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Evaluation of a microfluidic atmospheric-pressure plasma reactor for water treatment

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Abstract. A dielectric barrier discharge (DBD) microfluidic plasma reactor, operated at atmospheric pressure, was studied for its potential to treat organic contaminants in water. The proposed microfluidic plasma reactor (MPR) allows *in situ* production of plasma in a continuous flow, operated under atmospheric pressure, for plasma-based water treatment. The MPR operates with glass as the dielectric barrier, where plasma is generated in the continuous gas flow stream of a gas-liquid two-phase annular flow regime in the microchannels. The microchannels have dimensions of 100 μm depth, 250 μm width and the plasma is generated in an approximately 21 cm length of microchannel arranged in a serpentine pattern. Methylene blue (MB) in solution was used as a model organic to investigate its degradation by plasma generated in the microchannels. The influence of discharge time, residence time and gas sources, i.e. air, argon and oxygen, on MB degradation was studied. The percentage degradation increased with lower liquid flow rates, with maximum degradation of MB achieved at a liquid flow rate of 35 μL/min and inlet gas pressure of 1 bar using oxygen as the working gas. Liquid chromatography/mass spectrometry analysis of the MB solution after treatment suggests degradation through fragmentation of MB. It is intended that the device will be used as proof of concept to introduce plasma technology as an advanced oxidation process for water treatment, with the potential to achieve total mineralization of dissolved organic materials and microbial inactivation, replacing water treatment chemicals and consumables.

1. Introduction

Advanced oxidation processes (AOPs), based on the *in situ* generation of oxidising species with non-thermal plasma-based water treatment, have been widely studied for the degradation of soluble organics found in water, for their potential to outperform conventional water treatment methods [1]. The production of highly reactive oxidative species such as hydroxyl radicals ($\cdot$OH) by non-thermal plasma and plasma processes, i.e. pyrolysis and UV photolysis, allows *in situ* degradation of target pollutants [2]. The application of microfluidics presents a compelling approach for further examination of plasma-based water treatment as this methodology allows the control of spatial and temporal behaviour of fluids within dimensions

less than a millimetre [3]. Generation of plasma in microchannels opens the prospects of low power operation, large surface area-to-volume ratio and enhanced mass transfer of continuous flow milli-scale plasma reactor.

In the present work, a glass microfluidic atmospheric-pressure plasma reactor, operated as a dielectric barrier discharge (DBD), was studied for the removal of methylene blue (MB) in a gas-liquid two-phase flow regime. MB was selected as model organic compound due to its chemical stability and to further evaluate the effect of on-chip plasma treatment.

2. Experimental

The microfluidic plasma device used in this study was designed and fabricated in glass using standard photolithography techniques coupled with wet etching [4] and designed using AutoCAD to produce the design shown in Figure 1.
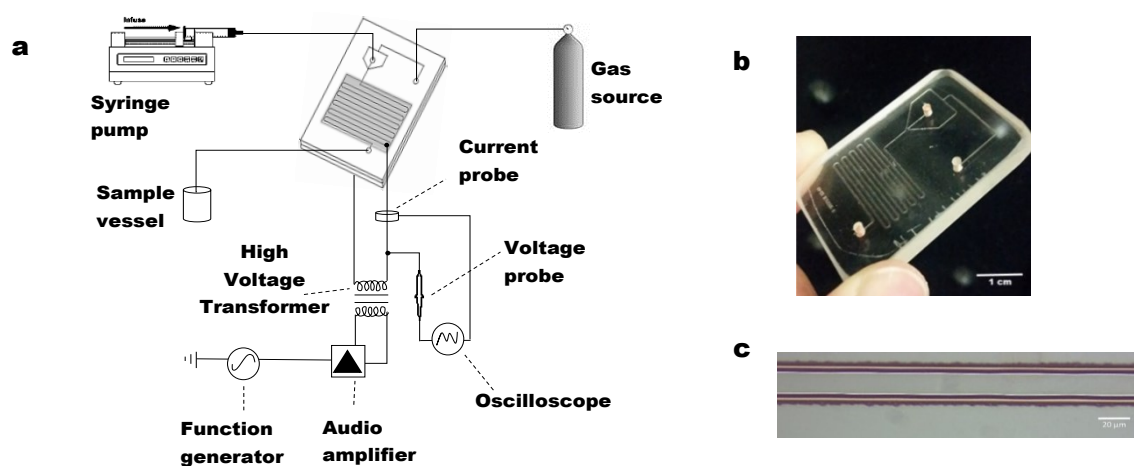

Fig. 1 Schematic illustration of the microfluidic plasma device system. (**a**) Experimental set-up. (**b**) Microfluidic plasma device. (**c**) Annular flow regime at 1 atm and 35 μL/minute gas and liquid flow rate, respectively.

Microchannels were etched in a 1 mm thick bottom glass plate, both inlet and outlet holes (1/16" outer diameter (OD)) were drilled through a 1 mm the top plate, and the two plates thermally bonded. Fluorinated ethylene propylene (FEP) tubing (1/16" OD x 0.030" inner diameter (ID)) was glued, using Araldite, onto the device. Sample solutions of methylene blue at 5 ppm were injected, with compressed gas, i.e. air, argon or oxygen, continuously flown in the device, and an annular flow was achieved as shown in Figure 1c. Sustained annular flow was achieved at various liquid flow rates of 35 to 100 μL/minute and gas flow kept at 1 atm. Copper was used as both the high voltage and ground electrode, with size 20 x 10 mm and 25 μm thickness, and positioned on either side of the glass chip over the serpentine microchannels. Voltage of 10 kV at 17 kHz was applied to the electrodes and the average power consumption, as estimated from Lissajous figures, was found to be P = 13.9 ± 0.05 W. The power supply consists of a signal generator (TTi TG1000), audio amplifier (ProSound 1600) and custom-built high voltage transformer (Amethyst Designs). Current and voltage measurements were made with a Pearson

4100 current monitor and a Tektronix 1000:1 voltage probe, recorded on a Tektronix DPO3014 digital oscilloscope. The microreactor chip was fixed into a compressive case made of poly(methyl methacrylate) (PMMA). Relative reactivity was affirmed by collecting treated solution from the outlet. The degree of MB degradation and presence of degradation products were determined using UV-Vis spectroscopy (Perkin Elmer Lambda 40) and LC/MS (Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS), respectively.

3. Results and Discussion

Concerning plasma generation, the gas space along the liquid-air interface of the annular flow was the focus of interest, providing a space for discharge. Residence time of the solution in the plasma discharge zone is an important parameter yielding different reactivity with the MB solution, resulting to MB degradation. The mean residence time was estimated as the ratio of the inner volume to the volumetric flow rate. Figure 2 shows decreasing degradation of MB by increasing liquid flow rate, attributed to decreasing residence time.
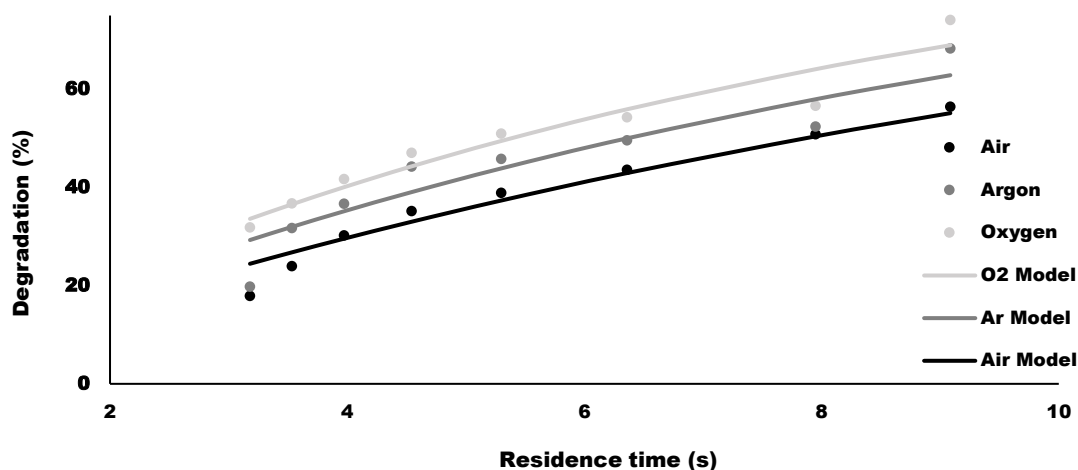

Fig. 2 MB degradation versus residence time, using various carrier gases. Error bars represent standard errors (n=3). Air (k = 0.088 s^{-1}, $R^2 = 0.9952$), argon (k = 0.11 s^{-1}, $R^2 = 0.9927$) and oxygen (k = 0.13 s^{-1}, $R^2 = 0.9898$) (P< 0.05)

Kinetic rates of degradation were obtained by fitting the data to a first-order kinetic reaction, using equation 1;

$$\eta = 1 - e^{-kt} \tag{1}$$

where t is the reaction time and η is the degradation efficiency. Under the reaction conditions studied, degradation of MB followed a pseudo-first-order kinetics. The apparent kinetic constant increased in the order of oxygen to argon to air. The optimal rate constant obtained was 0.13 s^{-1} using oxygen as the carrier gas, which is the most effective for promoting MB degradation. The result is attributed to the efficient production of reactive oxygen species such as ozone, O, $\cdot OH$ and H_2O_2, using pure oxygen which are found essential to the degradation of MB through oxidation [5]. Peaks in the mass spectra, as shown in Figure 3, indicates the breakdown products of MB after plasma treatment on chip. The result shows

fragmentation of MB as an initial step in the breakdown of MB rather than direct mineralization upon exposure to plasma [6]. The system is predicted to reach further degradation upon further effective area of exposure to plasma by elongating the serpentine channel.
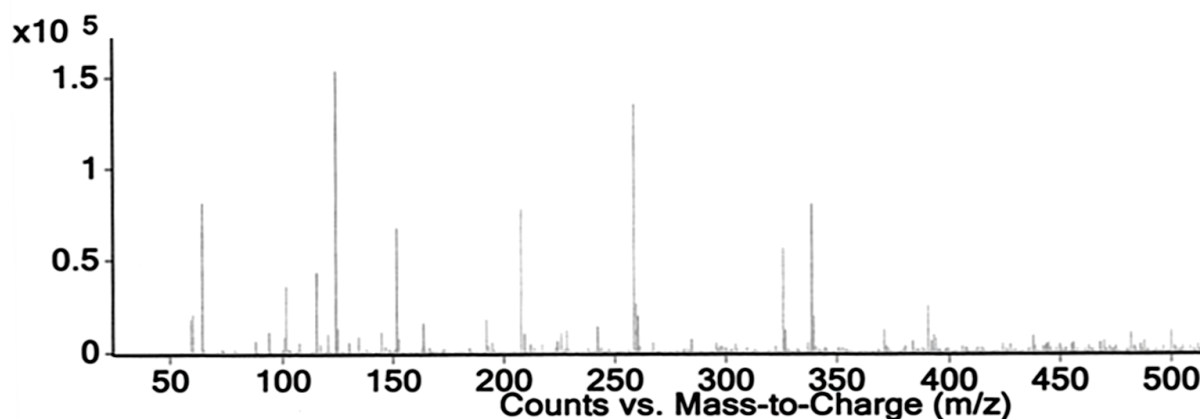

Fig. 3 Mass spectra of plasma treated MB solution with oxygen as the carrier gas.

Molecular ion $[C_{16}H_{18}N_3S]^+ = 284.12$

4. Conclusion

The decomposition of MB using a microfluidic chip was investigated using a DBD generated in a continuous two-phase annular flow. Results indicated successful degradation of MB in water. Degradation of MB was favoured by higher residence time in the plasma discharge zone, which can be manipulated by decreasing the liquid flow rate. Highest MB degradation was obtained with the lowest liquid flow rate, 35 µL/min, and oxygen as the carrier gas due to the nature of the reactive oxygen species formed. Kinetic behavior of MB degradation was found to follow a pseudo-first order reaction. Based on the MS spectra obtained, MB degradation through fragmentation favored other than mineralization. The microfluidic plasma reactor opens up promising prospects for plasma-based water treatment and other flow systems. Further optimization is required in terms of design and power supply to exploit plasma generated in the microchannel for higher degradation.

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