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

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Decolorization process of methylene blue (MB) in aqueous solution using nonthermal plasma is presented. Plasma reactor with dielectric barrier discharges (DBD) and air as a processing gas at normal pressure and room temperature is described. The influence of the reactive oxygen species (especially ozone) on the electrical and chemical properties of water is also checked. The experimental results have shown that the efficiency of decolorization process increases with rising treatment time and input power. The impact of the gas flow rate on ozone concentration responsible for oxidation process is also discussed.

1. 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 universe is filled with plasma. It is possible to distinguish two types of plasmas: nonthermal 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 the all particles are at thermal equilibrium, typically at high pressure (above 10^5 Pa) and large power (about 50 MW). In nonthermal 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. So this plasma is also defined as nonequilibrium 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 nonthermal 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.

DBD plasma system is characterized by the presence of one or more dielectric layers between electrodes. Strong electric field between electrodes covered with dielectric layer leads to gas breakdown. Large number of current filaments or microdischarges appears during this process [4]. DBDs are usually operated between line frequency (e.g. 50/60 Hz) and microwave frequencies (e.g. 10 MHz) [4]. Nonthermal plasma using DBD is used to induce physical and chemical reactions within gases at relatively low gas temperatures, e.g. hydrocarbons conversion, volatile organic compounds (VOCs) decomposition and ozone generation [5]-[7].

2. Experimental setup

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

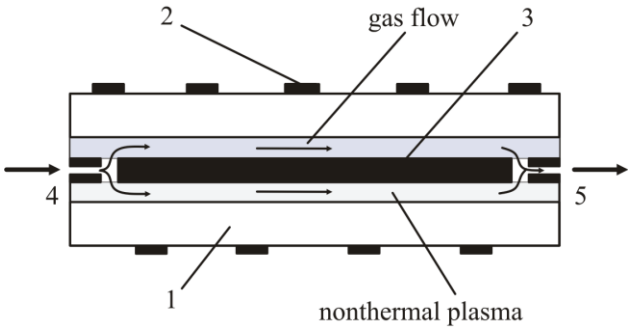

Figure 1. Scheme of the DBD plasma reactor.

A ceramic tube (composition of Al_2O_3 with ZrO_2) 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 195 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 aluminium rod having diameter of 8 mm (3) equipped with the inlet (4) and outlet (5) gas connections was used as a grounded electrode. The high voltage electrode was supplied from a pulse modulated power supply. The frequency of the modulation pulse were constant during the experiment and equal to 730 Hz. The waveform of discharge voltage without the modulation was continuous sine form with a frequency of 15 kHz. Total volume of the reactor was equal to 5,5 cm^3.

Using DBD energetic electrons, UV light and many reactive species as ions, free radicals, H_2O_2, O_3 are produced. The formation mechanisms for these species during the discharge can be described as given in Eqs. (1)-(10):

$$O_2 \xrightarrow{e^-} O^\bullet + O^\bullet \quad (1)$$

$$O^\bullet + O_2 \rightarrow O_3 \quad (2)$$

$$O^\bullet + H_2O \rightarrow {}^\bullet OH + {}^\bullet OH \quad (3)$$

$$O^- + H_2O \rightarrow {}^\bullet OH + OH^- \quad (4)$$

$$O_2^- + H_2O \rightarrow HO_2^\bullet + OH^- \quad (5)$$

$$2H_2O \xrightarrow{e^-} H_2O_2 + H_2 \quad (6)$$

$$O_3 + H_2O_2 \rightarrow {}^\bullet OH + O_2 + HO_2^\bullet \quad (7)$$

$$O_3 + HO_2^\bullet \rightarrow {}^\bullet OH + O_2 + O_2^- \quad (8)$$

$$O_3 + H_2O \xrightarrow{h\upsilon} H_2O_2 + O_2 \quad (9)$$

$$H_2O \xrightarrow{h\upsilon} {}^\bullet OH + {}^\bullet OH \quad (10)$$

Most of these chemically active species are the strongest oxidizing agents and play main role during decolorization process of MB. The main parts of the experimental setup used in the investigation of ozone generation in plasma reactor was shown in Figure 2.

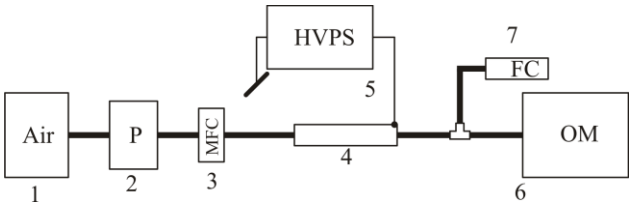

Figure 2. Schematic of the experimental apparatus: 1 –air chamber, 2 – pump, 3 – mass flow controllers, 4 – plasma reactor, 5 – high voltage power supply, 6 – ozone meter, 7 – flow controller.

The gas flow rate (air), in the range 100-2000 mL·min^{-1}, was regulated by mass flow controllers. Ozone concentration was checked using ozone meter. Also power dissipated during ozone generation was controlled.

The MB concentration was determined according to the Beer-Lambert law ate the maximum absorbance (λ_{max}=664 nm) ising a UV-Vis spectrophotometer (Thermo Scientific™ Evolution 300) with a spectral range of 200 to 800 nm. Decolorization of MB was performed at room temperature and atmospheric pressure of air.

3. Results

Ozone generation using nonthermal plasma reactor was performed for air as a processing gas at room temperature and atmospheric pressure. The influence of power dissipated for different gas flow rate on ozone concentration is shown in Figure 3.

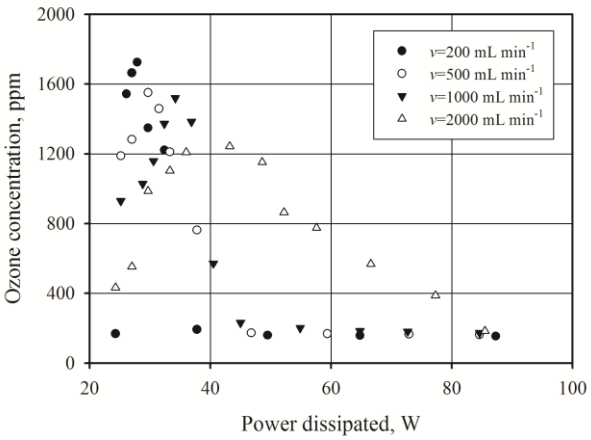

Figure 3. Influence of power dissipated in the reactor on ozone concentration. Results obtained in air at room temperature and atmospheric pressure.

The effect of active species from nonthermal plasma on water properties was checked. Experiments were performed at the initial pH and conductivity equal to 7,2 and 5,8 μS cm^{-1} respectively of the deionized water. 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 4.

The decrease of ph with plasma treatment time can be explained by the formation of acids from the nitrogen in air as given in Eqs. (11)-(15):

$$O_2 \xrightarrow{e^-} 2O^\bullet + e^- \quad (11)$$

$$N_2 \xrightarrow{e^-} 2N^\bullet + e^- \quad (12)$$

$$N^\bullet + O^\bullet \rightarrow NO \quad (13)$$

$$O^\bullet + NO \rightarrow NO_2 \quad (14)$$

$$NO_2 + {}^\bullet OH \rightarrow HNO_3 \quad (15)$$

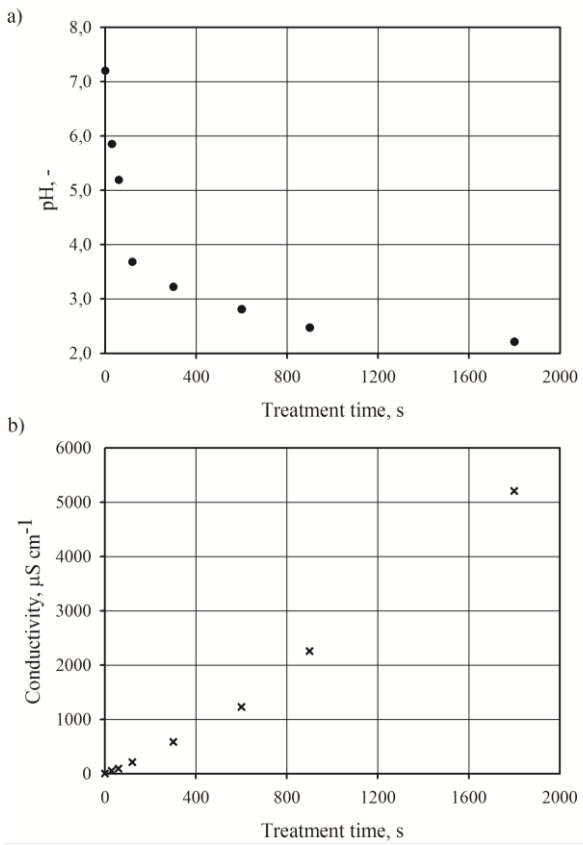

Figure 4. Influence of plasma treatment time on pH (a) and conductivity (b) of deionized water. Results obtained for dissipated power and gas flow rate equal to 43 W and 2000 mL·min^{-1} respectively.

UV-visible absorption spectra of the aqueous solutions before and after plasma treatment were presented in Figure 5.

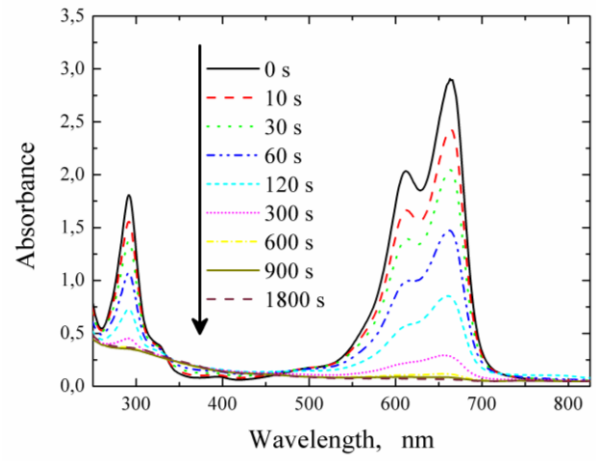

Figure 5. UV-Vis spectra of MB aqueous solution, untreated and treated by nonthermal plasma for different durations. Results obtained for initial concentration of MB at 23°C, gas flow rate and power dissipated in the plasma reactor equal to 20 mg L^{-1}, 2000 mL min^{-1} and 43 W respectively.

The concentration of MB in solution was determined from the absorption maximum at 664 nm, which was also used for the calibration curves. The decolorization percentage D% was calculated using Eq. (16) [8]:

$$D\% = \frac{C_0 - C_t}{C_0} \cdot 100\% \qquad (16)$$

where C_0 and C_t were the initial and the final concentrations of MB solution respectively.
The effect of plasma treatment time on degradation of MB was shown in Figure 6.

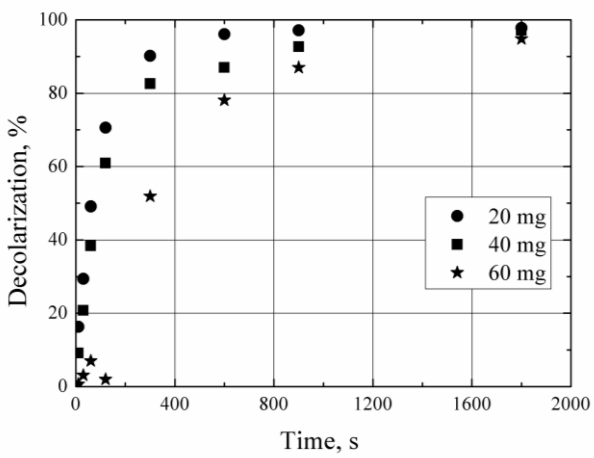

Figure 6. Influence of plasma treatment time on decolorization efficiency. Results obtained for gas flow rate and power dissipated in the plasma reactor equal to 2000 mL min^{-1} and 43 W respectively.

A photograph of decomposed dye solutions for different times of plasma treatment is shown in Figure 7.

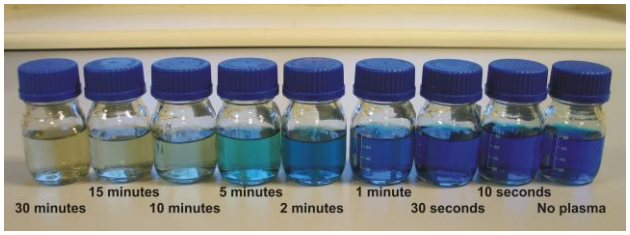

Figure 7. Photograph of MB samples after plasma treatment. Initial concentration of MB and power dissipated during processing were equal to 20 mg L^{-1} and 43 W respectively.

4. 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 (≥95%) for its different initial concentrations,
- energy yield of decolorization was equal to 0,8 g/kWh.

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