

## Decolorization of methylene blue in aqueous medium using dielectric barrier discharge plasma reactor

**Abstract.** Decolorization process of methylene blue (MB) in aqueous solution using non-thermal plasma is presented. Plasma reactor with dielectric barrier discharges (DBD) and air as a processing gas at atmospheric pressure and room temperature is described. The impact of the gas flow rate on ozone concentration responsible for oxidation process is also discussed. The experimental results have shown that the efficiency of decolorization process increases with rising treatment time and input power. The energy yield of decolorization is estimated and discussed.

**Streszczenie.** W artykule opisano wykorzystanie plazmy niskotemperaturowej do dekoloryzacji wodnego roztworu błękitu metylenowego. Proces dekoloryzacji prowadzono z użyciem reaktora plazmowego z barierą dielektryczną, w którym wyładowania występują w powietrzu przy ciśnieniu atmosferycznym. W pracy określono wpływ prędkości przepływu powietrza na koncentrację ozonu oraz na proces utleniania badanego związku rozpuszczonego w wodzie. Wyniki pomiarów optycznych wskazują na istotny wpływ mocy wyładowań oraz czasu trwania obróbki plazmowej wodnego roztworu błękitu metylenowego na skuteczność prowadzonego procesu. Ponadto oszacowano efektywność energetyczną prowadzonego procesu. (Dekoloryzacja wodnego roztworu błękitu metylenowego z wykorzystaniem reaktora plazmowego z barierą dielektryczną).

**Keywords:** decolorization, dielectric barrier discharges, non-thermal plasma.

**Słowa kluczowe:** dekoloryzacja, wyładowania z barierą dielektryczną, plazma niskotemperaturowa.

### Introduction

Plasma can be defined as a neutral ionized (partially or fully) gas consisting of various particles, such as electrons, ions, atoms, and molecules. It is also called as the fourth state of matter and more than 99% of the matter in the Universe exists as plasma state. It is possible to distinguish two types of plasmas: non-thermal and thermal. This classification is based on the relative energetic levels of "light" (electrons) and "heavy" species (ions, molecules and atoms) of the plasma. Thermal plasma occurs when all particles are at thermal equilibrium, typically at high pressure (above  $10^5$  Pa) and large power density. In non-thermal plasmas there is no equilibrium between particles – temperatures (kinetic energy) of electrons and other particles are totally different. The electron temperature is much (about 3 orders) higher than the gas temperature, which is close to ambient temperature. This kind of plasma is also defined as non-equilibrium or cold plasma and can be obtained at lower pressures and for lower power. High energetic electrons play an essential role in the initiation of plasma chemistry reactions so plasma is chemically active media. The main non-thermal plasma (NTP) applications are waste gas and water treatment, surface treatment of polymeric materials, sterilization process and deactivation of microorganisms [1-3]. There are many types of NTP reactors: corona discharge, dielectric barrier discharge (DBD), surface discharge, ferroelectric pellet packed-bed reactor, plasma jet, and gliding arc, etc.

Regarding the water treatment, the type of applied NTP reactor depends mostly on the medium, where discharges occur: in gas, liquid or gas-liquid phase. In consequence the phenomena leading to degradation of wastes differs depending on the medium, what result in various values of energy yield. The higher energy yields may be obtained when the reactive species are generated in gas and transported to liquid.

The dielectric barrier discharge (DBD) reactor is an example of NTP reactor which is characterized by the presence of one or more dielectric layers between electrodes. Strong electric field between electrodes covered with dielectric layer leads to the gas breakdown. Large number of current filaments or micro-discharges appears during this process [4]. DBDs are usually operated between line frequency (e.g. 50/60 Hz) and microwave frequencies (e.g. 10 GHz) [4]. Non-thermal plasma generated by DBD is

used to induce physical and chemical reactions within gases at relatively low (room) gas temperature, which may be applied for: hydrocarbons conversion, volatile organic compounds (VOCs) decomposition and ozone generation and others [5-7].

### Experimental section

DBD plasma reactor working with air as a processing gas at atmospheric pressure and room temperature was proposed to investigate decolorization process of methylene blue (MB) in aqueous solution in so called post-plasma system (aqueous solution was placed outside the plasma reactor). A cross-section of a cylindrical laboratory type non-thermal plasma reactor is shown in Figure 1.

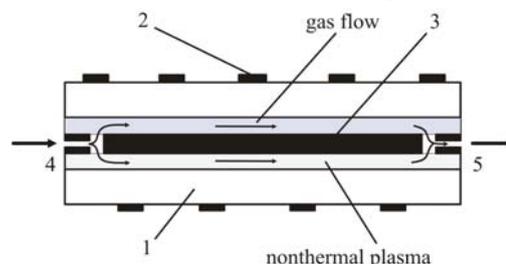


Fig. 1. Scheme of the DBD plasma reactor

A ceramic tube (made of  $\text{Al}_2\text{O}_3$ :  $\text{ZrO}_2$  composite) was used as a dielectric barrier (1). The length of the tube ( $l$ ), its inner and outer diameters ( $d_1$  and  $d_2$ ) were equal to 185 mm, 10 mm and 19.5 mm respectively. Copper tape placed on the surface of a ceramic tube operated as a high voltage electrode (2). An aluminum rod having diameter of 8 mm (3) equipped with the inlet (4) and outlet (5) gas connections was used as a grounded electrode. Total volume of the reactor was equal to  $5.23 \text{ cm}^3$ .

The high voltage electrode was supplied from a pulse modulated high voltage power supply (Dora PS). The power consumed by the reactor is regulated by change of modulation frequency. The carrier frequency of sine wave was constant and equal to 15 kHz.

The shape of the high voltage pulses supplying the reactor was recorded using oscilloscope Tektronix TDS 1002B. The typical voltage pulses are presented in Figure 2.

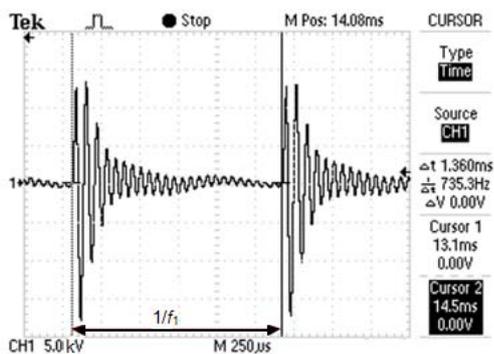


Fig. 2. High voltage pulses on the plasma reactor

The main parts of the experimental setup used in the investigation of ozone generation by a plasma reactor was shown in Figure 3. The gas flow rate (air), in the range from 100 to 2000 mL/min, was regulated by mass flow controllers (MFC). Ozone concentration was checked using ozone meter (OM). Power dissipated during ozone generation was controlled by the measurements of the total power consumed by the HVPS.

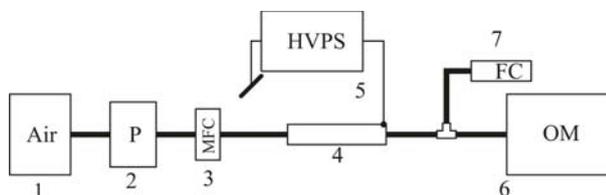


Fig. 3. Schematic of the experimental apparatus: 1 – air chamber (Air), 2 – pump (P), 3 – mass flow controllers (MFC), 4 – plasma reactor, 5 – high voltage power supply (HVPS), 6 – ozone meter (OM), 7 – flow controller (FC).

Three different solutions of the methylene blue (MB –  $[C_{16}H_{18}N_3S]^+Cl^-$ ) were prepared by dissolving required amount of dye in deionized water. The initial concentrations were equal to: 20, 40, 60 mg/L. The ozone treatment time were: 10 s, 1, 2, 5, 10, 15, 30 min. Results were obtained at 23°C and atmospheric pressure. Gas flow rate and the total power dissipated in the plasma reactor were equal to 2000 mL/min and 40 W respectively. The MB concentration was determined according to the Beer-Lambert law at the maximum absorbance ( $\lambda = 663$  nm) using a UV-Vis spectrophotometer (Thermo Scientific™ Evolution 300) with a spectral range of 200 to 800 nm.

## Results

Ozone generation using non-thermal plasma reactor was performed for air as a processing gas at room temperature and atmospheric pressure. Using DBD energetic electrons, UV light and many reactive species as ions, free radicals,  $O_3$  in a gas phase are produced. The formation mechanisms of ozone during the discharge can be described as given below:



where M is a third collision partner including : O,  $O_2$ ,  $O_3$  or  $N_2$  [7].

Power dissipated in the plasma reactor was estimated on the basis of known efficiency (estimated to be on the level of 52%) of the high voltage power supply

The influence of total power dissipated for different gas flow rates on the measured ozone concentration is presented in Figure 4.

It was found, that the maximum value of ozone

concentration is strongly dependent on the total power dissipated in the reactor and the operating gas flow rate. Moreover, an increase in gas flow rate leads to a decrease in the maximum ozone concentration. All of the investigated characteristics exhibit maxima. The width of the observed peaks increases with the increase of the gas flow rate. For the further research the gas flow rate equal to 2000 ml/min was chosen to obtain with the best stability of the discharge process. The maximum ozone concentration measured for the gas flow rate equal to 2000 ml/min was on the level of 1200 ppm, where the total power dissipated in reactor was equal to 40 W. During the experiment, the frequency of the modulation pulse was kept constant and equal to  $f_1 = 730$  Hz.

Decolorization experiments were performed at the initial pH and conductivity of the deionized water equal to 7.2 and  $5.8 \mu S/cm$  respectively.

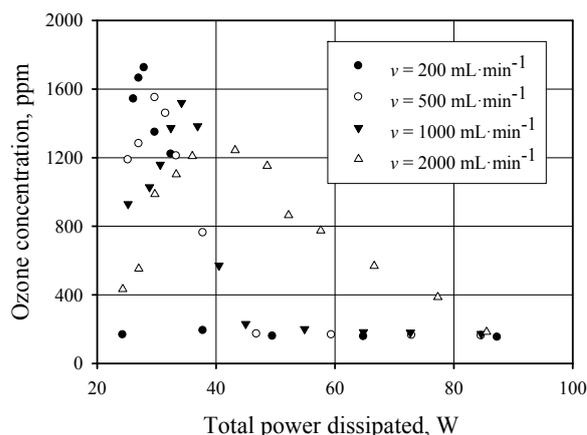


Fig. 4. Influence of total power dissipated in the reactor on ozone concentration. Results obtained in air at room temperature and atmospheric pressure

The gas with active species from plasma was added to a volume of 80 mL of water. The influence of the plasma treatment on water pH and conductivity was presented in Figure 5.

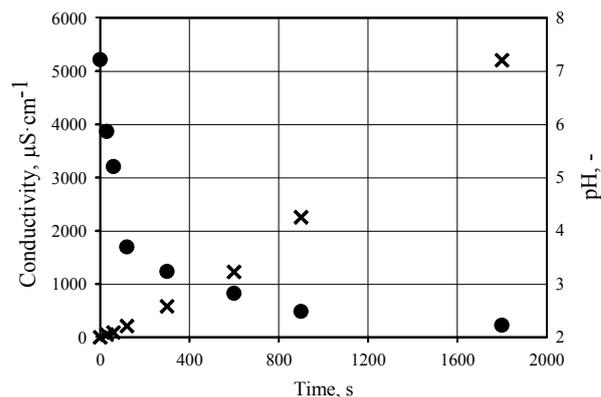


Fig. 5. Influence of plasma treatment time on pH and conductivity of deionized water. Results obtained for dissipated power and gas flow rate equal to 40 W and 2000 mL/min respectively

The decrease of pH with plasma treatment time can be explained by the formation of nitrogen acids and ions, which derive from solved in water excited nitrogen particles from the air [8,9].

The conductivity and pH of treated water samples were verified in 1, 2, 3 weeks after treatment. No changes of parameters' values were observed. It indicated that

chemical changes, which occur during ozone treatment were permanent.

Moreover, the ozonation and hydroxylation processes of MB lead to demethylation, deamination, ring breaking and finally degradation of a dye into inorganic products such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_2$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and water [10,11].

A photograph of decomposed dye solutions for different times of plasma treatment was shown in Figure 6.

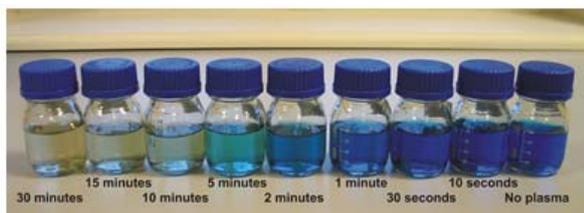


Fig. 6. Photograph of MB samples after plasma treatment. Initial concentration of MB and power dissipated during processing were equal to 20 mg/L and 23 W respectively.

Decomposition of dye results in fading of solution colour and may be investigated using spectrophotometric measurements. UV-visible absorption spectrums of the aqueous solutions before and after plasma treatment were presented in Figure 7.

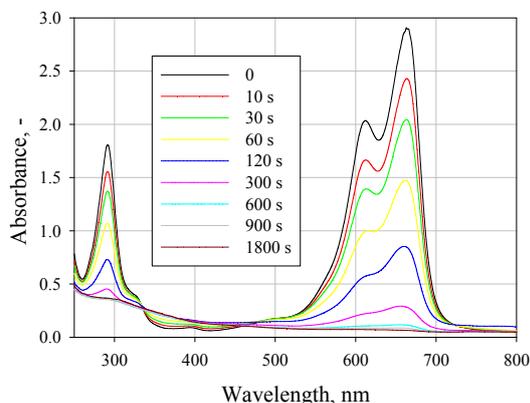


Fig. 7. UV-Vis spectra of MB aqueous solution, untreated and treated by non-thermal plasma for different durations. Results obtained for initial concentration of MB, gas flow rate and power dissipated in the plasma reactor equal to 20 mg/L, 2000 mL/min and 40 W at room temperature respectively

In the visible light spectrum two local maximum values were observed: at 663 and 612 nm, which correspond to reported in literature  $\text{MB}^+$  and  $(\text{MB}^+)_2$  species respectively [12]. The maximum value for 292 nm was also noticed. The decolorization rate ( $D_t$ ) in time  $t$  was calculated also for those maximum values using the following equation:

$$(3) \quad D_t = \frac{C_0 - C_t}{C_0} \cdot 100\%,$$

where  $C_0$  and  $C_t$  were the initial and the final concentrations of MB solution respectively [13].

The effect of plasma treatment time on degradation of water solution of MB for different wavelengths was shown in Figure 8. The concentrations of  $\text{MB}^+$  and  $(\text{MB}^+)_2$  decreased approximately with the same dynamics and reached almost 90% of decolorization levels after 5 minutes of ozone treatment. The decline of wave equal to 292 nm suggested that ozone treatment led to degradation of the phenothiazine structure of MB [14].

The effect of plasma treatment time on degradation of water solution of MB with different initial concentrations was

determined from the absorption maximum at 663 nm. The results were shown in Figure 9. For each initial concentration the decolorization rate reached 95% after 30 min of treatment.

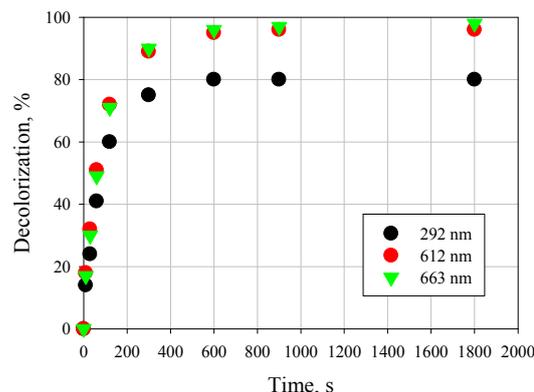


Fig. 8. Influence of plasma treatment time on decolorization efficiency for different wavelengths for initial concentration of MB equal to 20 mg/L

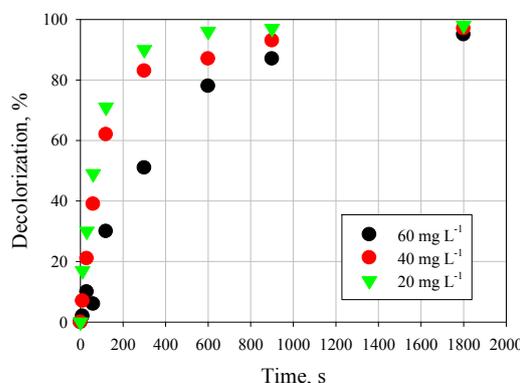


Fig. 9. Influence of plasma treatment time on decolorization efficiency for different initial concentrations

The dynamics of decolorization process depended on the initial concentration as it was shown in the Figure 9. The process of MB decolorization was more rapid for the lower initial concentration of MB.

The energy yield  $Y$  of the process of the dye degradation was illustrated using the following equation [9]:

$$(4) \quad Y \left( \frac{\text{g}}{\text{kWh}} \right) = \frac{C_0 \left( \frac{\text{g}}{\text{L}} \right) \cdot V(L) \cdot \frac{1}{100} \cdot D_t (\%) }{P_r (\text{kW}) \cdot t(\text{h})},$$

where  $C_0$  is initial MB concentration,  $V$  is the volume of the solution (80 mL),  $D_t$  is a decolorization at time  $t$ ,  $P_r$  – power dissipated in the reactor equal to 23 W.

The energy yield as function of treatment time was presented in Figure 10. Values of energy yield for different decolorization rate: 50% ( $Y_{50\%}$ ) and 90% ( $Y_{90\%}$ ) were presented in Table 1.

## Discussion

The  $Y_{50\%}$  parameter was chosen to compare constructed reactor with other presented in the literature [9, 13, 14]. Energy yield of the decolorization process mainly depends on dye type [15], so only reactors decolorizing same dye may be compared.

For different types of reactors used to decolorize MB water solutions the energy yield varies from 0.037 to 1.5 g·kWh<sup>-1</sup> [15]. The highest  $Y_{50\%}$  (around 1.3 and 6.1 g·kWh<sup>-1</sup>) was achieved for impulse corona discharge

reactor with discharges over the solution surface [16, 17]. The highest value of energy yield, reached to 67 g·kWh<sup>-1</sup> (for 93% decolorization) with very low consumed power [9].

Table 1. The energy yield of MB degradation for 50% decolorization ( $Y_{50\%}$ ) and 90% decolorization ( $Y_{90\%}$ ).

$C_0$ mg/L	$Y_{50\%}$ g·kWh <sup>-1</sup>	$Y_{90\%}$ g·kWh <sup>-1</sup>
60	1.34	0.68
40	2.95	0.64
20	2.09	0.87

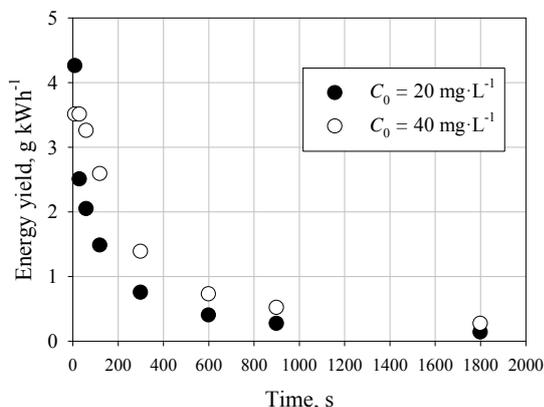


Fig. 10. Changes of energy yield due to the time of ozone treatment for initial concentrations of MB equal to 20 and 40 mg/L for the investigated reactor

## Conclusions

The results of the investigations indicated that:

- decrease of gas flow rate allowed to reach higher ozone concentration generated in DBD plasma reactor,
- maximum ozone concentrations (depending on the gas flow rate) were obtained for the different values of power dissipated in the plasma reactor,
- decrease of pH (due to the formation of acids) was observed during plasma treatment of water,
- increase of water conductivity (three orders of magnitude) was noticed,
- decolorization efficiency of MB was confirmed by UV-Vis measurements,
- decolorization efficiency and rate of oxidation reaction were dependent on the initial concentration of MB,
- practically total decolorization of MB was achieved ( $\geq 95\%$ ) for its different initial concentrations,
- energy yield of 50% decolorization and 40 mg/L initial MB concentration for the investigated reactor was found to be equal to 2.95 g·kWh<sup>-1</sup>,
- the dynamics of decolorization depended on initial concentration of dye.

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## REFERENCES

- [1] Hackman R., Akiyama H., Air Pollution Control by Electrical Discharges, *IEEE Trans. Dielectr. Electric. Insul.*, 7 (2000), 654-683.
- [2] Noeske M., Degenhardt J., Strudhoff S., Lommatzsch U., Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion, *Int. J. Adhes.*, 24 (2004), 171-177.
- [3] Akitsu T., Ohkawa H., Tsuji M., Kimura H., Kogoma M., Plasma sterilization using glow discharge at atmospheric pressure, *Surf. Coat. Technol.*, 193 (2005), 5829-5835.
- [4] Kogelschatz U., Dielectric-Barrier Discharges: Their History, Discharge Physics, and Industrial Applications, *Plasma Chem. Plasma Proc.*, 23 (2003), 1-46.
- [5] Petitpas G., Rollier J. D., Darmon A., Gonzalez-Aguilar J., Metkemeijer R., Fulcheri L., A comparative study of non-thermal plasma assisted reforming technologies, *Int. J. Hydrogen Energy*, 32 (2007), 2848-2867.
- [6] Evans D., Coogan J.J., Anderson G.K., Rosocha L.A., Kushner M.J., Plasma remediation of trichloroethylene in silent discharge plasmas, *J. Appl. Phys.*, 74 (1993), 5378-5386.
- [7] Eliasson B., Hirth M., Kogelschatz U., Ozone synthesis from oxygen in dielectric barrier discharges, *J. Phys. D: Appl. Phys.*, 20 (1987), 1421-1437.
- [8] Benstaali B., Moussa D., Fanmoe J., Njoyim-Tamungang E., Brisset J.L., Acidity control of plasma-chemical oxidation: applications to dye removal, urban waste abatement and microbial inactivation, *Plasma Sources Sci. Technol.*, 20 (2011), 1-12.
- [9] Reddy P., Raju B., Karupiah J., Reddy E., Subrahmanyam C., Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor, *Chemical Engineering Journal*, 217 (2013), 41-47.
- [10] Luan J., Hu Z., Synthesis, Property Characterization, and Photocatalytic Activity of Novel Visible Light-Responsive Photocatalyst Fe<sub>2</sub>BiSbO<sub>7</sub>, *International Journal of Photoenergy*, 2012 (2012), 1-11.
- [11] Panizza M., Barbucci A., Ricotti R., Cerisola G., Electrochemical degradation of methylene blue, Separation and Purification Technology, 54 (2007), 382-387.
- [12] Cenens J., Schoonheydt R., Visible spectroscopy of methylene blue on hectorite, laponite B and barasym in aqueous suspension, *Clays and Clay Minerals*, 36 (1988), no. 3, 214-224.
- [13] Feng J., Zheng Z., Sun Y., Luan J., Wang Z., Wang L., Feng J., Degradation of diuron in aqueous solution by dielectric barrier discharge, *J. Hazard. Mater.*, 154 (2008), 1081-1089.
- [14] Zhang T., Oyama T., Aoshima A., Hidaka H., Zhao J., Serpone N., Photooxidative N-demethylation of methylene blue in aqueous TiO<sub>2</sub> dispersions under UV irradiation, *Journal of Photochemistry and Photobiology A: Chemistry*, 140 (2001), 163-172.
- [15] Malik M., Water Purification by Plasmas: Which Reactors are Most Energy Efficient?, *Plasma Chem Plasma Process*, 30 (2010), 21-31.
- [16] Magureanu M., Bradu C., Piroi D., Mandache N., Pulsed Corona Discharge for Degradation of Methylene Blue in Water, *Plasma Chem Plasma Process*, 33 (2013), 51-64.
- [17] Grabowski L.R., van Veldhuizen E.M., Pemen A.J.M., Rutgers W.R., Breakdown of methylene blue and methyl orange by pulsed corona discharge, *Plasma Sources Science and Technology*, 16 (2007), no. 2, 226-232.