Comparison between plasma microbubbles and gas-liquid dielectric barrier discharge (DBD) plasma for pollutants degradation in water

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Abstract This study's main emphasis is the direct comparison between gas-liquid dielectric barrier discharge (GLDBD) and plasma microbubbles (PMB) concerning the kinetics related to the contaminant's destruction and plasma-activated water composition. As contaminants with different structures, methylene blue (MB), methyl violet (MV), methyl orange MO) and sunset yellow (SY) were investigated. For the PMB system, low concentrations of long-lived plasma species were measured and an almost neutral pH, while on the contrary for the GLDBD high long-lived species concentrations and a significant pH decrease was recorded. This study sheds light on how the GLDBD and PMB systems can be used to expand the use of cold plasma-based wastewater treatment.

Keywords: Plasma bubbles; Dielectric barrier discharge; Plasma-activated water; Wastewater treatment; Reactive oxygen and nitrogen species; Cold atmospheric plasma.

1. Introduction

By 2025, 3.5 billion people will experience water scarcity, since the demand for freshwater has more than doubled during the last 60 years [1]. The WHO claims that poisoning or diseases brought on by tainted water account for more than 500 million fatalities annually. The three primary categories of water contaminants are infections, inorganic substances (such as heavy metals), and harmful organic compounds (such as dyes, medicines, and endocrine disrupting chemicals). Conventional water treatment techniques, such as sedimentation, coagulation, and filtration units, which frequently only partially remove pollutants, are not always effective. On the other hand, processes like chlorination and adsorption may produce by-products and secondary pollution, necessitating additional depuration stages [2-4]. Advanced oxidation processes (AOPs), either by themselves or in conjunction with other techniques (such reverse osmosis), have been suggested as competitive options [5-7]. Cold atmospheric plasma (CAP), one of the many AOPs, has recently attracted a lot of attention. This might be explained by the quick pollutant degradation rates based on numerous highly reactive species working together and synergistically [8]. The key challenge is to identify the optimum conditions in order to fully utilize this beneficial technology for wastewater treatment [9]. Reactor design stands out as a very key factor in this regard. The rapid and effective removal rates depend on the mass transfer of plasma reactive species to the liquid in addition to the properties of the contaminants and the aqueous medium. Many studies have examined the plasma-water mechanisms that predominate in gas-liquid systems. Reactive oxygen and nitrogen species (RONS) are produced in the gas phase and afterwards diffuse into the formed in the gas-liquid interface and subsequently produce secondary RONS into the medium [9]. On the other hand, recent studies indicate the value of plasma bubbles in the wastewater treatment due to their positive impact on effective transfer of plasma species from the gas phase to water. The scope of this study is to comare in detail the plasma microbubbles and the gas-liquid DBD systems against the degradation of organic pollutants in water. Taken into account the different electrode arrangements of these reactors and the multiplicity of the process, we have conducted this comparison under the same pulse frequency and voltage, but also under their optimized design characteristics and experimental conditions which are responsible for the maximization of the pollutant degradation and energy efficiency. Pollutants with different structures, were examined based on the fact that these compounds exhibit a structural-dependent degradation [10]. The plasma-liquid interactions were also examined in both systems .

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2. Experimental section

2.1 *Chemicals and reagents*

All the reagents and chemicals, purchased from Merck, were used as is without further purification. The dyes methyl orange (MO), methylene blue (MB), sunset yellow (SY) and methyl violet (MV), were used as model pollutants. The compressed dry air used as plasma feeding gas was provided by Linde (Athens, Greece).

2.2 Experimental setup, treatment conditions and electrical measurements

The experimental set-up included a plasma reactor, a nanosecond pulsed HV power supply (NPG-18/3500), a plasma optical and electrical characterization arrangement (OES, AvaSpec-ULS2048CL-EVO), a feeding gas system, and tools for the chemical analysis of pollutants and plasma species detection in the aqueous phase. The gas-liquid DBD, has been discussed in detail in our previous study [10]. In this reactor the plasma discharges are generated above the water surface. The plasma microbubble (PMB) column was able to produce plasma bubbles directly inside the water. These two reactors were used in this study (Fig. 1a). Initial pollutant concentration was 40 mg/L. The time the solution was treated ranged from 2 to 40 min. The initial conductivity and the pH of 3D water were 4.6 μS/cm and 6.2 and, respectively. The pulse voltage and frequency were constant, being 26.0 kV and 200 Hz. The volume of the solution under treatment was 15 and 70 mL for the GLDB and PMB reactors, respectively.

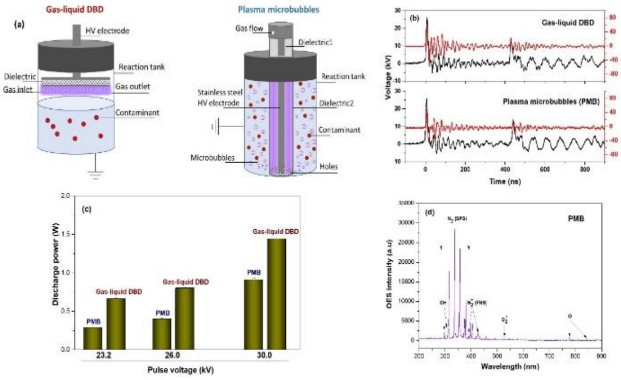

Figure 1. (a) The gas-liquid DBD and plasma microbubbles (PMB) reactors; (b) **C**urrent waveforms and instantaneous voltage of the two reactors at 26.0 kV; (c) Discharge power at different applied voltages; (d) Optical emission spectrum for the PMB reactor (air plasma gas).

3. Results and discussion

3.1 The degradation and energy efficiency for the PMB and gas-liquid DBD systems

The primary objective of the current investigation is the direct comparison of the degradation and energy efficiency of the plasma microbubble and the gas-liquid DBD. Complete degradation of MB, MV, and MO at pulse voltage 26 kV was accomplished after 10 minutes of treatment with PMB, as opposed to 15 minutes with gas-liquid DBD (Figs. 2a, b and c). In practice, this means that it could be achieved at the same or lower treatment time a treatment of a larger volume of polluted water (Fig. 1c) when PMB is used. The characteristics of the air-PMB, which are superior to the ones of the air-liquid DBD as for degradation kinetics, are evident in Figs. 2a, b, and c. The kinetic constant k for MB was 0.28 for air-liquid DBD, whilst 0.39 for air-PMB (Fig. 2a). Nevertheless, it should be noted that if the treated volume of each reactor is considered, the volume-normalized constant k' is 4.2 and 28.0 mL min^{-1} for air-liquid DBD and air-PMB, respectively (inset of Fig. 2a). An analogous trend is also noticed for the PMB system for MV (Fig. 2b) and MO as well (Fig. 2c). It should be noted though that the degradation kinetics are not the same for all dyes with the PMB system. It is noticeable that SY (Fig. 2d) was degraded by 46.8% in contrast to the almost complete degradation (>99.5%) of all other dyes when the solution was treated for 10 min. It is important to clarify that the 40 min that are required for almost complete SY degradation using the PMB reactor (70 mL), whilst 20 min are required for the air-liquid DBD (15 mL) with k values being 0.10 and 0.20 min^{-1}, respectively. However, the volume-normalized constant k' is higher for air-PMB compared to air-liquid DBD (inset of Fig. 2d). An explanation for the similar performance of the two reactors against SY may be assigned to the lower RNS concentrations detected for the PMB system. For the air-liquid DBD system important values of RNS were detected which led to the pH decrease from 6.2 to 3.5. It is important to note that previous knowledge indicates that RNS and low pH are important for the degradation of certain contaminants including [10].

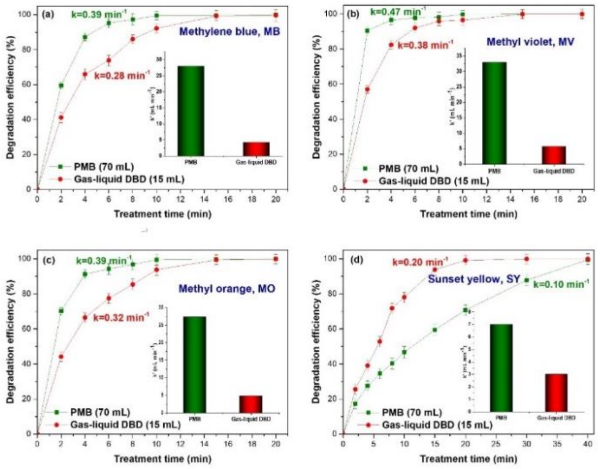

Figure 2. The PMB and gas-liquid DBD systems for the degradation of (a) MB; (b) MV; (c) MO and (d) SY (applied voltage: 26.0 kV; plasma gas: air; air flow rate in PMB: 3.0 L min^{-1}; air flow rate in gas-liquid DBD: 0.2 L min^{-1}).

3.2 Plasma species formation for the PMB and gas-liquid DBD

The concentrations of long-lived species were much lower in the PMB compared to the very high concentrations in the gas-liquid DBD (Fig. 3).

The rapid degradation, the high $^{\cdot}$OH concentration and the almost neutral pH are some of the advantages of combining plasma microbubbles with low-frequency high voltage nanopulses. In addition, since lower long-lived RONS are produced, it is anticipated that post-treatment effects will be less intense. On the other hand, the low long-lived species concentration and almost stable pH may have negative effects on the cases that the pollutants degradation is enhanced at lower pH and high RNS concentrations. In the context of the process sustainability, the plasma water deriving from the gas-liquid DBD could be exploited for irrigation since H_2O_2 is well known for its positive character for seed germination and NO_3^- promotes seedling/plant growth, while the water from PMB system may be potentially used as drinking water since very low quantities of RNS species are detected and the pH is slightly affected.

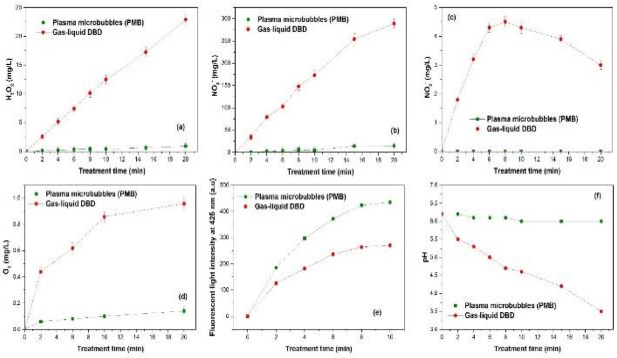

Figure 3. The composition of plasma activated water for the PMB and gas-liquid DBD (a) H_2O_2; (b) NO_3^-; (c) NO_2^-; (d) O_3; (e) Fluorescent light intensity at 425 nm; (f) pH (applied voltage: 26.0 kV; plasma gas: air; air flow rate in PMB: 3.0 L min^{-1}; air flow rate in gas-liquid DBD: 0.2 L min^{-1}).

4. Conclusions

The detailed comparison plasma microbubbles and gas-liquid DBD has been performed examining pollutants with different chemical structures. The different structures resulted different plasma-liquid interactions in the two systems, which subsequently led to varying properties and composition of the plasma water. In addition, the production of the RONS was different for the two systems being much higher in gas-liquid DBD than in PMB, while the pH remained unaffected in the PMB system when the pH decreased to 3.5 for gas-liquid DBD. The findings of this study indicate that the various RONS, the reactor configurations, and physicochemical properties of water play an important role for different pollutant structures showing therefore that PMB cannot be considered always a panacea.

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