Microwave plasma jet in water: effect of water electrical conductivity on plasma characteristics

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ABSTRACT

Plasma-induced water treatment is a novel water treatment technique that has shown high efficiency and flexibility. Although the electrical conductivity of impure water varies depending on the degree of pollution, its influence on plasma treatment efficiency is not well understood. In this study, we investigate the fundamentals of a microwave plasma jet submerged in water with electrical conductivities (σ_w) ranging from 10 to 10000 $\mu\text{S}/\text{cm}$. The plasma characteristics, namely composition, electron density, and temperature, and their variations as a function of σ_w , are derived using optical emission spectroscopy. The plasma-bubble dynamics is investigated using space- and time-resolved high-speed imaging. The results show that the plasma fills the bubble volume at relatively low flow rate (typically, < 2 L/min) and high σ_w (typically, > 1000 $\mu\text{S}/\text{cm}$). The influence of σ_w on the degradation of methylene blue, a standard water pollutant, is also assessed, and the obtained results indicate that the plasma becomes extremely inefficient at high σ_w . These findings are of great importance for the community of plasma-induced liquid processing, particularly wastewater treatment.

1. INTRODUCTION

Plasmas in- or in-contact with a liquid medium constitute a novel field of research that presents great potential for numerous applications, such as material processing [1]–[3], wastewater treatment [4], agricultural engineering [5]–[7], medical treatment [8]–[10], and others. To date, various plasma sources have been designed, developed, and studied for liquid processing. These can be classified into two categories: thermal (high temperature for all species—thousands of degrees kelvin) and non-thermal (high temperature for electrons—thousands of degrees kelvin—and low temperature for neutrals and ions—hundreds of degrees kelvin) [11]. Such (thermal and non-thermal) plasma sources can be powered using direct current (DC) [12], alternative current (AC) [13], and pulsed power [14] electrical excitation, as well as high-frequency electromagnetic fields (microwave and radio frequency) [15] and lasers [16]. Some plasma sources utilize electrodes, such as corona discharge, dielectric barrier discharge, spark, and arc discharge, whereas others are electrodeless, such as radio frequency and microwave discharge that use induced-field, antenna, or wave guide for coupling the power to a gas flowing in a dielectric tube.

In a plasma-assisted-water-treatment setup, it is preferable that a plasma-electrode interaction is minimized to avoid secondary contamination due to electrode's erosion [17]–[19]. Such erosion can contaminate the water with nanoparticles whose hazards are not clearly known. Recently, a submerged arc jet system has been proposed to generate plasmas that are independent of liquid properties [20], and it has been reported to effectively decompose phenols. However, as the use of metallic electrodes is essential for the arc discharges, there are strong plasma-electrode interactions leading to both decreased lifetime of the plasma device and the secondary contamination of water by metallic particles. In a subsequent study, a submerged electrodeless microwave plasma jet was designed to avoid such secondary contamination due to electrode erosion [21]. The system showed great potential for water processing as compared to other processes [22].

When a discharge location is geometrically decoupled from a target liquid as shown with the submerged arc jet [20] and the microwave plasma jet [21], we should investigate how liquid properties affect remotely generated plasmas. The influence of water conductivity, as an example, has been addressed in literature under various conditions. In this context, Bruggeman *et al.* [12]

have investigated its influence (by adding KCl) on the properties of a DC discharge in liquid. A change in the discharge mode is observed: streamer-like discharge in liquid is observed at low conductivity, whereas streamer discharge in liquid vapor is observed at conductivity higher than $\sim 45 \mu\text{S/cm}$. They also showed that, as liquid conductivity is increased from 1 to $700 \mu\text{S/cm}$, the breakdown voltage is decreased from ~ 11 to 1 kV and the electron density is decreased from $\sim 10 \times 10^{20}$ to $3 \times 10^{20} \text{ m}^{-3}$. Recently, Wang *et al.* [14] have investigated the influence of liquid conductivity (by adding KCl), in the range $10\text{--}36000 \mu\text{S/cm}$, on the properties of a nanosecond pulsed discharge in bubbled water (the used gases are He or Ar). They showed that the production rate of H_2O_2 was not significantly changed with liquid conductivity when He gas is used, however, it decreased by $\sim 13\%$ when Ar gas is used. Using an equivalent-circuit model, they also showed that decrease in the rise time of the applied voltage increased the breakdown voltage and improved the tolerance of the plasma system to the liquid conductivity allowing it to function in sea-water. The effect of water's electrical conductivity on the physical characteristics of electrical discharges in water with Ar gaseous bubbles is also studied by [16], and they reported, among others, that the discharge probability is reduced by 46% as the conductivity is increased from 10 to $1000 \mu\text{S/cm}$. In this context, it is clear that electrical conductivity has a great influence on in-liquid plasma properties and, therefore, on the induced physics and chemistry for required applications.

In this regard, the present study investigates the effect of water's electrical conductivity (by adding KCl) on the physical characteristics of remotely generated microwave plasma jet (MWPI). We characterize the plasma using optical emission spectroscopy and use a high-speed camera to investigate the relative plasma-bubble dynamics. To address the efficiency of the MWPI to degrade organic pollutants present in conductive liquids, we use methylene blue as a reference pollutant and monitor its degradation rate under various plasma conditions. Such research is particularly important considering that wastewater has a wide range of electrical conductivity (*e.g.*, $\sim 2\text{--}4 \text{ mS/cm}$ for cooling water and $\sim 30 \text{ mS/cm}$ for ballast water [4]).

2. EXPERIMENTAL METHODS

2.1. Setup Design and Working Conditions

Figure 1 Figure 1 depicts the scheme of the experimental setup. A solid-state microwave generator (Sairem, GMS200W) was used to deliver continuous microwave power (at 2.45 GHz)

to a surfatron device (Sairem, Surfatron60) using a coaxial cable. The surfatron's temperature was maintained by circulation of chiller-cooled water at 20°C, as well as a flow of dry air-cooled gas. The gaseous mixture is composed of argon and nitrogen (99.999% pure), and it flows through a quartz tube with outer and inner diameters of 6.0 and 4.0 mm, respectively. Mass flow controllers were used to control the rate of gas flow through the quartz tube and into a liquid cell (square cylinder quartz) filled with water where it generates bubbles.

To evaluate the effect of electrical conductivity (σ_w) on plasma characteristics and on methylene blue degradation efficiency, five samples of water solutions with different σ_w (10, 100, 1000, 5000, and 10000 $\mu\text{S}/\text{cm}$) were prepared by adding specific amounts of KCl to distilled water ($\sigma_w = 10 \mu\text{S}/\text{cm}$). The conductivity of water was measured using a conductivity meter (Mettler Toledo, Inlab 731-ISM).

A high-speed camera (LaVision, Image Pro HS) was used to study plasma-bubble dynamics. A diode lamp (Luminus, SST-90) was used to illuminate the backside of the liquid cell and to identify the interface between bubbles and the liquid. Exposure time and acquisition frequency were set to 0.47 ms and 2 kHz, respectively, with a spatial resolution of 1056×1312 pixels. Emission spectra were acquired using a spectrometer (Princeton Instruments, SP2750) equipped with a grating (900 grooves/mm, blazed at visible) and an ICCD camera (PI-MAX3). The spectra were acquired at an exposure time of 1 ms, and 50 spectra were averaged for each sample.

Figure 1. Schematic of the experimental setup used to create submerged MWPI: a) 3D view and b) 2D view. The zone delimited by dashed-blue line shows where the high-speed images are acquired.

Methylene blue (MB) was selected as a standard pollutant, and was added to water samples at a concentration of 50 mg/L. The MWPJ-induced degradation of MB was monitored by absorption spectroscopy using UV-Vis spectrophotometer (ThermoScientific, Genesys 10S) in the wavelength range of 350-1100 nm. The decoloration rate of MB was determined based on absorbance measurements at 663 nm. The shown values are an average of two series of measurements.

2.2. Determination of Gas Temperature and Plasma Electron Density

The rotational temperature (T_{rot}) of OH, that are supposed to have a Boltzmann distribution, was calculated by fitting its experimental spectrum, according to the method developed by Rodrigo *et al.* [23]. More details about the developed method and the various assumptions can be found in [23]. Although OH rotational temperature is very sensitive to the excitation and de-excitation mechanisms occurred in the plasma (a non-Boltzmann distribution can also be obtained), its consideration to represent gas temperature is not straightforward. In our case, we used OH rotational temperature as a first approximation to conduct a relative comparison between the different values of temperature and to establish a relationship between T_{rot} and σ_w . Good agreement between the simulated and the experimental spectra was usually observed, as illustrated in Figures 2a and 2b that correspond to the lowest ($T_{rot} \sim 2245$ K; at $\sigma_w = 100$ μ S/cm, 2 L/min) and the highest ($T_{rot} \sim 3500$ K; at $\sigma_w = 10000$ μ S/cm, 0.6 L/min) temperatures, respectively. Although each experimental spectrum is averaged over 50 accumulations, the error on temperature values has been deduced from the fit quality.

Figure 2. Comparison of experimental and simulated spectra of OH (A–X) at a) Ar flow rate = 2 L/min and $\sigma_w = 100$ μ S/cm, as well as b) Ar flow rate = 0.6 L/min and $\sigma_w = 10000$ μ S/cm; $P = 200$ W and water volume = 200 mL.

The variation of plasma electron density (n_e) as a function of σ_w was estimated through a detailed analysis of the $H\beta$ line ($\lambda = 486.1$ nm, $n = 4 \rightarrow n = 2$). The spectral shape of an excited species' emission line may be related to certain physical phenomena occurring in the plasma, mainly Doppler effect, van der Waals interactions, and Stark effect. Other factors that influence spectral shape include instrumental broadening and natural broadening. The FWHM (Full Width at Half-Maximum) of Gaussian shaped spectral lines affected by instrumental broadening was determined using a low-pressure light source and was found to be 0.054 nm. Natural broadening, on the other hand, originates from uncertainties in energy (Heisenberg's uncertainty principle), and it is usually negligible compared to other factors affecting spectral line breadth.

Doppler broadening ($\Delta\lambda_{Doppler}$) and van der Waals ($\Delta\lambda_{Van\ der\ Waals}$) broadening are given by equations (1) [24] and (2) [25], respectively,

$$\Delta\lambda_{Doppler}(nm) = 3.4804 \times 10^{-4} \sqrt{T(K)} \quad (1)$$

$$\Delta\lambda_{Van\ der\ Waals}(nm) = 5.24 / (T(K))^{0.7} \quad (2)$$

where λ is wavelength and T is temperature (assumed to be equal to T_{rot}). Broadening induced by Doppler effect (due to temperature) results in a Gaussian profile of the spectral emission lines, whereas broadening induced by van der Waals effect (due to pressure and temperature) yields a Lorentzian profile.

Stark broadening ($\Delta\lambda_{Stark}$) is due to the interaction between emitting species and surrounding charged species (electrons and ions) through their dynamic micro-electric field. Stark broadening of the $H\beta$ line has been theoretically investigated by Gigos and Cardenoso [26], and the extensively used relationship between n_e and $\Delta\lambda_{Stark}$ is given by equation (3) [24]:

$$n_e(cm^{-3}) = 10^{16} \times [\Delta\lambda_{Stark}(nm)]^{1.46808} \quad (3)$$

Under these conditions, the resulting experimental line shape can be fitted by a Voigt function (convolution product of a Lorentzian and Gaussian), where the Gaussian contribution (Doppler and instrumental broadenings) is known, and the Lorentzian contribution is deconvoluted from the Voigt profile. Knowing van der Waals broadening, Stark broadening can be deduced and

n_e can be measured. Note that, although each experimental spectrum is averaged over 50 accumulations, the error on electron density has been deduced from the fit quality.

3. RESULTS AND DISCUSSION

Recently, the plasma characteristics of MWPI in distilled water were studied in detail in [21], and the main results revealed that gas composition and flow rate strongly affect plasma dynamics and the degradation of MB. In this study, the influence of σ_w on various plasma properties and plasma-bubble dynamics was investigated. Note that the dissipation of microwave power in water is not considered here. **Section 3.1** presents the optical diagnostics of MWPI and the main plasma characteristics, such as the rotational temperature of OH radicals and electron density, as a function of σ_w . The influence of σ_w on plasma-bubble dynamics is presented in **Section 3.2**, whereas the influence of adding nitrogen is presented in **Section 3.3**. Finally, in **Section 3.4**, the influence of σ_w on the degradation of MB is discussed.

3.1. Effect of water electrical conductivity on MWPI characteristics

To investigate the plasma characteristics, namely reactive species composition, temperature, and electron density, of the submerged MWPI, a detailed analysis of the optical emission spectra, under various σ_w , was performed. Plasma-emitted light was collected near the inlet of the liquid cell using an optical fiber and analyzed with the spectrometer. The spectra presented in Figures 3a and 3b were acquired for various σ_w values, at Ar flow rates of 2 L/min and 0.6 L/min, respectively. In all measured spectra, the OH (A–X) band and the atomic Ar lines exhibit high intensity. H (α , β , and γ), O, and NH (A–X) lines are also identified. The intensities of these lines are relatively low compared to those of OH and Ar. Note that NH emission at 336 nm is due to an impurity in Ar and/or to dissolved air in water. The spectral lines at 766 and 769 nm correspond to emissions of potassium (K) atoms in KCl, and they are visible only at higher σ_w .

Figure 3. Optical emission spectra acquired at the inlet of the liquid cell for four σ_w values (10, 100, 1000, and 10000 $\mu\text{S/cm}$) at Ar flow rates of **a)** 2 L/min and **b)** 0.6 L/min. $P = 200$ W, exposure time = 1 ms, and number of accumulations = 50.

All the previously mentioned species were identified at low Ar flow rate (0.6 L/min) and low conductivity ($\sigma_w = 10 \mu\text{S/cm}$) (Figure 3b), albeit at lower band intensities than those observed at the higher flow rate. For $\sigma_w \geq 100 \mu\text{S/cm}$, K and Na lines are clearly visible in the spectra. Although it is known that K originates from KCl, Na may be present as impurity in KCl salt. The intensities of K and Na increase with increasing σ_w . Note that at $\sigma_w = 10000 \mu\text{S/cm}$, the spectrum is clearly dominated by K lines.

The data presented so far confirms that the MWPJ effectively dissociates water molecules to produce OH radicals together with H and O radicals; via a mechanism detailed in [27]. As strongly oxidative species, OH radicals are highly efficient in degrading water-bound organic molecules, and are thus, of great importance for the purpose of water treatment. The recombination of these radicals leads to the production of hydrogen peroxide, H_2O_2 ($\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$), an important agent in the chemical reactivity of plasmas in and in-contact with water [27]. The production rate of OH radicals is augmented with increased Ar flow rates, as evidenced by its relative intensity (this observation is valid for flow rates up to at least 5 L/min) and results in an increase in H_2O_2 concentration in water.

Variations in major emission intensities for OH, O, H, Ar, and K species as a function of σ_w , at Ar flow rates of 2 and 0.6 L/min, are depicted in Figure 4. The results indicate that as σ_w increases from 10 to 1000 $\mu\text{S/cm}$, the intensity of the Ar line increases monotonically. Further increase of σ_w to 10000 $\mu\text{S/cm}$ results in a slight decrease of the Ar emission intensity. Although this trend is evident for both Ar flow rates, the measured intensities at 2 L/min are two orders of magnitude higher than those measured at 0.6 L/min (note that the acquisition parameters were kept the same in both cases). The spectroscopic band intensities of OH, H, and O radicals also depend on σ_w . At 2 L/min, the variation of OH intensity as a function of σ_w is not significant, whereas the band intensities of H and O show a slight decrease as σ_w increases from 10 to 100 $\mu\text{S/cm}$, an effect that is not manifested at higher σ_w . Meanwhile, at Ar flow rate of 0.6 L/min, emission intensities of OH, H, and O radicals are significantly dependent on σ_w . H and O emissions continuously increase with increasing σ_w , within the tested range, while OH emission shows somewhat saturated behavior when σ_w is increased from 1000 to 10000 $\mu\text{S/cm}$. Note that, at 2 L/min, K emission is observed only at $\sigma_w = 10000 \mu\text{S/cm}$, while, at 0.6 L/min, it is detectable for $\sigma_w \geq 100 \mu\text{S/cm}$ demonstrating increasing emission intensity with increased σ_w .

Figure 4. Intensity variations of OH (309 nm), Ar (696.5 nm), H (656.3 nm), O (777 nm), and K (769.8 nm) spectroscopic bands as a function of σ_w for Ar flow rates of **a)** 2 L/min and **b)** 0.6 L/min. $P = 200$ W and water volume = 200 mL.

The results obtained in this study show that the spectroscopic band intensities of plasma species in submerged MWPI are dependent on σ_w . Such dependency has also been reported by Bruggeman *et al.* [12] who studied the emission intensities of plasma species in DC-excited discharge in water for σ_w between 1 and 700 $\mu\text{S/cm}$. Our results show that the investigated band intensities depend on the gaseous flow rate, and, interestingly, the trend reported in [12] (without gas) is similar to what we found at Ar flow rate of 2 L/min. However, at lower Ar flow rate, we observed a different trend (*i.e.*, continuous increase) suggesting that our MWPI plasma is very sensitive to both parameters, flow rate and water conductivity.

In fact, Ar flow rate is a very important parameter that can influence species concentrations, as it defines the environment in which the plasma is injected. Evidently, high Ar flow rate produces

a larger bubble, and vice versa. There is a specificity related to a surfatron device, and more generally to devices using electromagnetic surface wave plasma devices, that is the absorption of the microwave power requires a plasma (a critical electron density) to be developed. Therefore, high Ar flow rate will produce a larger bubble in which a longer plasma can be sustained; this has been previously confirmed by a high-speed imaging [21]. In this context, the plasma composition as well as the concentration of various species are closely related to Ar flow rate.

The electrical conductivity dependence of major plasma properties, such as rotational temperature and electron density, was also investigated using optical spectroscopy. The variation of T_{rot} as a function of σ_w , for the two typical flow rates (2 and 0.6 L/min), is presented in Figure 5. The results show that at higher flow rate, T_{rot} values are relatively lower than those measured at lower flow rate. Figure 5 also shows that T_{rot} decreases with increasing σ_w in the range of 10 - 100 $\mu\text{S/cm}$, by values of ~ 500 K and ~ 85 K at 2 L/min and 0.6 L/min, respectively. Further escalation in σ_w (up to 10000 $\mu\text{S/cm}$) augments T_{rot} from ~ 2245 K to 2640 K at 2 L/min, and from ~ 3030 K to 3500 K at 0.6 L/min. Conversely, the σ_w -dependence of the OH rotational temperature was found to be less significant ($\sim 3000 \pm 500$ K) in the case of DC-excited discharge in water [12]. This can be related to the investigated range of conductivity. Indeed, our temperatures obtained in the range of 10-1000 $\mu\text{S/cm}$ show a good agreement with [12], but further increase in σ_w to 10000 $\mu\text{S/cm}$ leads to an increase of OH rotational temperature, probably due to a change in plasma composition that modify the production mechanisms of OH(A) as well as its deexcitation mechanisms towards OH(X) state.

Figure 5. Variation of OH rotational temperature as a function of σ_w for two Ar flow rates; $P = 200$ W and water volume = 200 mL.

Figure a depicts the Voigt function fit of a typical $H\beta$ line profile determined at Ar flow rate = 2 L/min and $\sigma_w = 10 \mu\text{S/cm}$, whereas Figure 6b presents the variation of measured n_e values as a function of σ_w . Regrettably, it was not possible to estimate n_e at low Ar flow rate, due to relatively weak line intensities. The plotted data show a slight decrease of n_e , from $\sim 6.7 \times 10^{14} \text{ cm}^{-3}$ to $\sim 5.5 \times 10^{14} \text{ cm}^{-3}$, as σ_w increases from 10 to 10000 $\mu\text{S/cm}$. In the case of DC-excited discharge in water [12], a similar observation was reported, with n_e values decreasing from $\sim 10 \times 10^{14} \text{ cm}^{-3}$ to $\sim 3.0 \times 10^{14} \text{ cm}^{-3}$ as σ_w increases from 1 to 700 $\mu\text{S/cm}$. The relatively high values reported at low conductivity and relatively low values reported at high conductivity can be related to a variation in plasma-bubble dynamic. Indeed, at low conductivity the discharge is about a streamer-like in liquid. Such a discharge mode is known to produce high electron density because of the confinement of a plasma channel in liquid. Whereas, at high conductivity, it becomes a plasma in bubble (attached at gas-liquid interface): a mode that has relatively low electron density.

Figure 6. *a) Typical experimental and simulated profile of the $H\beta$ line. b) Variation of the electron density (n_e) as a function of σ_w . $P = 200 \text{ W}$, water volume = 200 mL, and Ar flow rate = 2 L/min.*

3.2. The effect of σ_w on plasma-bubble dynamics

To better understand the effect of electrical conductivity, spatially and temporally resolved plasma dynamics was investigated at the entry of MWPI to the liquid cell, under various conditions of Ar flow rate and σ_w , using high-speed imaging technique. Instantaneous plasma/bubble images were recorded at selected elapsed times, and are depicted in Figure 7. Initial time ($t = 0$) indicates the moment right after the detachment of a previous bubble from the entry of the MWPI during a periodic cycle. It is worth noting that the residence time of a bubble in water is highly dependent on both gas flow rate and microwave power; however, its dependence on σ_w is not significant (typically, at Ar flow rate = 2 L/min and $P = 200$ W, the residence time is ~ 400 ms). At flow rate = 0.6 L/min and $\sigma_w = 10$ or $100 \mu\text{S/cm}$, the plasma does not penetrate the bubble (Figures 7a and 7b), and the observed dynamics corresponds to that of a gaseous bubble in water. Meanwhile, the images recorded at $\sigma_w = 1000 \mu\text{S/cm}$ (Figure 7c), exhibit a tiny plasma in the bubble. Finally, for $\sigma_w = 5000$ and $10000 \mu\text{S/cm}$ (Figures 7d and 7e), a strong plasma is observed while the bubble is attached to the entry. This indicates a strong influence of water electrical conductivity on the remotely generated MWPI.

Figure 7. Plasma-bubble dynamics for various σ_w , at Ar flow rate = 0.6 L/min, $P = 200$ W, and water volume = 200 mL: **a)** $\sigma_w = 10 \mu\text{S/cm}$, **b)** $\sigma_w = 100 \mu\text{S/cm}$, **c)** $\sigma_w = 1000 \mu\text{S/cm}$, **d)** $\sigma_w = 5000 \mu\text{S/cm}$, and **e)** $\sigma_w = 10000 \mu\text{S/cm}$.

Similarly, Figure **Figure 8** shows the time evolution of the plasma-bubble dynamics for various σ_w , but at an Ar flow rate of 0.8 L/min. The results show that the dynamics are not significantly affected by the small increase in Ar flow rate from 0.6 to 0.8 L/min when $\sigma_w \leq 1000$ $\mu\text{S/cm}$. However, at $\sigma_w = 5000$ $\mu\text{S/cm}$, the strongly inhomogeneous plasma, particularly for $t < 6$ ms (see *zoom presented as 1 in Figure 8*), is likely to fill a larger portion of the bubble volume. Such bubble filling is an important feature as it may increase the plasma-water interaction, thereby enhancing the treatment efficiency. For $t \geq 6$ ms ($\sigma_w = 5000$ $\mu\text{S/cm}$), the plasma becomes asymmetric: decrease in the left-hand side region and increase in the right-hand side region (see *zoom presented as 2 and 3 in Figure 8*). The superposition of the magnified plasma boundaries measured at 4, 8, and 12 ms indicates that the ionized volume increases in the direction of the carrier flow (*i.e.*, momentum), as well as towards the surface of the liquid (*i.e.*, buoyancy). Finally, at $\sigma_w = 10000$ $\mu\text{S/cm}$, the plasma is filamentary-shaped, and is attached to the gas-water interface at the bottom of the bubble. The global plasma volume is relatively smaller than that observed at $\sigma_w = 5000$ $\mu\text{S/cm}$.

Figure 8. Plasma-bubble dynamics for various σ_w , at Ar flow rate = 0.8 L/min, $P = 200$ W and water volume = 200 mL.

Further increase in Ar flow rate to 1 L/min induces additional changes in plasma dynamics (Figure 9a). For $\sigma_w \leq 1000 \mu\text{S/cm}$, filamentary shaped plasma is observed in the bubble starting at $t = 0 \text{ ms}$, which indicates improved bubble penetration with increasing gas flow rate. Meanwhile, at $\sigma_w = 5000 \mu\text{S/cm}$, the plasma fills the bubble, with maximum filling rate at $t = 10 \text{ ms}$. The asymmetrical shape of the plasma observed at $t \geq 12 \text{ ms}$ ($\sigma_w = 5000 \mu\text{S/cm}$) is probably due to the instability (due to momentum and buoyancy) of the bubble interface. Finally, at $\sigma_w = 10000 \mu\text{S/cm}$, the plasma homogeneously fills the bubble for a few milliseconds ($t \leq 2 \text{ ms}$), before turning into a thin filament, as shown in Figure 9a. The plasma filament is also observed for Ar flow rates $\geq 2 \text{ L/min}$ (the tested upper limit is 5 L/min), regardless of the magnitude of electrical conductivity (Figure 9b). Plasma-bubble dynamic is weakly dependent on σ_w under such conditions.

Figure 9. Plasma-bubble dynamics recorded at Ar flow rates of **a)** 1 L/min and **b)** 2 L/min, for various σ_w ($P = 200 \text{ W}$ and water volume = 200 mL).

The results presented thus far show that the influence of σ_w and Ar flow rate on plasma dynamics seems to be coupled. We remark that plasma propagation in the bubble is enhanced upon increasing σ_w , and that the plasma completely and homogeneously fills the bubble at flow rates lower than 2 L/min. Maximum plasma volume and intensity were observed for Ar flow rate = 1 L/min and $\sigma_w = 5000 \mu\text{S/cm}$. Both, high-speed images and optical emission data concur that σ_w exhibits greater effects on plasma characteristics at lower gaseous flow rates. In fact, increasing σ_w is due to increased amount of dissociated K^+ and Cl^- by adding more KCl in water. Injecting gas into liquid results in a bubble formation that is rich in vapor inside, and the concentration of vapor is dependent on temperature, an interfacial surface area, and a volume of a bubble. At $\sigma_w = 10 \mu\text{S/cm}$, without KCl addition, the bubble composition should be Ar and water vapor only. As σ_w is increased, for a given Ar flow rate, concentrations of K^+ and Cl^- should increase in the bubble. However, for a given σ_w , increasing Ar flow will produce a larger bubble in which concentration of K^+ and Cl^- are expected to decrease, since a volume to surface ratio of a bubble ($\sim d_3/d_2 \sim d$; d is the bubble diameter) is increased as the volume of the bubble increases. When MWPI is injected into such a liquid medium, its composition is thus significantly influenced by a bubble composition. On the other hand, as the electrons have a mobility three orders of magnitude higher than those of ions, electrons diffuse (radially and axially) towards a gas-liquid interface. Therefore, at high σ_w , *i.e.*, high concentration of ions due to dissolved KCl, it would be easier for electrons to recombine with K^+ to produce K. As K has low ionization/excitation energies, they can be easily ionized/excited and emits radiation. For a couple Ar flow rate and σ_w (for instance: 1 L/min and $5000 \mu\text{S/cm}$ – Figure 9), since K^+ (and thus K atoms) should be distributed throughout a volume of the bubble, a light emission can partially or completely fill the gaseous volume. This may explain the various plasma-bubble dynamics.

3.3. The effect of N_2 on MWPI characteristics and plasma dynamics

Adding N_2 to Ar significantly influences plasma properties, including electron density, electron temperature, and gas temperature [28], [29]. Recently, we have shown that the addition of 1-2% N_2 to the Ar flow in MWPI improves the efficiency of MB degradation [21]. In this study, we investigate whether such enhancement can be achieved for highly conductive wastewater.

Specifically, we assess the effect of increasing N₂ content on the plasma characteristics of MWPI and degradation kinetics of MB, under various conditions of σ_w . Since the emission intensities are too low to allow for confident analysis at lower flow rates, the N₂ effect was evaluated only at 2 L/min. Figures 10a and 10b present variations in spectral line intensities of major species (OH, Ar, H, O, K, and NH) as a function of N₂ percentage, at $\sigma_w = 10000$ and 10 $\mu\text{S/cm}$, respectively. Meanwhile, the effects of N₂ addition on T_{rot} and n_e are illustrated in Figures 10c and 10d, respectively. The spectra acquired at $\sigma_w = 10000 \mu\text{S/cm}$ are presented in *supplemental material 1*. For both tested values of electrical conductivity, the NH (A-X) emission intensity increases from a non-zero value at 0% N₂ (signal due impurity and/or dissolved air in water) to a maximum at 0.5% N₂. The signal intensity subsequently decreases upon further increasing N₂ content. At 10000 $\mu\text{S/cm}$ NH exhibits the highest signal compared to other lines in the emission spectrum; however, at 10 $\mu\text{S/cm}$, the highest intensity is that of OH. The intensities of Ar, OH, and O lines continuously decrease with increasing N₂ content at both investigated conditions. For $\sigma_w = 10000 \mu\text{S/cm}$, maximum H line intensity is observed at 1% of N₂, but it decreases monotonically for $\sigma_w = 10 \mu\text{S/cm}$. As for K, its line intensity continuously increases with increasing N₂ percentage for $\sigma_w = 10000 \mu\text{S/cm}$. The K signal is absent in the spectrum recorded for the 10 $\mu\text{S/cm}$ sample since no KCl was added. Finally, nitrogen lines, namely N₂ and N₂₊, are observed, but their data are not shown due to relatively low intensities compared to the other lines. This observation indicates that, except for K, all signals decline upon the addition of N₂, regardless of σ_w .

Figure 10. Emission intensity variations of OH (309 nm), Ar (696.5 nm), H (656.3 nm), O (777 nm), and K (769.8 nm) as a function of N₂ percentage for water samples with electrical conductivities of 10000 μS/cm (a) and 10 μS/cm (b) (spectra recorded at Ar-N₂ flow rate of 2 L/min). Variations of rotational temperature (c) and electron density (d) variation as a function of N₂ percentage in Ar. P = 200 W, water volume = 200 mL.

Figure 10c shows that, regardless of water conductivity, T_{rot} continuously increases from ~2700 K to ~3400 K as N₂ content increases from 0 to 2.5%. Previous studies have shown that such increase in temperature is due to the excitation of N₂ rotational levels, with contributions from other phenomena such as excitation of vibrational and electronic levels, ionization, and dissociation [25], [28], [29]. Although this explanation is very well accepted for gas-phase microwave plasmas, our results show that it is also valid for the submerged MWPI investigated in this study.

The variation of n_e as a function of N₂ percentage is presented in Figure 10d. The illustrated results indicate that at $\sigma_w = 10 \mu\text{S/cm}$, n_e slightly decreases from $\sim 6.7 \times 10^{14} \text{ cm}^{-3}$ to

$\sim 5.2 \times 10^{14} \text{ cm}^{-3}$ as N_2 percentage increases from 0 to 2.5%. However, at $\sigma_w = 10000 \text{ }\mu\text{S/cm}$, n_e reaches a maximum of $\sim 9 \times 10^{14} \text{ cm}^{-3}$ at 1% N_2 , then continuously decreases down to $\sim 5.2 \times 10^{14} \text{ cm}^{-3}$ at 2.5 % N_2 . Previously, the influence of N_2 addition (up to 10%) on the properties of Ar surface-wave atmospheric-pressure plasmas was extensively investigated, both, experimentally and theoretically. The results reported a similar increase in temperature and decrease in n_e upon increasing N_2 content. For instance, Bravo *et al.* [28] show that increasing N_2 percentage from 0 to 10% results in a drop of n_e by one order of magnitude (from $\sim 10^{14}$ to 10^{13} cm^{-3}). In fact, the addition of N_2 to Ar, even at very low percentages ($< 1\%$), leads to power loss due to molecular excitation/ionization phenomena that undermine the ionization of Ar and generation of electrons. The results obtained herein for $\sigma_w = 10 \text{ }\mu\text{S/cm}$ agree with those observed in previous studies; however, at $\sigma_w = 10000 \text{ }\mu\text{S/cm}$, discrepancies are detected. Thus, further investigation is needed to discern the underlying plasma physics and chemistry of MWPI at high σ_w .

The effect of N_2 on plasma-bubble dynamics is investigated using the high-speed imaging technique. Figure 11 depicts the plasma emission images for experiments run at various conditions of N_2 percentage and σ_w (flow rate = 2 L/min); all the presented images correspond to $t = 18 \text{ ms}$. The results show that at $\sigma_w = 10 \text{ }\mu\text{S/cm}$, plasma length decreases with increasing N_2 content between 0 and 5%. At 5% N_2 , no plasma channel is perceived in the bubble, but a tiny plasma close to the inlet can be observed. Appreciable effects of σ_w on plasma dynamics are detected at N_2 percentages $\geq 2\%$ wherein the plasma channel becomes thicker and longer with increasing conductivity. This indicates that discharge channel (represented by the emission intensity in Figure 11) deterioration due to increased N_2 content can be compensated by increasing the conductivity of water. However, this does not signify greater efficiency for water treatment, since the process depends on chemical and physical phenomena other than the photon emission.

Figure 11. Plasma-bubble dynamics at $t = 18$ ms for varying conditions of σ_w and N_2 percentage. Flow rate = 2 L/min, $P = 200$ W, and water volume = 200 mL.

3.4. Methylene blue degradation as a function of σ_w

As previously mentioned, our goal is to investigate whether the MWPJ can be a feasible candidate for a wastewater treatment, especially a degradation of organic pollutants presented in water. In a recent study, we had shown that the addition of 1-2% N_2 to Ar promotes the degradation of MB in distilled water by the MWPJ [21]. Meanwhile, wastewater has a wide range of electrical conductivity (*e.g.*, up to 30 mS/cm for ballast water [4]), and the degradation of pollutants by plasma under such high conductivity conditions is not investigated. Moreover, the efficiency of direct electrical discharges in water is highly reduced as water conductivity is augmented [14], [16]. In this regard, to maintain a generation of a plasma in a conductive media, advanced technology is usually needed, *e.g.*, high-voltage source with very fast rising time [14], although electrode erosion is always manifesting once it is in contact with plasma. Very recently, a MWPJ in TIAGO (*Torche à Injection Axiale sur Guide d'Onde*, in French) configuration has been studied and it shows very high potential to remove organic pollutants from water at high conductivity [30].

Here, to highlight the combined influence of σ_w and N_2 on MB degradation efficiency, experiments were run at the same conditions as in [21] (microwave power of 200 W, treated water volume of 200 mL, and total processing time of 10 min), for varying conditions of electrical conductivity and N_2 percentage. Figure 12 presents the variation of normalized absorbance

intensities at 663 nm as a function of σ_w and compares the profiles obtained at different conditions of N₂ added and flow rate. At 2 L/min of pure Ar, normalized MB absorbance values decrease from ~0.82 to ~0.55 as σ_w increases from 10 to 100 $\mu\text{S}/\text{cm}$; however, further increase in σ_w (up to 10000 $\mu\text{S}/\text{cm}$) does not significantly influence the degradation of MB. These results indicate that MB degradation is significantly enhanced as σ_w increases from 10 to 100 $\mu\text{S}/\text{cm}$. Previously shown physical characteristics of the MWPIJ (n_e , temperature, and plasma-bubble dynamics) do not show any significant changes, showing only Ar intensity is significantly increased (Ar intensity shows a similar trend to MB removal rate). Although a relationship between Ar (including those in metastable states) and MB degradation rate cannot be readily provided, we believe that the production of reactive species is enhanced as the conductivity is increased from 10 to 100 $\mu\text{S}/\text{cm}$. Further increase in conductivity does not show further improvement in the degradation rate.

The incorporation of 1% N₂ into the gaseous flow (both flows are tested 2 L/min and 1 L/min) slightly enhances the degradation efficiency for $\sigma_w = 10$ $\mu\text{S}/\text{cm}$, which has been already observed in [21]. However, as σ_w increases from 100 to 10000 $\mu\text{S}/\text{cm}$, MB absorbance increases linearly from 0.88 to 0.97, indicating a decline in MB degradation efficiency. This means that adding a few percent of N₂ in Ar enhances MB degradation in water at very low conductivity, but not that effective at higher conductivities. To deeply investigate the fundamental mechanisms of these results, a model development is needed.

Figure 12. Variation of normalized MB absorbance as a function of σ_w for varying conditions of % N₂ added and flow rate.

Compared to distilled water [21], the increased electrical conductivity of water seems to have a negative effect on the degradation of MB, even with the addition of N₂. Meanwhile, high-speed images show that the increased conductivity has a positive impact on the emission volume of the plasma channel (Figures 7, 8, 9, and 11). Spectroscopic analyses indicate that K emission lines dominate upon the augmentation of conductivity (Figure 4) due to increased amounts of dissociated KCl, as well as the low ionization/excitation energy of K. In solution, KCl breaks up into K⁺ and Cl⁻. K⁺ captures plasma electrons to give K atoms. Conductivity is increased upon augmenting the quantity of added KCl, which results in higher concentrations of K⁺ and ultimately leads to greater amounts of K, as well as lower electron densities. However, K is not a reactive species, and thus, it cannot contribute to MB degradation. Therefore, when the amount of K in solution is high, the degradation efficiency of MB is relatively low. Although, these statements can explain the obtained results, the characterization of the liquid phase, by measuring the concentration of various reactive species under various experimental conditions, is highly recommended.

4. CONCLUSION

In this study, the effect of the electrical conductivity of water (σ_w) on plasma characteristics of MWPJ is investigated using optical emission spectroscopy. Variations of σ_w between 10 and 10000 $\mu\text{S/cm}$ are achieved by manipulating the amount of KCl added to distilled water. The obtained results show that at high Ar flow rates (typically ≥ 2 L/min), the plasma composition does not significantly depend on σ_w , but the intensities of OH, H, O, and Ar emission lines do. Moreover, as electrical conductivity increases, n_e decreases. Meanwhile, T_{rot} decreases with increasing σ_w between 10 to 100 $\mu\text{S/cm}$, then it continuously increases as σ_w is augmented to 10000 $\mu\text{S/cm}$.

High-speed images show that at low σ_w and Ar flow rates < 2 L/min the plasma is a thin ionized channel in the bubble. As σ_w is augmented, the plasma tends to fill the whole bubble volume, with maximum filling at $\sigma_w = 5000$ $\mu\text{S/cm}$ and Ar flow rate = 1 L/min. At low σ_w , the addition of N₂ to the gaseous flow decreases plasma length (and intensity), eventually leading to its extinction at N₂ % $> 5\%$. As σ_w increases, the plasma can be sustained in the bubble for higher N₂ percentage.

Finally, the influence of σ_w on water treatment efficiency is tested by analyzing the degradation rates of MB. The results indicate that the investigated MWPI becomes less efficient in removing MB as σ_w increases, even with the addition of N_2 . This may be due to the loss of electrons via electron-ion (here K_+) recombination, followed by power loss through excitation/ionization of low-energy species (here K). These findings are of great importance for plasma-induced wastewater treatment applications, as the electrical conductivity of polluted water varies within a wide range.

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Figure captions:

Figure 1. Schematic of the experimental setup used to create submerged MWPI: a) 3D view and b) 2D view. The zone delimited by dashed-blue line shows where the high-speed images are acquired.

Figure 2. Comparison of experimental and simulated spectra of OH (A–X) at a) Ar flow rate = 2 L/min and $\sigma_w = 100 \mu\text{S/cm}$, as well as b) Ar flow rate = 0.6 L/min and $\sigma_w = 10000 \mu\text{S/cm}$; $P = 200 \text{ W}$ and water volume = 200 mL.

Figure 3. Optical emission spectra acquired at the inlet of the liquid cell for four σ_w values (10, 100, 1000, and 10000 $\mu\text{S/cm}$) at Ar flow rates of **a)** 2 L/min and **b)** 0.6 L/min. $P = 200 \text{ W}$, exposure time = 1 ms, and number of accumulations = 50.

Figure 4. Intensity variations of OH (309 nm), Ar (696.5 nm), H (656.3 nm), O (777 nm), and K (769.8 nm) spectroscopic bands as a function of σ_w for Ar flow rates of **a)** 2 L/min and **b)** 0.6 L/min. $P = 200 \text{ W}$ and water volume = 200 mL.

Figure 5. Variation of OH rotational temperature as a function of σ_w for two Ar flow rates; $P = 200 \text{ W}$ and water volume = 200 mL.

Figure 6. a) Typical experimental and simulated profile of the H β line. **b)** Variation of the electron density (n_e) as a function of σ_w . $P = 200 \text{ W}$, water volume = 200 mL, and Ar flow rate = 2 L/min.

Figure 7. Plasma-bubble dynamics for various σ_w , at Ar flow rate = 0.6 L/min, $P = 200 \text{ W}$, and water volume = 200 mL: **a)** $\sigma_w = 10 \mu\text{S/cm}$, **b)** $\sigma_w = 100 \mu\text{S/cm}$, **c)** $\sigma_w = 1000 \mu\text{S/cm}$, **d)** $\sigma_w = 5000 \mu\text{S/cm}$, and **e)** $\sigma_w = 10000 \mu\text{S/cm}$.

Figure 8. Plasma-bubble dynamics for various σ_w , at Ar flow rate = 0.8 L/min, $P = 200 \text{ W}$ and water volume = 200 mL.

Figure 9. Plasma-bubble dynamics recorded at Ar flow rates of **a)** 1 L/min and **b)** 2 L/min, for various σ_w ($P = 200 \text{ W}$ and water volume = 200 mL).

Figure 10. Emission intensity variations of OH (309 nm), Ar (696.5 nm), H (656.3 nm), O (777 nm), and K (769.8 nm) as a function of N₂ percentage for water samples with electrical conductivities of 10000 $\mu\text{S/cm}$ (**a**) and 10 $\mu\text{S/cm}$ (**b**) (spectra recorded at Ar-N₂ flow rate of 2 L/min). Variations of rotational temperature (**c**) and electron density (**d**) variation as a function of N₂ percentage in Ar. $P = 200 \text{ W}$, water volume = 200 mL.

Figure 11. Plasma-bubble dynamics at $t = 18 \text{ ms}$ for varying conditions of σ_w and N₂ percentage. Flow rate = 2 L/min, $P = 200 \text{ W}$, and water volume = 200 mL.

Figure 12. Variation of normalized MB absorbance as a function of σ_w for varying conditions of % N₂ added and flow rate.

SUPPLEMENTAL MATERIAL

Supplemental material 1. Optical emission spectra acquired at the inlet of the MWPI to the liquid cell for six N_2 percentages (0, 0.5, 1, 1.5, 2, and 2.5 %). Flow rate = 2 L/min, $\sigma_w = 10000 \mu\text{S/cm}$, $P = 200 \text{ W}$, exposure time = 1 ms, and number of accumulations = 50.