Characterization of radial plasma discharge in contact with water by Optical Emission Spectroscopy and correlation with organic contaminants degradation results

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Abstract: Optical Emission Spectroscopy has been used to characterize an atmospheric radial plasma (RAP) discharge in contact with water. Specifically, the effects of the liquid conductivity and of the presence of oxygen on the behaviour of the RAP discharge in terms of continuous emission intensity, characteristic emission lines and electron density dynamics were studied. Additionally, the effect of dissolved organic contaminants was investigated and the data correlated with the pollutants degradation efficiency.

Keywords: Non-thermal plasma, RAP, PFAS, Optical Emission Spectroscopy.

1. Background

A radial discharge plasma (RAP) reactor has been developed for the degradation of surfactants, in particular for removal of Per- and Poly-fluoroalkyl substances (PFAS) from water [1]. PFAS have become a major environmental problem being resistant to natural degradation mechanisms and thus having widely spread throughout aquatic environments and soil. Conventional water treatments have proved to be ineffective in the removal of PFAS, likewise Advanced Oxidation Processes (AOPs) that utilize hydroxyl radical, which is ineffective in attacking the very strong C-F bonds in PFAS alkyl chains [2].

Advanced oxidation/reduction processes appear to be promising [2] and, among them, atmospheric pressure plasma is reported as the most energy efficient in achieving high degrees of PFAS mineralization [3]. Since electrons produced in plasma are expected to play an important role in initiating the degradation of PFAS at the gas/liquid interface [1], [4], the optimization of the production of high energy electrons is crucial to enhance the efficiency of the process. The characterization of the plasma system is therefore a powerful tool to achieve this purpose.

This study was focused on the characterization of the RAP discharge through Optical Emission Spectroscopy and investigated in particular the effects of the liquid conductivity, the presence of oxygen and the presence of dissolved organic contaminants on the behaviour of the RAP discharge in terms of electron density dynamics, continuous emission intensity and emission lines due to the specific species generated by the discharge.

2. Methods

A radial plasma (RAP) discharge reactor was used consisting of a 92 mm high and 46 mm diameter cylindrical quartz vessel closed by an airtight plexiglass cover.

A concentric hole supports the pointed edge high voltage tungsten electrode (2 mm diameter) placed 6 mm above the liquid surface. The counter electrode is a stainless-steel ring (37 mm diameter) held partially submerged in the liquid. Two additional holes on the cover are used for gas inlet and gas outlet, respectively, allowing the gas to flow through the reactor above the liquid surface. In an alternative mode of operation, the inlet port on the reactor cover is stoppered and the gas is bubbled inside the liquid from the bottom of the reactor through a fritted glass septum. Argon and argon/oxygen mixtures were used as plasma feed gas and were flushed through the reactor at 100 mL/min.

55 mL of tap water (initial conductivity = 0.5 mS/cm) and solutions of Na_2SO_4 in Milli-Q water at different initial conductivities were treated.

Plasma was ignited with Glassman (60 kV, 20 mA) high voltage power supply with negative polarity protected by 2.5 M Ω high voltage resistor. The specific configuration and reciprocal arrangement of the opposing electrodes lead to the formation of numerous random radial discharges contacting the liquid surface and sweeping across the opposing electrodes. These discharges cover the entire area encircled by the grounded electrode, providing a dense and most effective plasma-liquid interface. The frequency was fixed at 100 Hz and the power was maintained around 4 W by adjusting voltage and current by charging a high voltage capacitor (2.0 nF) connected in parallel to the reactor.

The voltage was measured using a high voltage probe, Tektronix P6015A, connected to a Tektronix TDS 2024B oscilloscope (200 MHz, 2 GS/s) while the current was measured by determining the voltage drop across a noninductive resistor (1.2 Ω) mounted between the ring electrode and the grounding point, using an ordinary voltage probe (Tektronix TPP0201).

Typical voltage and current waveforms of the radial discharge studied are represented in Fig. 1.



Fig. 1. Electrical properties of radial plasma discharge: voltage and current signals of one pulse.

The power dissipated in the RAP reactor corresponds to the product of energy deposited in the capacitor before the breakdown and the discharge frequency. The energy of a single pulse was measured by integrating the product of voltage (u) and current (i) waveform over time using Eq. (1), where τ is the average pulse duration.

$$E_{pulse} = \int_0^\tau u(t) \cdot i(t) \cdot dt \tag{1}$$

Overall spectra in the 190-900 nm range were recorded by using an Ocean Optics USB 4000 Spectrometer, while spectra in the UV range (200-390 nm) where recorded by using an Ocean Optics QE65000 Spectrometer.

Electron densities were determined based on the analysis of Stark broadening of Hydrogen Balmer alpha (H α) line emission at 656.3 nm [5], [6]. High spectral resolution images were recorded by using a Minuteman Spectrometer, with a 1 m focal length, 1200 grooves/mm grating and a slit of 50 µm, connected to a Princeton Instruments PiMax iCCD: 1024 x 256 pix (size of pixel 26x26 µm). The instrumental profile of the spectral apparatus obtained with the low-pressure spectral lamps had a Gaussian shape with the full width at the half maximum of 0.042 nm.

To perform temporally resolved measurements of electron density, a trigger unit was connected to the iCCD.

3. Results

Spectra in the UV-Vis range (190-900 nm) were recorded using two different modes of gas supply: by flushing the feed gas from the top of the reactor, above the liquid surface, and by bubbling the gas through a fritted glass septum from the bottom of the reactor into the treated solution. The resulting spectra obtained in 100% argon atmosphere are represented in Fig. 2. As it is visible, no significant differences have been recorded by comparing the two spectra in terms of continuous emission intensity and production of active species. So, the way of flushing the gas does not influence the emitted spectrum.

The effect of oxygen on continuous emission intensity and electron density was studied by adding different percentages of oxygen to the feed gas (from 2% to 5%).

The resulting spectra in the UV region are compared in Fig. 3, where it is visible an increase in continuous emission intensity due to the higher power required to ignite the plasma at higher oxygen percentages.

At higher power a higher electron density was expected, but this effect is not so evident in the experiments run by adding different percentages of oxygen to the feed gas. This is due to the quenching effect operated by oxygen, caused by its high electron affinity (Fig. 4a).

Moreover, through temporally resolved measurements of the intensity of the H α emission an average electron lifetime of 9 µsec has been observed in the presence of 3% of oxygen, while a value of 11 µsec was obtained in the absence of oxygen (Fig. 4b). So, the presence of oxygen in the gas phase reduces the electrons average lifetime.



Fig. 2. Typical spectra emitted in the radial plasma discharge in the 190–900 nm range: comparison between emission recorded by flushing argon from the top of the reactor (black) and bubbling argon from the bottom (red).



Fig. 3. Spectra emitted between 190 and 400 nm at different oxygen percentages.



Fig. 4. a) Electron density in the presence of different percentage of oxygen in the plasma feed gas; b) Temporally resolved electron density in argon 100% (black) and with addition of 3% of oxygen (red).

The effect of the liquid conductivity on the discharge properties was studied by using as aqueous media Na_2SO_4 solutions in Milli-Q water at different concentrations. The comparison of the resulting emitted spectra in the 190-400 nm range (Fig. 5) shows a decrease in continuous emission intensity with the increase in conductivity from 0.5 mS/cm to 2.5 mS/cm; as conductivity is further increased, from 4.0 to 10.0 mS/cm, the opposite trend is observed, so the continuous emission intensity increases again with increasing conductivity.

The applied power was almost the same for all the conductivities tested and this is reflected in the measured electron densities: in fact, no significant differences were observed in terms of electron density (Fig. 6a). Moreover, the same electrons lifetime (11 μ sec) was observed using tap water (0.5 mS/cm) and Na₂SO₄ solutions at 2.5 mS/cm and 4.0 mS/cm (Fig. 6b).



Fig. 5. Spectra emitted between 190 and 400 nm at different initial conductivity.



Fig. 6. a) Electron density at different initial conductivity; b) Temporally resolved electron density in tap water (purple), in Na₂SO₄ 2.5 mS/cm (orange) and in Na₂SO₄ 4.0 mS/cm (green).

4. Conclusions

In summary, the study found that neither the presence of oxygen (3-5%) in argon plasma nor changes in the liquid conductivity do significantly affect the production of active species or electron densities. However, the intensity of continuous emission was higher in the presence of 5% oxygen, due to the higher power required to ignite the plasma. Additionally, the presence of oxygen lowered the electrons lifetime due to its high electron affinity. Finally, the continuous emission intensity in the UV region decreased as conductivity levels increased up to 2.5 mS/cm, then increased again at higher conductivities.

In the poster presentation these data will be correlated with the results obtained in experiments of degradation of various PFAS and other organic contaminants characterized by different structures and physicochemical properties.

5. References

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