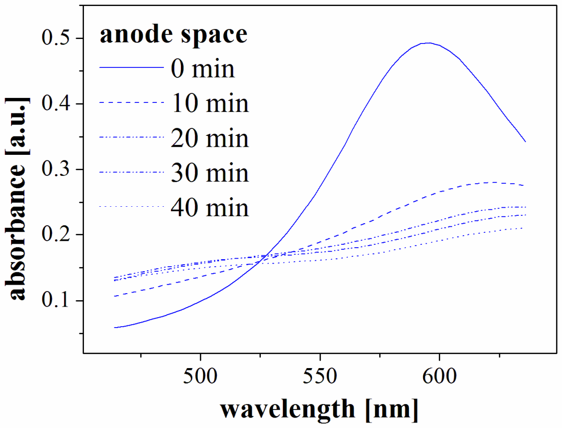

Fig. 1: Absorption spectra of Direct Blue 106 dye during the diaphragm discharge (170 W) in NaCl solution (500 μS·cm^{-1}) and in the anode space.

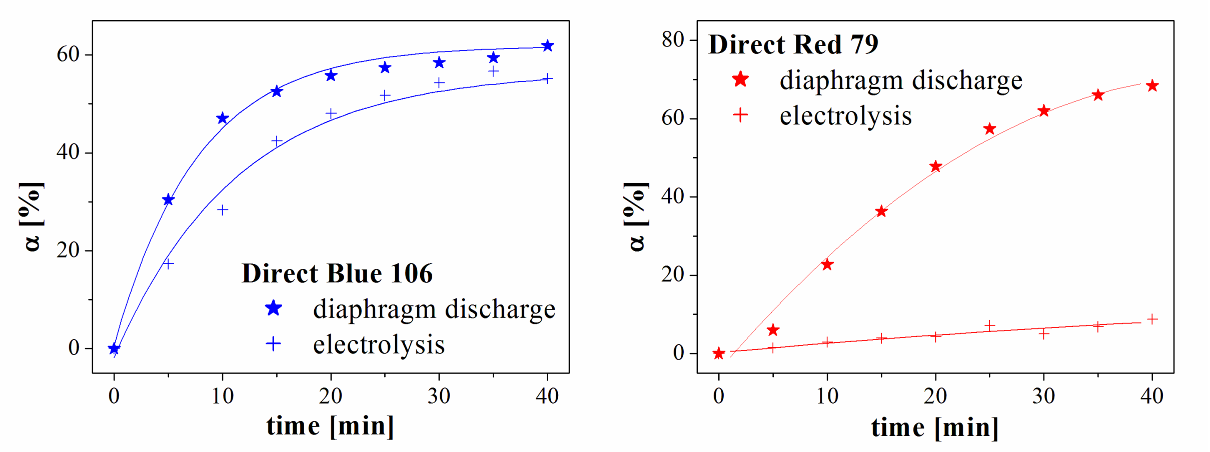

Fig. 2: Decomposition rates of Direct Blue 106 (left) and Direct Red 79 (right) dyes during the diaphragm discharge (170 W) and electrolysis (30 W) in NaCl solution (500 µS·cm^{-1}) and in the anode space.

The results obtained by electrolytic treatment of both dye solutions are presented in Fig. 2. Decomposition rates during the treatment are compared from the viewpoint of the diaphragm discharge and of the pure electrolysis, both given for the anode space of the reactor. In both tested dyes, the decoloration process in the discharge ran almost exponentially and the final decomposition rate after 40 minutes of the treatment reached the value over 60 %. However, the situation in the electrolysis went in a different way. While Direct Blue dye was electrochemically oxidized up to 60 % (Fig. 2 left), i.e. to the almost same value as by the discharge, Direct Red dye removal by electrolysis was hardly 10 % after 40 minutes of the treatment (Fig. 2 right). Moreover, the DR79 decoloration went more or less linear while the DB106 degradation followed up the exponential trend like in the discharge. The difference in the obtained data could be caused by various degradation mechanisms due to the different structure of each dye (molecular weight, number of substitutes, various size of double bond system). The molecule of DB106 is smaller and with only a few substitutes and therefore it could be easily attacked by OH radicals as well as decomposed by lower energy supplied into the system by pure electrolysis.

Influence of UV radiation on the dye decoloration was studied in water solutions of both dyes (DR79 and DB106). Deuterium lamp was used as a light source. Its emission spectra included the region of OH radical (around 310 nm) that simulated similar conditions as in the diaphragm discharge. Tested cells with samples were exposed by the radiation for 1 and 1.5 hour, respectively. Absorption spectra of both dye solutions were analyzed after the treatment and compared to the initial dye spectrum. The final results are given for the Direct Red 79 in Fig. 3. It is evident that the UV treatment did not provide any remarkable difference in absorption spectra. More or less the same results (i.e. no change is observed in the absorption spectrum) were obtained for the Direct Blue 106 dye, too. Thus we have assumed that contribution of UV radiation in the diaphragm discharge is only negligible.

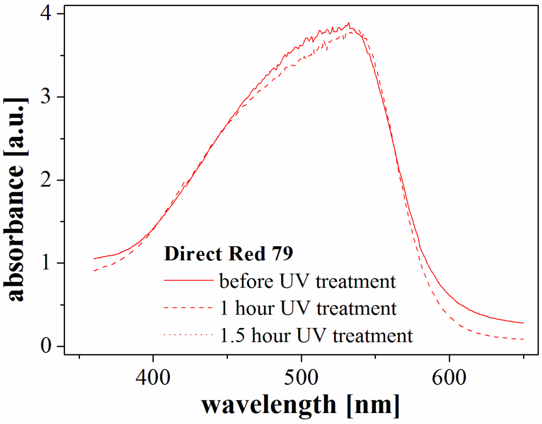

Fig. 3: Absorption spectra of Direct Red 79 dye during the UV treatment.

Conclusions

This paper compares and discusses contributions of particular degradation mechanisms taking place during the DC diaphragm discharge in water solutions of selected organic dyes Direct Red 79 and Direct Blue 106. The dye decomposition by the diaphragm discharge was strongly influenced by the electrode polarity. The degradation process ran almost exponentially in both dyes and reached the decomposition rate value of 60 % after 40 minutes of plasma treatment in the anode space. Electrochemical reactions significantly influenced the dye oxidation in the anode space. However, power of their effect was different due to the structure of the used dye. The Direct Red dye decomposition was much weaker than the blue ones. There was only a negligible effect of UV radiation on the dye decoloration.

Acknowledgements

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