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DECOMPOSITION OF HUMIC ACID AND METHYLENE BLUE BY ELECTRIC DISCHARGE IN FOAM[1]

J. Pawłat *, **K. Hensel** [2†], **S. Ihara** ‡

*Graduate School of Information, Production and Systems, Waseda University, Kitakyushu, 808 Fukuoka, Japan

†Department of Astronomy, Earth Physics and Meteorology, Comenius University, 84248 Bratislava, Slovakia

‡School of Science and Engineering, Saga University, 840 Saga, Japan

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Generation of the oxidants and decomposition of the organic compounds using pulsed electric discharge in the foaming column was investigated. Hydrogen peroxide, dissolved and gaseous ozone formations at various discharge power, pulse repetition rates, gas flow rates and substrate gases were evaluated. The potential of the system for the decomposition of methylene blue and humic acids was tested. The foaming reactor presents a promising method for simultaneous treatment of both gaseous and liquid pollutants.

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1 Introduction

Numerous methods and technologies have been developed in the last decades to protect natural resources and reduce the quantity of pollutants in the environment [1, 2]. Very efficient and promising among them are advanced oxidation technologies (AOTs). The key of the AOTs is a production of highly reactive oxidants (e.g. OH, O_3, H_2O_2) that initiate a sequence of reactions resulting in the destruction and removal of organic pollutants in water. Usually the oxidants are produced separately and dosed individually, causing transportation loses and a decrease of the total efficiency of the process. The advantage of the AOTs is that the generation of the oxidants and the removal of the pollutants take place in the same vessel and therefore these losses are avoided.

The paper presents a new approach of a simultaneous generation of the oxidants and treatment of pollutants. The method uses an electric discharge generation in the foaming environment in one compact apparatus. The foam inside the reactor vessel is formed without the addition of surface active components surfactants. The formation is rather achieved by using the reactor of

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[2]E-mail address: hensel@fmph.uniba.sk

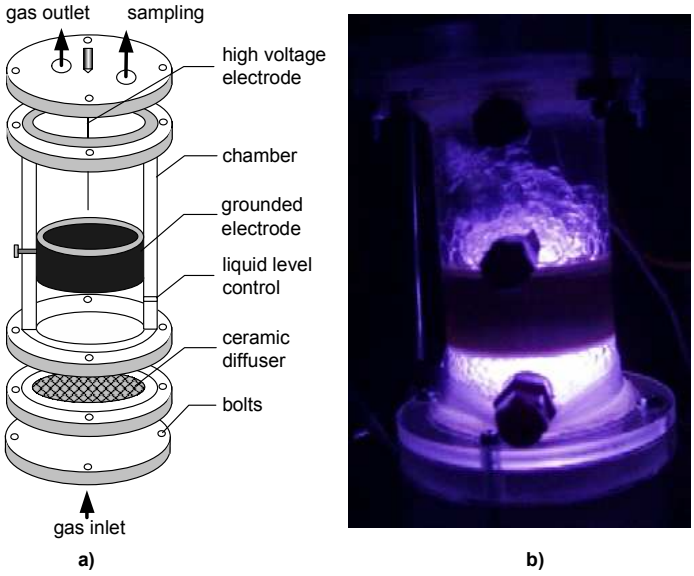

Fig. 1. Cylindrical vessel of the foaming column (a) and photograph of the electric discharge in the foam (b).

a special construction with porous diffusers and operation in strict conditions of gas/liquid ratio and of gas flow rate [3]. To create a dynamic foam without surfactants the required conditions are: a) perforation level (porosity) of the diffuser must be 5-20%, b) linear velocity of the substrate gas for the cross-section of the diffuser must be 0.1-4.0 m/s and c) velocity of the substrate gas in the pore of the diffuser must be 10-20 m/s.

2 Experimental Setup and Methods

The main reactor vessel is depicted in Fig. 1a. It was designed to maintain the appropriate flow of media necessary for dynamic surfactant-free foam formation. It consisted of a cylindrical polyacrylate column (inner diameter 50 mm, height 200 mm) with alumina diffuser (type IA-500) located at the bottom of the vessel. The vessel was connected to the liquid and gas providing systems. Distilled water (60 ml) was used as a substrate liquid and was injected through the inlet above the diffuser. The substrate gas, air or oxygen, was sampled at the bottom of the vessel perpendicularly to the diffuser layer. The formation of the dynamic foam was achieved at the gas flow rate 3 l/min and more. The height of the stable dynamic foam column was 8-10 cm. Average diameter of a single bubble ranged from 1 to 5 mm and increased with the distance from the diffuser and with increasing substrate gas flow.

The stainless-steel electrodes in the coaxial geometry were located above the ceramic diffuser within the dynamic foaming region. The inner high voltage electrode consisted of 1.5 mm diameter needle. The grounded ring electrode had diameter of 40 mm and height of 30 mm.

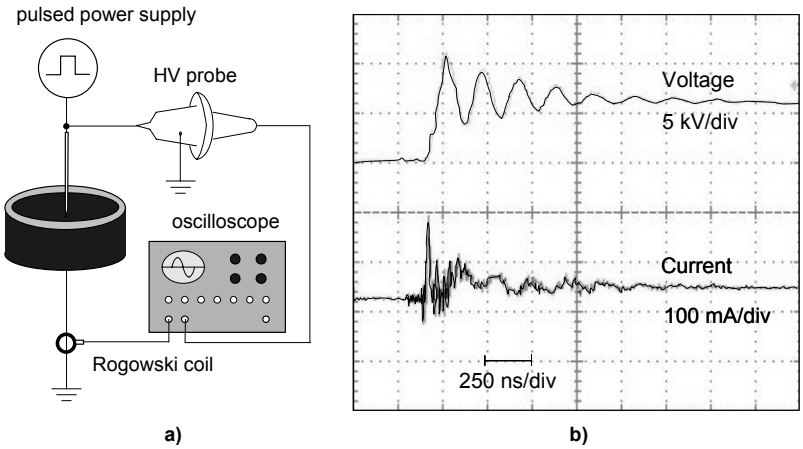

Fig. 2. The used electric circuit (a) and typical waveforms of discharge voltage and current (air, 5 l/min, 40 W) (b).

The electrical circuit used to drive the reactor and generate the discharge inside the vessel is presented in Fig. 2a. The magnetic-pulse-compression pulsed-power generator was employed as a repetitive high voltage power supply. The discharge voltage and current were measured by the high voltage probe (Tektronix, P6015A) and the Rogowski coil (Pearson Electronics, model 110), respectively, connected to the digital oscilloscope (Tektronix, TDS 380).

Upon the application of the pulsed high voltage on the electrodes a uniformly distributed electric discharge formed between the electrodes. The photograph of the discharge is shown in Fig. 1b. The typical waveform of the applied pulsed voltage and the discharge current are presented in Fig. 2b. More details about the discharge properties and optimal conditions for the foam generation in the foaming column can be found elsewhere [4, 5].

The chemical analysis of the liquid and the gas was performed to evaluate the formation of the oxidants and the removal of the pollutants. The hydrogen peroxide concentration was determined by the titration method using hydrogen peroxide Test Kit (Hach, model HYP-1). The dissolved ozone concentration was measured by spectrophotometer (Hach, DR/4000) and the gaseous ozone was measured by the ozone gas probes (Kitagawa, Gastec). The decomposition of the selected organic pollutants was determined by UV absorption spectrometry.

3 Results and Discussion

Generation of the oxidants in the foam was examined in a batch experiments. The 60 ml of distilled water was injected into the reactor to form a foaming column and exposed to the action of the electric discharge for 5 minutes. After the discharge, the gas flow was cut off and the liquid from the reactor was strained off and analyzed. Figure 3 and 4 presents the concentrations of hydrogen peroxide and gaseous ozone as a function of gas flow rate and the total power. The results were obtained using average pulsed voltage of 25 kV and different pulse repetition rates

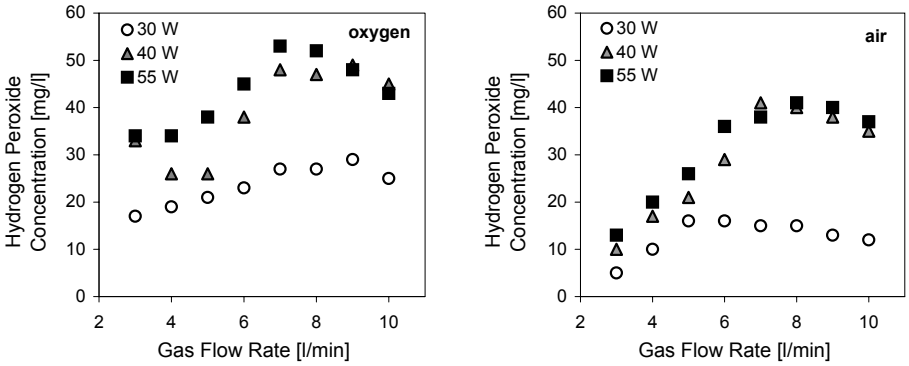

Fig. 3. Hydrogen peroxide H_2O_2 formation in oxygen (left) and air (right) as function of gas flow rate for various total power.

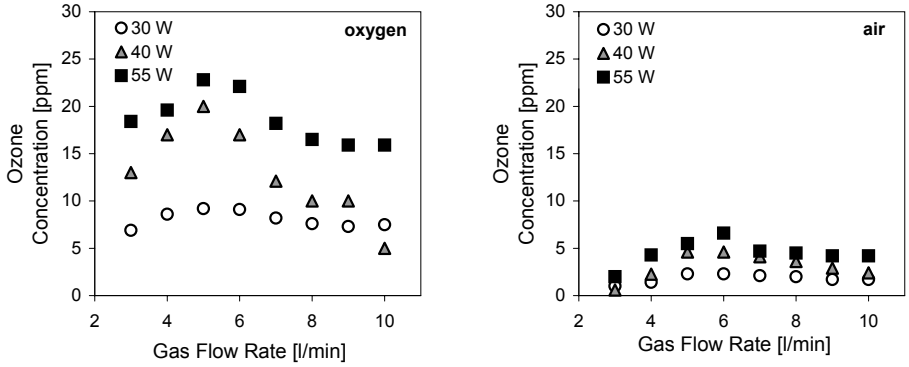

Fig. 4. Gaseous ozone O_3 formation in oxygen (left) and air (right) as function of gas flow rate for various total power .

(30–90 Hz), corresponding to total power 30–55 W. The concentration of the oxidants increased with the increasing applied voltage and with the increasing pulse repetition rate. The highest concentrations of hydrogen peroxide and dissolved ozone generated in air were 40 mg/l and 0.25 mg/l, respectively. Concentration of the gaseous ozone was relatively low, resulting from the ozone solvation in the liquid. A little higher concentrations of the oxidants were obtained if oxygen was used as the substrate gas. The optimal generation of the oxidants was observed for the gas flow rates of 4.5-6.5 l/min. Too small or high gas flows resulted into bubbling or water splashing, respectively, instead of foaming. The discharge character changed and the production of the oxidants decreased significantly.

Compared to other AOT studies, the presented foaming system produces relatively small concentrations of gaseous O_3 and significantly high concentration of H_2O_2. Miichi et al. [6] generated the discharge inside bubbles in water by pulsed power and obtained up to 3000 ppm

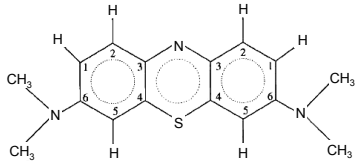

Fig. 5. Methylene blue.

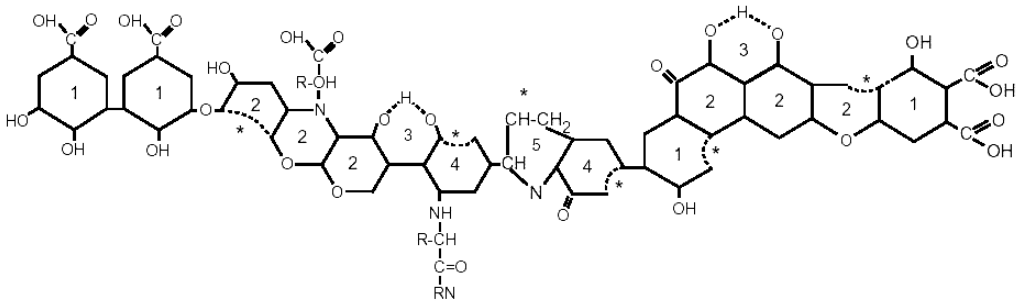

Fig. 6. Fragment of humic acid molecule.

of ozone (22 kV, 150 Hz, 0.3 l/min). The concentration of ozone decreased with the decreasing pulse repetition rate and the increasing gas flow rate. In the same system, when using 18kV, 15Hz pulse and the gas flow rate of 1 l/min, 300 ppm was generated only [7]. At the same time, the concentration of H_2O_2 was reported to be negligible (less than 0.5 mg/l after 10 minutes of the applied discharge) [8]. Lukes et al. [9] investigated generation of active species in a hybrid gas-liquid discharge. They reported generation of 3000 ppm of ozone and 17 mg/l (0.5 mmol/l) of H_2O_2 in the specific conditions (40 kV, 60 Hz, 0.35 l/min). The amount of H_2O_2 is less than in the presented foaming system. The concentration of H_2O_2 is very important for e.g. the decomposition of various contaminants in water. To enhance the decomposition efficiency of AOT process the amount of H_2O_2 is often increased by its direct addition into the water [10, 11].

Solution of methylene blue (MB) was selected as a model compound for the test of the system's performance at the removal of dyes from waste waters. The MB is an odorless, green crystalline powder, soluble in water. It is used to aid in the transport of oxygen in blood and it is also used as a dye to stain certain parts of the body before or during surgery. The catalyst supported oxidization of the MB was found difficult, if only ozone was used [12]. The molecule of methylene blue is depicted in Fig.5.

Second selected model pollutant were humic acids (HA), the organic compounds arising from the physical, chemical and microbiological transformation (humification) of biomolecules, which primarily can be found in manure, peat, lignite coal, and leonardite [13, 14]. The HA are fraction of humic substances, which are ubiquitous in the environment and may constitute as much as 95% of the total dissolved organic matter in aquatic systems. In many cases they act as the major buffering system and absorbent, which has serious implications for acidification of lakes and rivers. Example of the fragment of humic acid molecule is shown in Fig. 6.

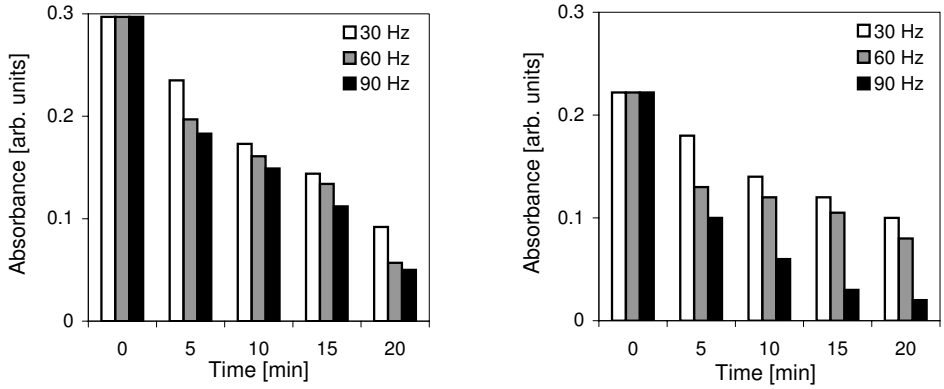

Fig. 7. Decomposition of methylene blue and humic acid in time with various pulse repetition rate (4.5 l/min, air).

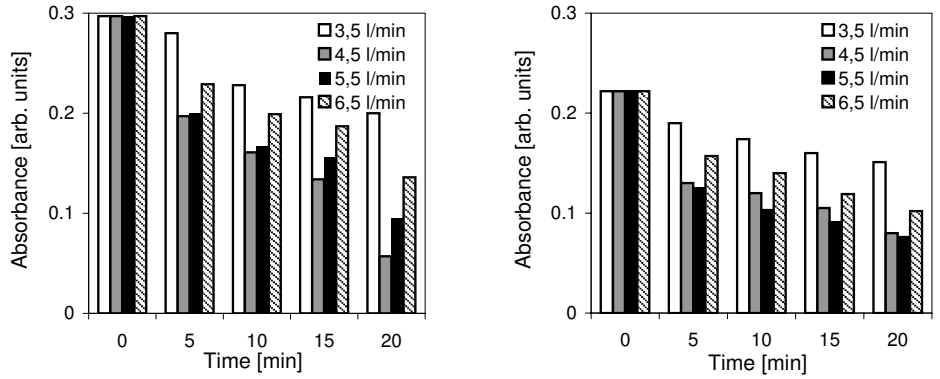

Fig. 8. Decomposition of methylene blue and humic acid in time with various gas flow rate (60Hz, air).

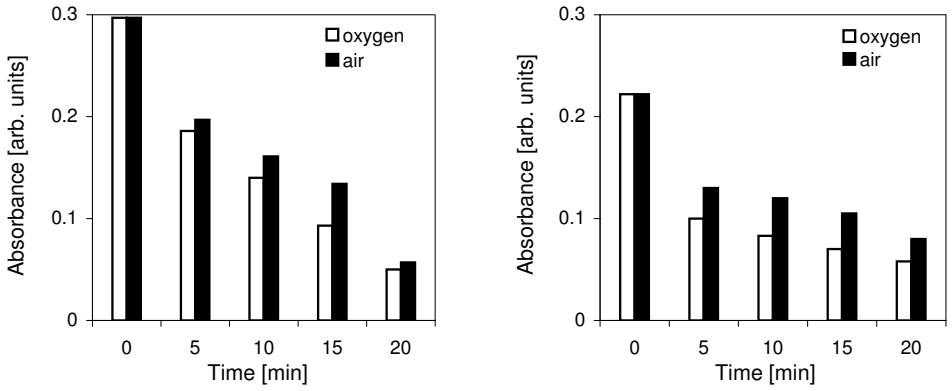

Fig. 9. Decomposition of methylene blue and humic acid in time with various substrate gas (60Hz, 4.5 l/min).

The treatment potential of the system was tested on the solutions of 35 mg/l of MB or 100 mg/l of HA suspended in 60 ml of pure water dosed into the reactor. The characteristic UV absorption lines of the MB (550–665 nm) and the HA (260 nm) were used to determine their concentration in the liquid. The experiments were performed for various pulse repetition rates (pulsed frequency), gas flow rates and substrate gases. The concentration was measured after each 5 minutes of the discharge treatment. After 20 minutes of the treatment the color of the solution became much weaker and the amount of suspended matter after the sedimentation significantly decreased. Full discoloration of the solutions was achieved in the case of oxygen with the pulse frequency of 90 Hz. The treatment time must be extended to obtain complete purification also in other cases. Figures 7, 8 and 9 presents the decomposition of MB and HA with time. It was shown that the amount of the pollutant removed increased with treatment time and pulse frequency. The best treatment results were observed for 4.5–5.5 l/min of the gas flow rate (Fig. 8). Decomposition was slightly better using oxygen as a substrate gas (Fig. 9).

4 Conclusions

System utilizing electric discharge in the foam for the treatment of the pollutants was build and used. The dynamic foam was formed without the addition of surface active compounds. Hydrogen peroxide and dissolved ozone were generated simultaneously in the foaming environment and used for the treatment of methylene blue and humic acid dissolved in water. The most efficient generation of the oxidants and the highest treatment efficiency was observed for pulse repetition rates of 90 Hz and gas flow rate of 4.5–5.5 m/s.

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