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## Destruction of Direct Blue 106 Dye in Underwater Discharge

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**Abstract.** An application of underwater discharge is one possible way how make the destruction of organic dyes. This contribution presents results of Direct Blue 106 destruction in discharge generated in bubbles. The initial conductivity value of  $30 \mu\text{S}\cdot\text{cm}^{-1}$  was obtained using electrolyte; the starting dye concentration was  $20 \text{ mg}\cdot\text{l}^{-1}$ . The DC voltage from 1.5 kV to 3.0 kV was applied to generate the discharge at the mean current of 10–30 mA. The system was bubbled through the high voltage capillary electrode by He, Ar and N<sub>2</sub> at the constant gas follow of 200 sccm. The dye destruction rate was directly proportional to the applied discharge current, so the highest efficiency was reached at the current of 30 mA. The destruction rate was strongly dependent on the filling gas. While using He and Ar only 4% destruction was obtained during the 20 minutes treatment at 10 mA of discharge current but the decomposition of 52 % was reached if nitrogen was introduced into the high voltage electrode. The destruction efficiency of about 40 % (He, Ar) and over 60 % in nitrogen was reached at discharge current of 30 mA. This enormous difference was probably connected not only to the production of hydrogen peroxide that seems to be usually the main oxidative specie in under water discharges but also atomic and excited nitrogen particles, both atomic and molecular, can have very positive effect in the dye destruction. The detailed study of the kinetic mechanisms leading to the Direct Blue 106 dye destruction will be a subject of the further studies.

### 1. Introduction

Direct Blue 106 dye belongs under the group of Organic Synthetic Dyes. By definition, dyes are colored, ionizing and aromatic organic compounds which show an affinity towards the substrate to which it is being applied. One characteristic of dye is that the dyes must get completely or at least partially soluble in which it is being put to. The rule that we apply to other chemicals is similarly applicable to dyes also. For example certain kind of dyes can be toxic, carcinogenic or mutagenic and can pose as a hazard to health. Direct Dyes are one of the most popular dye groups. They have a wide range of applications because they are often cheap and easy to apply. Their chemical composition consists of salts of complex sulfuric acids. They are usually soluble in water and they show a good affinity for vast fibre types and thus they are applied to numerous substrates for example to textiles, leather, plastic, paper, etc. in liquid form. Due to their wide range of applications, the waste water containing these dyes can be a great environmental problem. It is easier to decompose these dyes directly in the liquid phase. The dye concentration in waste water is usually not very high and thus the dye decomposition should be completed in liquid phase directly. Unfortunately, many of organic dyes are not possible to decompose using microorganisms due to the presence of multiple bounds mainly in



the benzene ring (see Fig. 1). Thus, and due to the increasing demand for purification of dye containing industrial wastewaters by advanced oxidation processes (AOP), a large number of papers are published on the subjects. In AOP, generally reactive, strongly oxidizing  $\cdot\text{OH}$  radicals play the main role in destruction of the dye molecules. The decoloration of the dye is generally followed by spectrophotometry at the absorbance maximum between 350 and 700 nm [1-2].

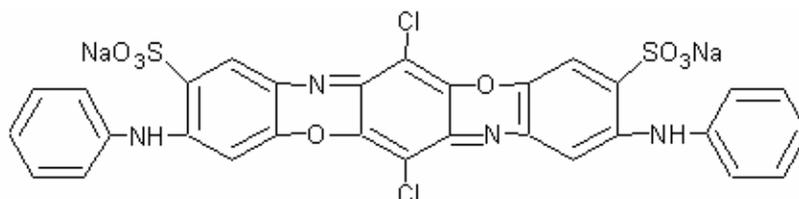


Figure 1. Direct blue 106 chemical structure

Underwater discharge is a promising environmental process to water treatment. Nowadays there are more different configurations suitable for the underwater discharge ignition. Besides well described pulsed corona like systems in point to plane [3] and coaxial configurations [4] and so called electrode less configurations (diaphragm [5] and capillary [6]), the discharge created in the bubbles introduced into the systems can be applied. All these discharges generate the non thermal plasma very similar to gas corona discharge but it presents several physical differences. There is a lower ionic mobility in the bulk liquid; on the other hand, the electron density and electron collision frequency are much higher than in the gas phase. This underwater bubble discharge configuration is relatively new one and fully combines both gas and liquid phase discharges. The gas bubbles are introduced into the system by thin stainless steel capillary that play simultaneously a role of HV pin electrode. Thus the HV pin electrode is covered by a thin gas layer and the discharge is generated in the gas phase in pin to plane configuration. The discharge streamers (plasma channels) generated in the gas phase are long enough (up to 1 cm) and thus they introduce into the liquid phase and further propagate in it [7, 8].

## 2. Experimental technique

The principal scheme of the set-up for the generation of the underwater discharge in gas bubbles is presented in fig. 2.

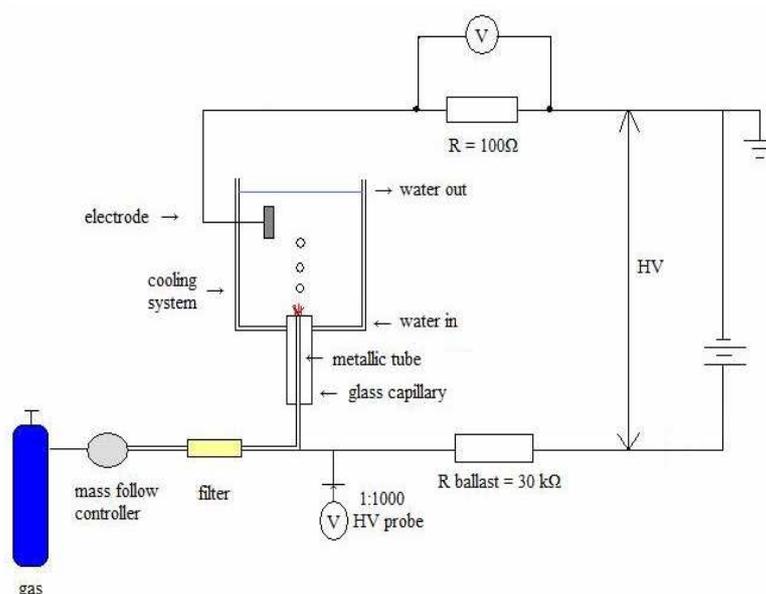


Figure 2. Scheme of the experimental set-up

The discharge reactor consisted of perspex discharge chamber (volume of 1 L), on the bottom of which a glass capillary (the inner diameter of 1.2 mm, length of 50 mm) is placed. Liquid was connected through a shunting resistance of 100  $\Omega$  to the ground potential by stainless steel electrode placed at the upper part of the chamber. The reactor was water cooled in order to avoid thermal destruction of hydrogen peroxide at temperatures above 30  $^{\circ}\text{C}$  [9]. HV electrode was a stainless steel tube (the diameter of 0.5 mm) which was placed inside glass capillary. The gas (Ar, He or  $\text{N}_2$ ) has been applied through this tube in order to produce bubbles. Gas flow in the system was supplied by mass flow control system (MKS 4000). Flow rate of used gases was fixed at 200 sccm in all experiments. The electric discharge was located directly on the surface of the metallic tube inside of bubbles. The DC power supply for the discharge sustaining has been connected to the reactor through a ballast resistor 30 k $\Omega$ . The applied voltage was varied from 1.5 to 3.0 kV at mean current from 10 mA to 30 mA.

### 3. Results and discussion

The kinetic plots for discharge currents of 15 and 30 mA are presented in Figure 3. Discharge generated at 10 mA was not stable and thus the destruction of direct blue dye was not sufficiently effective as it is demonstrated in Table I. One can see that in the case of He and Ar plasmas the destruction efficiency of the direct blue dye molecules was much lower than in the case of  $\text{N}_2$ . Maximal destruction of about 64 % was achieved in  $\text{N}_2$  plasma at the highest applied current. We suppose that this effect is connected to the formation of  $\text{HNO}_3$  in case of  $\text{N}_2$  due to oxidation of  $\text{N}_2$  that leads to the decrease of solution pH down to 2. Used dye has lower stability in acidic solutions with  $\text{pH} < 6$  and the oxidative ability of plasma is stronger in acidic conditions (e.g. the oxidative potential of the hydroxyl radical is 2.70 V at  $\text{pH} 3.0$  and 2.34 V at  $\text{pH} 9.0$ ). A new set of experiments will be arranged to confirm this hypothesis.

As it was pointed in Introduction, the underwater discharge is a source of different reactive particles (aqueous electrons, OH, O, H radicals,  $\text{O}_3$ ,  $\text{H}_2\text{O}^*$ ,  $\text{HO}_2$ , and many other reactive species) as well as UV radiation. Besides them, also the temperature in the bubble surrounding should be taken into account. Gas temperature inside the bubble estimated by fitting the emission spectra of OH bands can reach 1500-2000 K [10] and thus it can influence the destruction of organic compounds due to thermal dissociation. In order to estimate an importance of different mechanism in chemical destruction of the dye additional experiments with scavenger of OH radicals [11] have been carried out. The full understanding of the dye destruction mechanism and its kinetic is thus very complicated task that is impossible to solve without further studies including the exact analyzes of the discharge products by various analytical techniques.

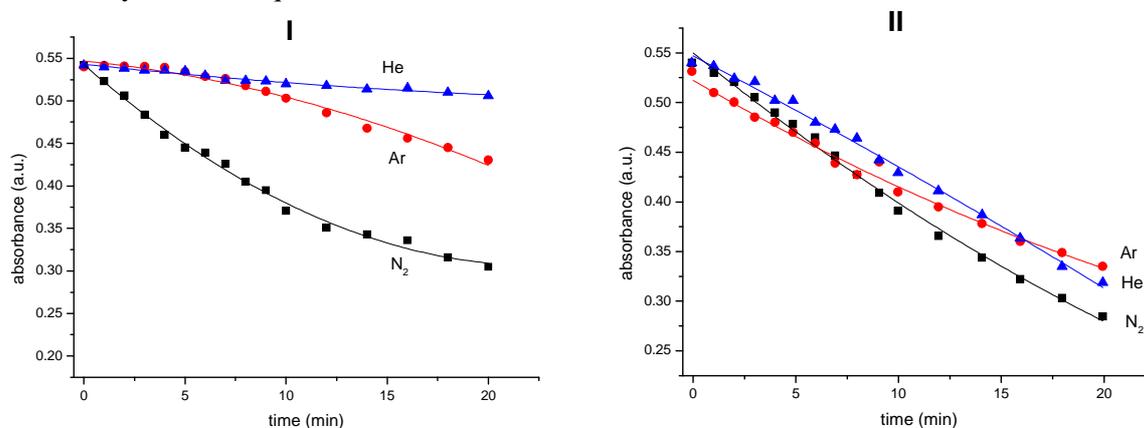


Figure 3. Kinetic plots of Direct Blue 106 dye destruction at the current of 15 mA (I) and 30 mA (II)

Table I. Efficiency of the Direct Blue 106 destruction after 20 minutes plasma treatment.

Current [mA]	Decomposition of the dye [%]		
	He	Ar	N <sub>2</sub>
10	4	4	52
15	6	15	53
20	21	24	55
25	32	30	59
30	36	43	64

#### 4. Conclusion

This work has been focused on chemical efficiency of the electric discharge in water solution generated in gas bubbles. The influence of the used gas (He, Ar, N<sub>2</sub>) was studied at the constant gas flow. The destruction of Direct Blue 106 dye was observed as a function of applied discharge current. A great difference between used gases was found. By using lower current of 10 mA and 15 mA (He, Ar) the plasma was not fully stable and efficiency of decomposition was very low of a few percents. It increased up to 40 % at the current of 30 mA in both cases. On the other hand a 52 % destruction of dye during 20 minutes was observed in N<sub>2</sub> bubbles even at very low current of 10 mA and it increased up to about 65 % at 30 mA. The possible explanation of this great difference is in the creation of HNO<sub>3</sub> acid molecules when nitrogen is introduced into the system. These molecules decrease the pH of solution that accelerates the dye decoloration.

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