

Generation of oxidants and removal of indigo blue by pulsed power in bubbling and foaming systems

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Generation of dissolved ozone (O_3) and hydrogen peroxide (H_2O_2) in water, bubbling and foaming systems by a pulse powered electric discharge was studied. The concentrations of the species in the systems increased with operation time and a pulse repetition rate. In the foaming column generation of more than 70 mg/l H_2O_2 was observed after 20 minutes of discharge operation. The concentration of H_2O_2 was an order of the magnitude bigger than in the case of the bubbling column and two orders of the magnitude bigger than in the case of still water. The highest concentration of dissolved O_3 (2.17 mg/l) was obtained in the bubbling system, after 20 minutes of discharge operation at 90 Hz pulse repetition rate. Similar results were achieved also in the foaming column. However, the amount of dissolved ozone in still water was only 0.97 mg/l. Due to the effective overall generation of the oxidants, the system of foaming column provided the best results also in indigo blue treatment.

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1 Introduction

Numerous systems and processes has been developed to control and reduce the quantities of pollutants in the environment. Despite enormous effort, there are still many hardly treatable compounds, where traditional decomposition techniques are not efficient enough to meet the present standards. Advanced oxidation processes (AOP) are considered to be promising alternatives to remove many hazardous chemicals from contaminated water. Among many AOP processes (e.g. ultraviolet photolysis, direct ozonation, high-energy electron irradiation), the process utilizing a pulsed discharges in gas or liquid phase has been found to be effective in removing and degrading organic contaminants from aqueous solutions.

In the paper, generation of dissolved ozone and hydrogen peroxide in the water, foaming and bubbling columns is presented. The systems of bubbling and foaming columns are promising alternatives allowing a simultaneous generation of oxidants and a treatment of the pollutants in one reaction vessel. The applicability of the presented AOP systems was confirmed by using them for indigo blue treatment.

2 Experimental apparatus

The experimental apparatus consisted of a discharge reactor vessel. The vessel was a cylindrical acrylic column of 50 mm diameter and 200 mm height. An alumina type diffuser was placed at the bottom of the vessel and set perpendicularly to the gas flow. The electrode system consisted of a stainless steel ring electrode (diameter 40 mm, height 30 mm) and a needle electrode (diameter 1.5 mm) set in the centre of the ring electrode. The used substrate gas was air. The gas flow rate and the amount of water in the vessel determined the phenomena occurring inside the reactor vessel, resulting either in bubbling or foaming. Average diameter of a single bubble in the foaming column and bubbling column was 1–5 and 4–12 mm, respectively. In both systems, the diameter of the bubble increased with the vertical distance from diffuser. The foam was formed without the addition of surface-active components in a strict gas flow regime and controlled by gas/liquid ratio [1, 2]. Overall, the systems under the investigation were as follows:

- still water (Fig. 1a): pure water (130 ml) without any gas flow,
- bubbling column (Fig. 1b): pure water (130 ml) with air flow (4 l/min),
- foaming column (Fig. 1c): pure water (60 ml) with air flow (4 l/min).

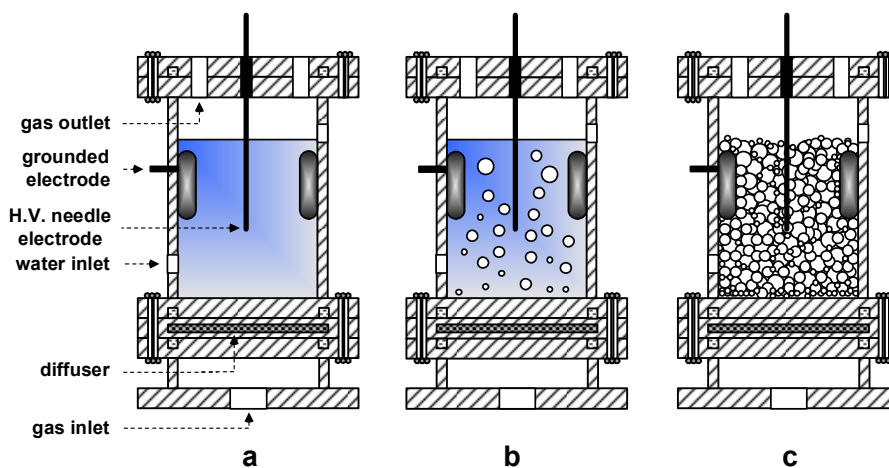


Fig. 1. Reactor vessels: a) still water, d) bubbling column, c) foaming column.

The discharge reactor vessel was powered by magnetic-pulse-compression pulsed power supply operated at variable frequencies. The pulse of positive polarity was applied to the central needle electrode. The discharge voltage and current characteristics were measured by high voltage probe (Tektronix, P6015A) and current probe (Pearson Electronics, model 110), respectively, both connected to the digital oscilloscope (Tektronix, TDS380). The electrical circuit and a typical characteristics of the voltage and current are presented in Fig. 2. The current waveform in the foaming column was very alike bubbling, therefore it is not presented.

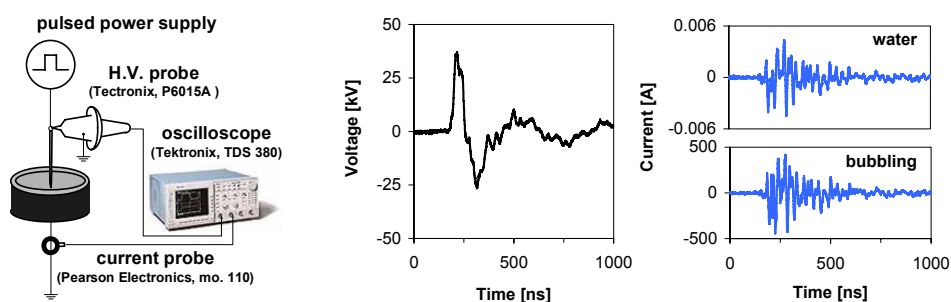


Fig. 2. Electric circuit and typical voltage and current waveforms.

3 Experimental results and discussion

Upon the application of the high voltage pulse the discharge occurred in the reactor vessels. The discharge was applied for 5, 10, 15 or 20 minutes. After each experimental cycle, a sample of the liquid was taken for the chemical analysis to determine the presence of the oxidants. Concentrations of dissolved ozone and hydrogen peroxide were determined by spectrophotometer (Hach, DR/4000) and hydrogen peroxide Test Kit (Hach, model HYP-1), respectively. The results of the oxidants generation in all three systems are presented in Fig. 3.

The concentration of the oxidants increased with the operation time and the pulse repetition rate. The highest concentration of dissolved ozone (2.17 mg/l) was observed in the bubbling system after 20 minutes of discharge operated at 90 Hz. Similar results were obtained also in the foaming column (2.01 mg/l). On the contrary, with no air flow, the amount of dissolved ozone was much lower and in the same conditions reached only 0.97 mg/l. Foaming system was very efficient also for hydrogen peroxide generation. 74 mg/l of H_2O_2 was generated after 20 minutes of discharge operation at 60 Hz. The concentration of H_2O_2 was an order of the magnitude bigger than in the case of the bubbling column and two orders of the magnitude bigger than in the case of still water. Due to the high water conductivity the energy provided by the discharge to the reaction zone in still water was not sufficient to generate enough oxidants. Generation of oxidants in this system is therefore ineffective. Foaming environment is more favorable for the

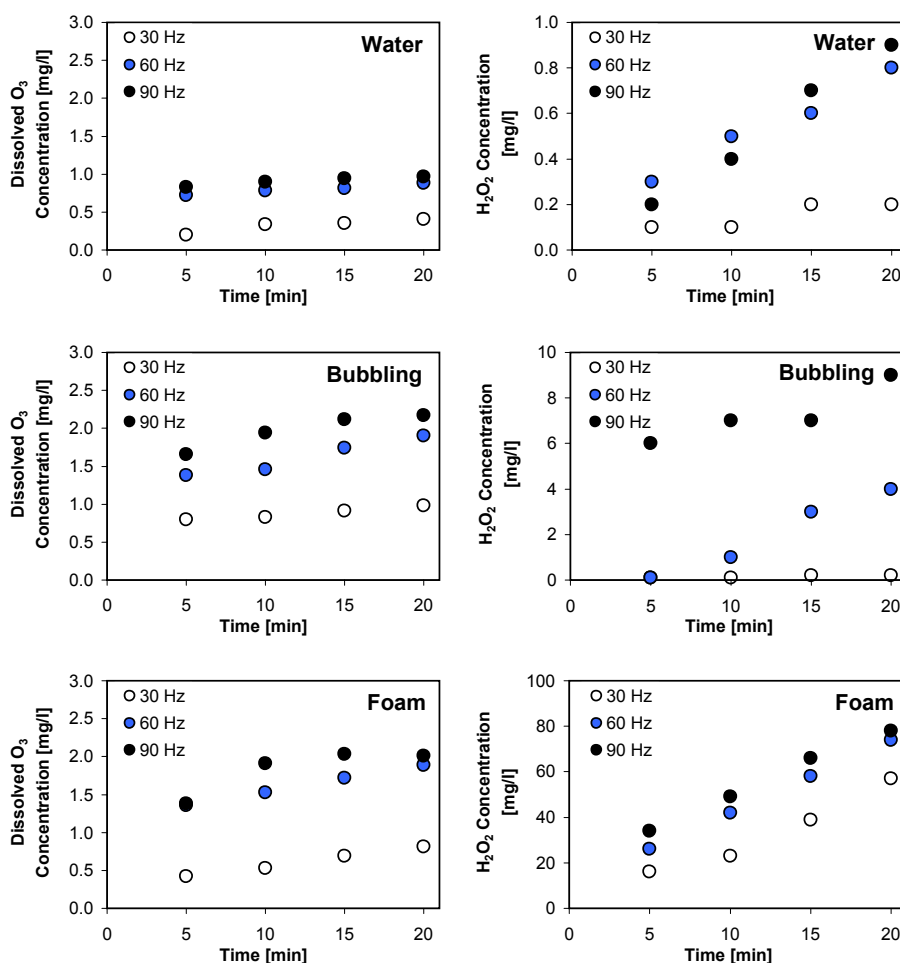


Fig. 3. Generation of dissolved O₃ and H₂O₂ in time as function of pulse repetition rate in water, bubbling and foaming systems.

hydrogen peroxide generation, while, the highest concentrations of gaseous ozone may be expected in the bubbling system.

Indigo blue was selected for the test of the removal of dyes from water to evaluate the performance of all three systems. The indigo molecule, presented in Fig. 4 (left), has two -N-H groups (electron donors) and two -C=O groups (electron acceptors). The terminal O and H atoms may engage in hydrogen bonding with atoms of a solvent or they may hydrogen bond with one another. The relative amounts of these two possibilities determine the colour of the indigo solution. Colour disappears after the indigo molecule is decomposed onto the isatin and further onto more simple by-products [3].

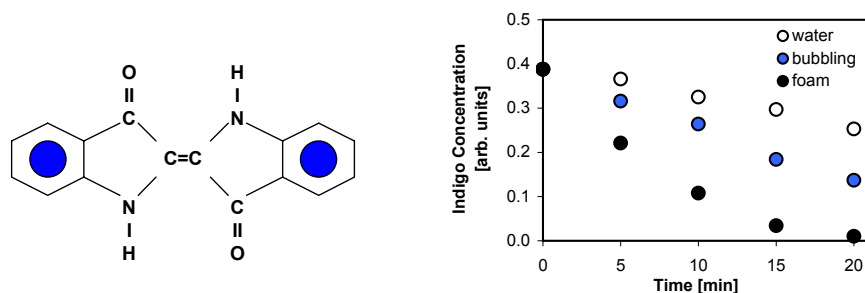


Fig. 4. Chemical structure of indigo blue molecule (left). Decomposition of indigo blue in water, bubbling and foaming systems at 60 Hz (right).

The removal of indigo blue was evaluated using UV absorption spectrometer. The absorption band of indigo blue at 612 nm was used for the analysis. The level of decomposition was confirmed also visually. The results of the decomposition of indigo blue resulting from the action of the pulsed discharge operated at 60 Hz are presented in Fig. 4 (right). As the figure shows, the most efficient removal was observed in the foaming column. It is the results of the oxidation of indigo by ozone (dissolved, but also gaseous) with minor support of H_2O_2 . Visually, the full discoloration was observed after about 30 minutes of the discharge treatment.

4 Conclusion

The systems of water, bubbling and foaming columns powered by the electrical discharge were tested for the generation of the oxidants and the removal of indigo blue. The highest amount of hydrogen peroxide was found in the foaming column. Concentration of dissolved ozone in bubbling and foaming systems were comparable. In water system, the generation of the oxidants was not satisfactory. In all the systems, the concentration of the oxidants increased with operation time and pulse repetition rate. The best results of indigo blue treatment were obtained in the foaming column.

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