

Université de Montréal

Décharge à courant alternatif (AC) dans l'air et en contact avec l'eau :
Caractérisation fondamentale et application au traitement des eaux

Par

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**Décharge à courant alternatif (AC) dans l'air et en contact avec l'eau :
Caractérisation fondamentale et application au traitement des eaux**

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Résumé

Les décharges en phase gazeuse couplées avec les liquides est une branche relativement nouvelle de la physique des plasmas. Le développement des applications technologiques basées sur les plasmas-liquides dans des domaines tels que la médecine, le traitement de matériaux, la remédiation environnementale, etc., est très prometteur. Cependant, la compréhension de la nature de l'interaction plasma-liquide est indispensable pour pouvoir développer les applications. Dans ce mémoire, composé de trois sections, nous avons étudié l'interaction d'un plasma d'air, généré par une décharge à courant alternatif (AC), et couplé directement avec l'eau. Tout d'abord, une présentation générale des systèmes plasmas-liquides et ses applications pour le traitement des eaux est faite dans le Chapitre 1. Chapitre 2, un article publié dans *Journal of Physics D: Applied Physics*, est une étude de la dynamique spatio-temporelle d'un plasma d'air produit par une décharge AC entre une électrode pointe et la surface de l'eau. Chapitre 3, un article publié dans *Plasma Chemistry and Plasma Processing*, représente une investigation sur les différents modes de décharges AC en contact avec l'eau et sur l'efficacité de chaque mode pour dégrader un polluant organique modèle (bleue de méthylène).

Mots-clés : Interaction plasma-liquide, décharge électrique, imagerie résolue en temps, structuration de l'émission, traitement des eaux.

Abstract

Gas phase discharges in contact with liquids is a relatively novel research field in plasma physics. Plasma-liquid systems are very promising for various technological applications, such as medicine, solid-state physics, and environmental remediation. However, further development of the applications requires understanding of plasma-liquid interactions. In this thesis, interaction between an air plasma directly coupled in contact with water is studied. This thesis includes three chapters. Chapter 1 presents a general introduction of the plasma-liquid interactions and their applications in water treatment. Chapter 2, an article published in *Journal of Physics D: Applied Physics*, is an investigation of the spatial and temporal dynamics of an air plasma produced by AC discharge between a pin electrode and water. Chapter 3, an article published in *Plasma Chemistry and Plasma Processing*, is an investigation of the various modes produced by an AC-driven air discharge in contact with water. The electrical characteristics of each discharge mode are presented in detail, and variations in water properties (namely water acidity and conductivity) are also discussed. The efficiency of each discharge mode on the degradation rate of methylene blue, a standard pollutant, is also reported.

Keywords: Plasma-liquid interface, electrical discharge, time resolved imaging, plasma structuration, water treatment; methylene blue degradation.

Table des matières

| | |
|--|-----------|
| Résumé | v |
| Abstract | vii |
| Table des matières | ix |
| Liste des tableaux | xiii |
| Liste des figures | xv |
| Liste des sigles et abréviations..... | xxi |
| Remerciements | xxv |
| 1. Introduction | 1 |
| 1.1 Contexte du mémoire | 1 |
| 1.2 Interaction plasma-liquide..... | 2 |
| 1.2.1 Plasma direct dans le liquide..... | 3 |
| 1.2.2 Plasmas multiphasiques..... | 6 |
| 1.2.3 Plasma en phase gazeuse..... | 11 |
| 1.2.3.2 Plasma en couplage indirect avec un liquide | 11 |
| 1.1.3.1 Plasma directement couplé avec un liquide | 13 |
| 1.3 Application au traitement des eaux | 26 |
| 1.3.1 Méthodes d'oxydation avancées | 27 |
| 1.3.2 Traitement de l'eau par plasma | 28 |
| 1.4 Objectifs du mémoire | 30 |
| 1.5 Bibliographie..... | 30 |
| Chapitre 2 – Time and space-resolved imaging of an AC air discharge in-contact with water | 37 |
| Résumé | 38 |

| | |
|---|-----------|
| Abstract | 39 |
| 2.1 Introduction | 40 |
| 2.2 Experimental setup | 42 |
| 2.3 Results | 44 |
| 2.3.1 Time-averaged characterization of AC air discharge in contact with water | 44 |
| 2.3.1.1 Water polarity: Cathode | 45 |
| 2.3.1.2 Water polarity: Anode | 49 |
| 2.3.1.3 Plasma emission at the water surface | 53 |
| 2.3.2 Time resolved imaging of AC air discharge in contact with water | 57 |
| 2.4 Discussion | 63 |
| 2.5 Conclusion | 69 |
| Acknowledgement | 69 |
| References | 71 |
| Chapitre 3 – Characterization of various air plasma discharge modes in contact with water and their effect on the degradation of reactive dyes | 75 |
| Résumé | 77 |
| Abstract | 78 |
| 3.1 Introduction | 79 |
| 3.2 Experimental setup and discharge modes | 81 |
| 3.2.1 Experimental Setup | 81 |
| 3.2.1 Electrical Waveforms and Discharge Modes | 82 |
| 3.3 Result and discussion | 86 |
| 3.3.1 Characteristics of electrical discharges and their influence on water properties | 86 |
| 3.3.2 Effect of MB on discharge characteristics and on water properties | 91 |
| 3.3.3 Degradation of MB by various discharge modes | 94 |

3.4 Conclusion..... 100

Acknowledgement..... 101

References 103

Chapitre 4 – Conclusion 107

Bibliographie..... 109

Annexes 113

Liste des tableaux

| | |
|--|-----|
| Table 3.1. <i>Summary of the discharge modes (1-5) and the related parameters</i> | 86 |
| Table 3.2. <i>$Y_{50\%}$ values for each discharge mode and other useful data.</i> | 99 |
| Table 3.3. <i>Energy yields needed to remove 50% of MB ($Y_{50\%}$) using various plasma reactors.</i> | 100 |

Liste des figures

| | |
|--|----|
| Figure 1.1 Configuration expérimentale typique pour produire un plasma dans le liquide. [10] ... | 3 |
| Figure 1.2 : Signal de tension et image ICCD résultantes d'un streamer produisant une ionisation directe dans l'eau [11]. | 4 |
| Figure 1.3 : Schéma de l'initiation d'un streamer en liquide selon la théorie des bulles [14]. | 5 |
| Figure 1.4 : Schéma montrant les différentes zones du plasma ainsi que les réactions principales dans chaque zone. [16] | 6 |
| Figure 1.5 : Configuration expérimentale typique pour produire un plasma dans des bulles en liquide..... | 7 |
| Figure 1.6 : Différent modes d'initiation d'un plasma dans les bulles. La distance interélectrode est de 1 mm et le gaz dans la bulle est de l'argon [23]. | 8 |
| Figure 1.7 : Simulation du champ électrique de la configuration des trois modes d'initiation d'une décharge [23]. | 8 |
| Figure 1.8 : Simulation de la propagation de la densité électronique ($[e]$), de la source d'impact électronique (S_e) et de la densité de charge positive (ρ). Le temps indiqué en ns est le moment de la simulation où l'image est prise et le nombre indiqué dans chaque case est la valeur maximale de la caractéristique dans l'image. La permittivité relative ϵ/ϵ_0 du liquide augmente du haut vers le bas et la bulle est formé à partir de l'air ($\epsilon/\epsilon_0 = 1$) [25]. | 9 |
| Figure 1.9 : Images de l'évolution d'un plasma impulsif dans une bulle d'air dans l'eau. La bulle est produite sur une aiguille ou la haute tension est appliquée. [26]..... | 10 |
| Figure 1.10 : Un jet du plasma à pression atmosphérique en contact avec la surface d'un liquide [1]. | 12 |
| Figure 1.11 : Photo d'un plasma jet microonde produite à l'aide d'une Torche à Injection Axiale sur Guide d'Ondes (MWPJ-TIAGO) et est en contact avec l'eau pour différentes distances plasma-eau. [29]..... | 13 |
| Figure 1.12 : Distribution 2D de radicaux OH par Fluorescence induite par laser (LIF). La figure a) présente la distribution de radicaux OH d'un plasma jet à pression atmosphérique à l'air libre, tandis que b) présente la distribution de radicaux OH d'un même plasma jet avec la présence d'un volume d'eau [30]. | 13 |

| | |
|---|----|
| Figure 1.13 : une représentation d'un dispositif typique pour produire un plasma directement couplé avec un liquide. [10] | 14 |
| Figure 1.14 :(a) Cône de Taylor avant le claquage. (b) et (c) Cône de Taylor au claquage pour lorsque la pointe métallique a une polarité négative ou positive, dans l'ordre présenté. Dans le coin à droite, le temps par rapport au temps du claquage $t = 0$. Le temps d'ouverture de la caméra est de $15 \mu\text{s}$ [31] | 15 |
| Figure 1.15 : Motif d'émission lumineuse dans l'écart pour de décharge en courant continu à $30,9 \text{ mA}$ pour la polarité négative (à gauche) et positive (à droite) lorsque le temps d'ouverture de la caméra est de $5 \mu\text{s}$. L'écart est de 5 mm [3]..... | 16 |
| Figure 1.16 : Motif d'émission à la surface lorsque la pointe métallique est cathode. Le temps d'ouverture de la caméra est de 20 ms , à gauche, et de $100 \mu\text{s}$, à droite [3]..... | 16 |
| Figure 1.17 : Composition du spectre d'émission d'une décharge lumineuse près de l'eau. Une comparaison entre les polarités de l'eau, anode et cathode, est faite. [3] | 17 |
| Figure 1.18 : Courbes de courant et de tension de la transition de la charge lumineuse vers la décharge spark lorsque la solution de NaCl a une conductivité de $100 \mu\text{S/cm}$ est anode. La position temporelle des images est indiquée sur la figure, de gauche à droite. [35]..... | 18 |
| Figure 1.19 : Comparaison de la transition de la décharge lumineuse vers la décharge de type spark. Les figures (a) et (d) montrent la transition pour l'eau distillée. Les figures (b) et (e) pour une solution de NaCl une conductivité de $50 \mu\text{S/cm}$. Les figures (c) et (f) pour une solution de NaCl avec une conductivité de $5000 \mu\text{S/cm}$. Le temps d'ouverture de la caméra est indiqué en bas à droite de l'image [35] | 19 |
| Figure 1.20 : Morphologie d'une décharge lumineuse soutenue à $1,25 \text{ mA}$ et 1 kV lorsque l'eau est anode. L'espace interélectrode est de 3 mm . [3] | 20 |
| Figure 1.21 : (a) Image de l'émission lumineuse d'une décharge en courant continu lorsque la pointe métallique est cathode. (b) Spectre de l'émission lumineuse résolue spatialement selon l'axe de la pointe [4]..... | 21 |
| Figure 1.22 : Profil axial des raies OH (A-X) (309 nm), NO (A-X) ($236,3 \text{ nm}$), N_2 (C-B) ($337,1 \text{ nm}$) et l'émission totale avec l'intensité sur une échelle logarithmique [4]. | 21 |
| Figure 1.23 : Motif d'autoorganisation de l'émission anodique à la surface de l'eau lorsqu'elle est anode. La solution contient 1% de NaCl. La distance interélectrodes est de 10 mm [38]..... | 22 |

Figure 1.24 : Motif d’autoorganisation de l’émission anodique à la surface de l’eau en fonction de la distance et du courant et de la tension mesurée pour le même liquide qu’à la figure 1.23. [38]22

Figure 1.25 : Modification du motif à la surface de l’eau en fonction de la composition du gaz à la surface. Le flux de gaz est dirigé vers la surface, ce qui déplace le motif. (a) présente le motif sans flux de gaz (b) avec un flux de N₂ de 300 et 700 sccm et (c) avec un flux de O₂ de 100 à 700 sccm [38].23

Figure 1.26 : Motifs à la surface de l’eau en fonction de la conductivité du liquide (du haut vers le bas) et en fonction de l’ouverture de la caméra (de gauche à droite). [39]24

Figure 1.27 : Motif à la surface de l’eau d’une décharge en courant alternatif à une fréquence de 7 kHz. L’eau désionisée est acidifiée à partir du HNO₃. [6]24

Figure 1.28 : Motif à la surface de l’eau d’une décharge lumineuse pour trois conductivités, 10 mS/cm, 57 mS/cm et 150 mS/cm, pour trois acides différents : (a) H₂SO₄ (b) HCl et (c) HF [32].25

Figure 1.29 : Schéma moléculaire et propriétés chimiques du méthylène bleu. [40]26

Figure 1.30 : Spectre d’absorption du méthylène bleu en solution en fonction du temps de traitement par ozonation [40].27

Figure 1.31 : Répartition des espèces réactives pour une décharge pointe-plan pour un plasma couplé directement avec l’eau dans l’air ambiant [50].29

Figure 2.1 -Scheme of the experimental setup.42

Figure 2.2. Voltage and current waveforms recorded at a) d = 1.5 mm, b) d = 3.5 mm, and c) d = 7 mm during the first half-period (i.e., water as cathode). d) Variation of the injected charge, current peak, and energy as a function of gap distance.46

Figure 2.3. a) ICCD images (integrated during the 50 μs when water is cathode) of the plasma column emission recorded under various gap distance in the range of 0.5 - 4.5 mm; each image is normalized to a maximum value that is shown in supplementary Figure S1. b) The plasma-edge emission profiles determined using the threshold method.48

Figure 2.4. ICCD images (integrated during the 50 μs when water is cathode) of the plasma column emission recorded under various gap distances in the range of 5-9 mm. The color scale is common for all the images and ranges from 0 to 7%.49

Figure 2.5. Voltage and current waveforms recorded at a) $d = 1.5$ mm, b) $d = 3.5$ mm, and c) $d = 7$ mm during the second half-period (i.e., water as anode). d) Variation of the injected charge, current peak, and energy as a function of the gap distance.....50

Figure 2.6. ICCD images (integrated over $50 \mu\text{s}$ when water is anode) of the plasma column emission recorded under various gap distances in the range of a) $0.5 - 4.5$ mm and b) $5-9$ mm. Each image in a) is normalized to a maximum value that is shown in supplementary Figure S2, while images in b) have a common scale that ranges from 0 to 80%.52

Figure 2.7. ICCD images (integrated during the $50 \mu\text{s}$ when water is cathode) of the plasma emission at the water surface recorded under gap distances in the range of $0.5 - 9$ mm. The maximum intensity is 20% and 1% for images recorded at $0.5 < d < 4.5$ mm and $5 < d < 9$ mm, respectively. The inset at $d = 5$ mm shows the same image at maximum intensity of 20%.54

Figure 2.8. a) ICCD images (integrated during the $50 \mu\text{s}$ when water is anode) of the plasma emission at the water surface recorded under various gap distances in the range of $0.5 - 9$ mm (the maximum intensity is 40%). b) Normalized horizontal profiles extracted from the ICCD images (specifically, the area marked by a white-dashed rectangle in the $d = 0.5$ mm image).56

Figure 2.9. ICCD images (integrated during $5 \mu\text{s}$) showing the temporal evolution of the plasma a) in the gap (maximum intensity is 50%) and b) at the water surface (maximum intensity is 15%) over a whole period for $d = 3$ mm. c) Electrical characteristics (voltage, current, and power) corresponding to the ICCD images.59

Figure 2.10. ICCD images (integrated during $5 \mu\text{s}$) showing the temporal evolution of the plasma a) in the gap (maximum intensity is 7%) and b) at the water surface (maximum intensity is 7%) during the first half-period (when water is cathode) for $d = 5$ mm. c) Electrical characteristics (voltage, current, and power) corresponding to the ICCD images.....61

Figure 2.11. ICCD images (integrated during $5 \mu\text{s}$) showing the temporal evolution of the plasma a) in the gap (maximum intensity is 35%) and b) at the water surface (maximum intensity is 20%) during the second half-period (when water is anode) for $d = 5$ mm; the white lines superimposed to the images are the horizontal profiles. c) Electrical characteristics (voltage, current, and power) corresponding to the ICCD images. d) $1\text{-}\mu\text{s}$ -integrated ICCD images of the plasma at the water surface (maximum intensity is 10%) acquired at specific times during the half-period.62

| | |
|--|----|
| Figure 2.12. The evolution of power as a function of the gap distance for a discharge generated at 5 kHz. The ICCD images (integrated during 100 μ s, i.e., half-period when water is anode) show the corresponding structures of the plasma at the water surface..... | 68 |
| Figure 3.1. a) Schematic of the experimental setup used to generate electrical discharge in-air that is in-contact with water. b) Schematic of the absorption setup used to monitor the degradation of MB..... | 82 |
| Figure 3.2. Current-voltage (I-V) characteristics of the various discharge modes: a) Mode 1, b) Mode 2, c) Mode 3, d) Mode 4, and e) Mode 5. | 83 |
| Figure 3.4. Temporal evolution of water acidity and conductivity during plasma processing in discharge modes 1, 2 and 3. | 89 |
| Figure 3.5. Current-voltage (I-V) characteristics in deionized water with and without MB at a) $t=2.5$ minutes and b) $t=30$ minutes..... | 91 |
| Figure 3.6. Temporal evolution of the injected charge (Q_{inj}) during discharges in modes 1 (a and c) and 2 (b and d) in deionized water with and without MB..... | 93 |
| Figure 3.7. Temporal evolution of water acidity and conductivity, with and without MB, for discharge modes 1 (a) and 2 (b). | 94 |
| Figure 3.8. Temporal evolution of MB degradation percentage during plasma processing in discharge modes 1, 2, and 3. | 95 |
| Figure 3.9. (a) and (b) Temporal evolution of profiles of the injected charge (Q_{inj}), water acidity, and water conductivity in modes 1 and 4. (c) and (d) Temporal evolution of the injected charge (Q_{inj}), water acidity, and water conductivity in modes 3 and 5..... | 96 |
| Figure 3.10. Temporal evolution of MB degradation percentage during plasma processing in modes 4 and 5. For the purpose of comparison, MB degradation rate profiles of modes 1 and 3 are added to the figure. | 98 |

Liste des sigles et abréviations

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1. Introduction

1.1 Contexte du mémoire

Dans ce mémoire, l'interaction plasma-liquide est à l'étude. Ce domaine est un nouveau champ de recherche qui devient de plus en plus important dans la science et les technologies plasma. Ce domaine est en expansion puisque les interactions des plasmas hors équilibre avec un état liquide sont importantes pour une vaste gamme d'applications, allant de la remédiation environnementale au traitement des matériaux et de la santé [1]. La production efficace de différentes espèces réactives ainsi que la richesse en physique fondamentale produite par l'interaction plasma-liquide [2] sont les motivations du travail produit dans ce mémoire.

Les buts de ce mémoire sont ceux-ci : améliorer la compréhension des plasmas en contact avec les liquides et développer une application technologique peu coûteuse et qui utilise seulement l'électricité comme source d'énergie pour le traitement des eaux usées. Ainsi, ce mémoire investigate l'aspect fondamental de l'interaction plasma-liquide et présente les résultats et les conditions optimales d'un montage pour le traitement d'un polluant organique standard. Avant d'aborder une revue de littérature, qui permet de situer les travaux de ce mémoire dans la littérature scientifique, il est important de situer le contexte général de ces travaux.

Dans un premier temps, les travaux de ce mémoire servent de continuité aux travaux de compréhension de l'interaction plasma-liquide, surtout à l'interface du liquide et du plasma. Les travaux précédents ce mémoire présentent déjà les caractéristiques typiques d'une décharge plasma produite dans l'air en contact avec de l'eau pour différentes conditions. Spécifiquement, la polarité de la tension appliquée [3] et la conductivité du liquide en contact avec le plasma [4] ont été étudiées. Cependant, l'utilisation d'un générateur de tension par courant alternatif pour l'étude des plasmas en contact avec les liquides est peu documentée [5,6]. De plus, certains phénomènes restent encore incompris, comme la formation de structures autoorganisées sur la surface de l'eau [4]. La caractérisation d'un plasma en contact avec les liquides avec un générateur de tension à courant alternatif et l'évolution de la formation de structures autoorganisées sur la surface de l'eau seront étudiées dans ce mémoire.

Dans un deuxième temps, les travaux de ce mémoire servent à développer une nouvelle technologie pour le traitement des eaux usées. Le développement de nouvelles applications pour le traitement des eaux usées s'établit dans un contexte où la demande pour une eau de haute qualité pour des besoins de consommation, d'assainissement, d'irrigation et d'utilisation industrielle augmente continuellement [7]. Ainsi, dans le but de développer une méthode peu coûteuse et qui utilise l'électricité comme source principale d'énergie, les plasmas sont des candidats idéaux [1]. L'étude des plasmas en contact avec les liquides a permis de comprendre que ce genre d'interaction permet de produire des espèces hautement réactives en liquides. Ces espèces sont les radicaux $\bullet\text{OH}$, l'ozone (O_3) et le peroxyde d'hydrogène (H_2O_2), des espèces qui sont à la base de processus chimiques appelés Advanced Oxidation Processes (AOP), qui sont déjà utilisés à grande échelle. Malgré leur grande efficacité pour le traitement des eaux usées, les AOPs demandent de grandes quantités de produits chimiques [8], tandis que les procédés plasma n'ont besoin que d'électricité. Ainsi, le développement et l'optimisation de cette technologie pour le traitement des eaux usées à grande échelle permettraient de faire de cette technologie une technologie du futur utilisant seulement l'électricité comme source d'énergie [9]. Dans ce mémoire, l'efficacité du montage plasma en contact avec les liquides en utilisant un générateur de tension en courant alternatif sera évaluée. L'efficacité sera comparée avec d'autres montages utilisant la technologie plasma pour le traitement de polluants organiques.

1.2 Interaction plasma-liquide

Après une étude détaillée de la littérature, il est possible de classer les décharges plasmas-liquides dans trois catégories [1] :

1. Plasma direct dans le liquide,
2. Plasma multiphasique,
3. Plasma en phase gazeuse en contact avec un liquide.

Bien que les travaux présentés dans ce mémoire se trouvent dans la catégorie 3 (plasma en phase gazeuse en contact avec un liquide), les deux autres catégories sont présentées brièvement dans les prochaines sections.

1.2.1 Plasma direct dans le liquide

La production d'un plasma dans le liquide est souvent étudiée dans une configuration expérimentale relativement simple : deux électrodes immergées dans le liquide (figure 1.1). Une impulsion de haute tension est appliquée sur le système ; souvent, la pointe est reliée à la haute tension et l'autre électrode est reliée à la masse.

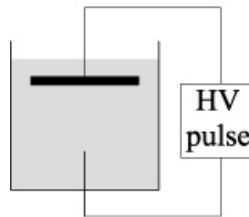


Figure 1.1 Configuration expérimentale typique pour produire un plasma dans le liquide. [10]

Historiquement, il existe deux théories qui expliquent la formation de décharge dans le liquide. La première théorie est basée sur l'ionisation directe des molécules du liquide. Selon cette théorie, les mécanismes impliqués sont similaires à ceux de l'ionisation d'un gaz à travers des collisions électroniques. Cependant, l'ionisation directe de l'eau implique beaucoup plus de phénomènes que l'ionisation dans un gaz, puisque la densité de molécules en liquide est beaucoup plus importante. Cette densité fait en sorte que le libre parcours moyen des électrons est plus petit qu'en phase gazeuse et que les interactions molécule-molécule sont beaucoup plus importantes [11]. Ainsi, l'intensité du champ électrique doit être intense, entre 10 et 20 MV/cm [12], pour être en mesure d'ioniser directement l'eau, selon l'approche d'un gaz dense. De plus, la montée en tension doit être de l'ordre de la nanoseconde pour que l'énergie soit seulement distribuée aux électrons, et non au chauffage du liquide [11]. La figure 1.2 montre le signal électrique et l'image ICCD produite par le signal pulsé.

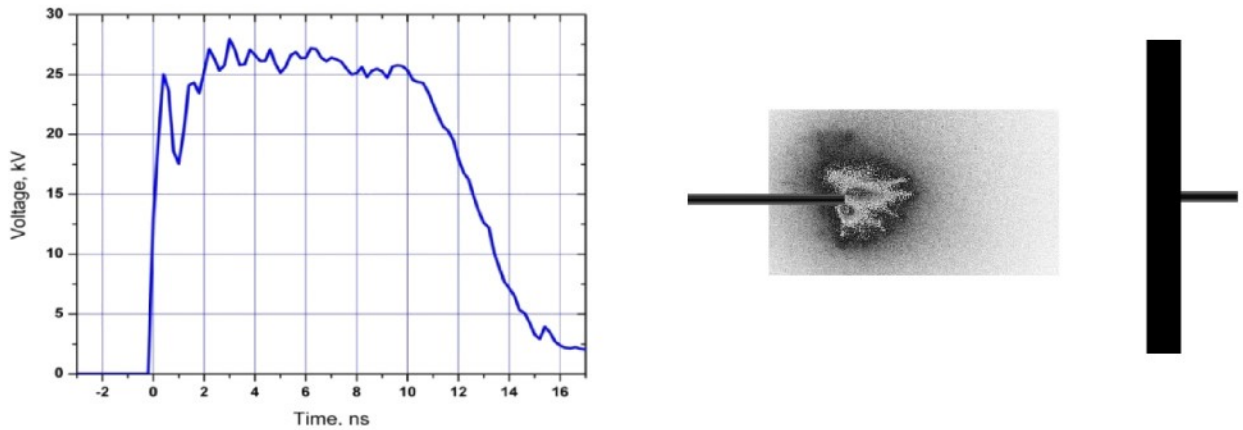


Figure 1.2 : Signal de tension et image ICCD résultantes d'un streamer produisant une ionisation directe dans l'eau [11].

La deuxième théorie s'appelle la théorie des bulles [13]. Un schéma de l'initiation d'un streamer selon la théorie des bulles est présenté à la figure 1.3. Tout d'abord, lorsqu'un champ électrique est appliqué à la pointe, un chauffage de Joule produit des fluctuations dans le liquide près de la pointe. Ces fluctuations provoqueront des zones de basses pressions. On appellera ces zones des microbulles. L'accumulation de microbulles créera une zone de basse pression suffisamment grande pour qu'il puisse se produire une décharge lumineuse de faible intensité. Cette décharge déformera l'amas de bulles autour de la pointe pour former une protrusion. Cette protrusion joue le rôle d'une pointe virtuelle. Comme le rayon de cette pointe virtuelle est beaucoup plus petit que la pointe métallique où la tension est appliquée, le champ électrique local à la protrusion sera beaucoup plus élevé. Il y sera suffisant pour provoquer l'ionisation du liquide. Cette ionisation, appelée streamer primaire, créera des canaux gazeux. Ces canaux seront les précurseurs d'une deuxième luminescence, appelée streamer secondaire, si le champ électrique est appliqué suffisamment longtemps. Les streamers secondaires allongeront les canaux gazeux et, encore une fois, si le champ électrique est appliqué suffisamment longtemps, une réillumination d'un ou plusieurs canaux gazeux est possible. Ceci étant dit, la formation de streamer selon la théorie des bulles peut être utilisée pour décrire les streamers induits par un signal de tension avec un temps de montée dans l'ordre de grandeur du μs .

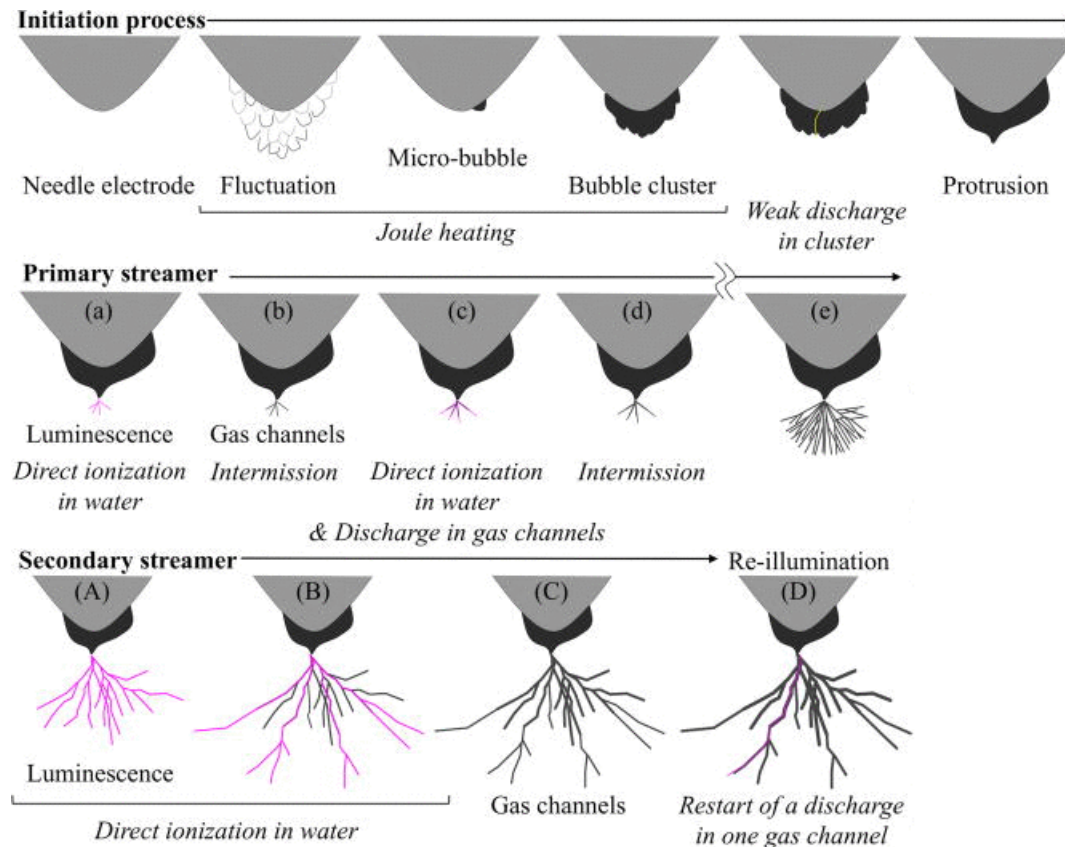


Figure 1.3 : Schéma de l'initiation d'un streamer en liquide selon la théorie des bulles [14].

D'autres chercheurs se sont aussi penchés sur la production des différentes espèces chimiques dans l'eau. Entre autres, Mededovic et Locke [15] ont modélisé une décharge microseconde impulsionnelle décrivant un filament plasma entouré d'eau. La modélisation est présentée en 2 parties : 1) un cœur de plasma, là où se produit la décharge, et 2) une région de recombinaison. La séparation de l'eau et la production de radicaux, tels que $H\bullet$ et $OH\bullet$, s'effectuent dans la première région. La production d'espèce ayant une longue durée de vie, telle que H_2O_2 , H_2 et O_2 , à partir des radicaux s'effectue dans la deuxième région. Il est possible de mesurer dans l'eau des concentrations de H_2 , de H_2O_2 , de O_2 et $OH\bullet$ de $3,9 \text{ mmol/cm}^3$, $2,4 \text{ mmol/cm}^3$, $0,93 \text{ mmol/cm}^3$ et $0,036 \text{ mmol/cm}^3$, dans l'ordre présenté. Un schéma (figure 1.4) montre les différentes zones du plasma dans l'eau ainsi que les réactions principales dans chaque zone.

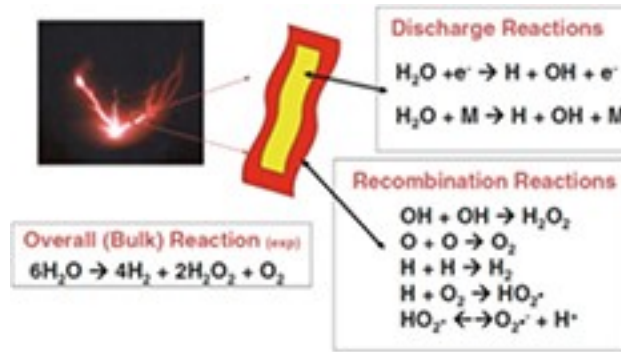


Figure 1.4 : Schéma montrant les différentes zones du plasma ainsi que les réactions principales dans chaque zone. [16]

Lorsque générées dans le liquide, les espèces réactives sont en mesure d'interagir avec le milieu supportant la décharge sur de petites échelles de temps. Lorsque comparée aux décharges en phases gazeuses, l'efficacité des réactions et des taux de réaction peut être très différente. Par exemple, le radical hydroxyle, OH^\cdot , avec des taux de réaction contrôlés par la diffusion, va réagir à l'interface plasma-liquide ou après la pénétration de quelques micromètres en liquide [17]. Ainsi, la compréhension de la formation des espèces réactives et des composés chimiques secondaires par les plasmas en liquide, incluant les taux de réaction, demeure un défi pour les méthodes diagnostiques et le développement de modèle.

1.2.2 Plasmas multiphasiques

Les plasmas multiphasiques incluent deux catégories de plasma : les plasmas en phase gazeuse avec aérosols et les plasmas formés à l'intérieur de bulles injectés en liquide.

Les plasmas en phase gazeuse avec aérosols ont généralement été étudiés pour l'identification de composés atomiques [18], la spectroscopie de masse, pour le traitement de surface [19] et pour la déposition de matériaux [20]. Ainsi, dans la plupart des montages, l'ajout d'aérosols dans les plasmas en phase gazeuse se résulte en dissolution des gouttes, et les espèces formées sont incorporées dans le plasma. Shan et Mostaghimi [21] ont démontré, par modélisation d'un plasma

radiofréquence, que l'injection de gouttelettes mène à une réduction de la température de l'espace occupé par les gouttelettes et que cette baisse en température est plus importante lorsque la masse des gouttes est plus importante. Plus cette baisse de température est importante, plus le délai sur la dissolution de la goutte dans le plasma est important. Ce temps de dissolution est important, puisque c'est durant ce moment que l'interaction entre les gouttes et le plasma se produit. Cette interaction permet de produire des espèces réactives de grande importance pour différentes applications. Par exemple, des résultats montrent que des gouttes qui survivent $\approx 100 \mu\text{se}$ dans le plasma dans des conditions de température du gaz $< 400 \text{ K}$ [22] sont les conditions optimales pour produire le maximum d'espèces réactives.

La deuxième catégorie du plasma multiphasique est celle produite dans des bulles dans un liquide. Bien que la production de bulles dans les liquides soit souvent inévitable lors de décharges dans le liquide, à cause du chauffage à l'électrode, il est aussi possible d'injecter les bulles intentionnellement dans le liquide et d'ioniser le gaz dans la bulle. Une configuration possible pour l'étude des plasmas dans des bulles en liquide est donnée à la figure 1.5.

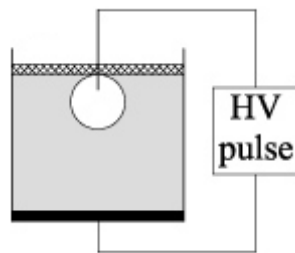


Figure 1.5 : Configuration expérimentale typique pour produire un plasma dans des bulles en liquide.

Dans une configuration pointe-pointe, comparativement à une configuration pointe-plan présentée dans la configuration typique, on peut étudier différents modes d'initiation d'un plasma dans des bulles. Les différents modes d'initiations sont présentés à la figure 1.6. Avec des bulles qui ont en moyenne un diamètre équivalent à l'espace interélectrode, il existe 3 modes d'initiations : 1) Initiation anodique 2) Initiation cathodique et 3) Initiations conjointes. Ces modes d'initiation sont dues à l'emplacement de la bulle lors de l'initiation du pulse nanoseconde. Pour chacun des modes, la bulle se trouve : 1) près de l'anode 2) près de la cathode et 3) entre les deux électrodes.

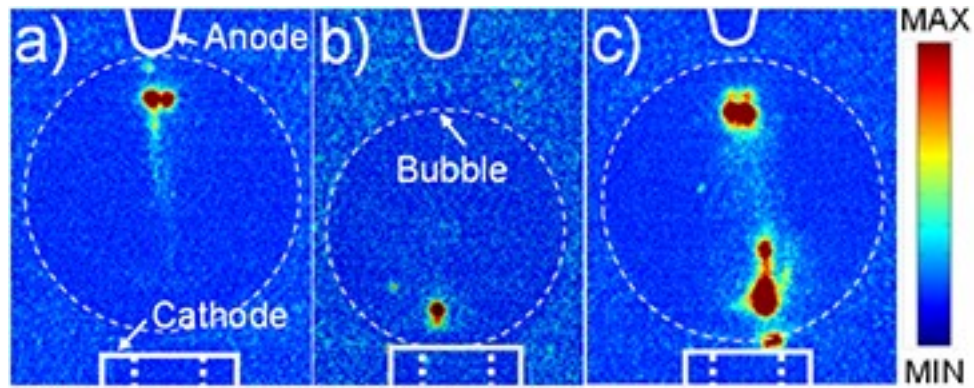


Figure 1.6 : Différent modes d’initiation d’un plasma dans les bulles. La distance interélectrode est de 1 mm et le gaz dans la bulle est de l’argon [23].

Ce qui rend possible ce type de décharge est la discontinuité de la permittivité électrique qui amplifie champ électrique aux frontières de la bulle. Une simulation du champ électrique des différents modes d’initiation est présentée à la figure 1.7.

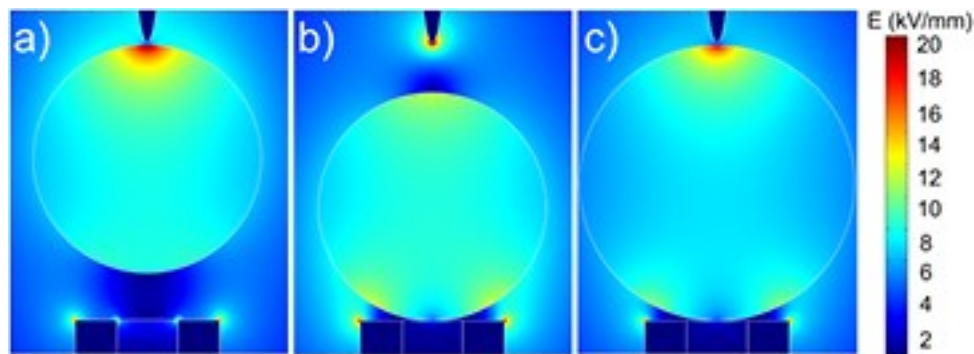


Figure 1.7 : Simulation du champ électrique de la configuration des trois modes d’initiation d’une décharge [23].

Ainsi, il est possible de modifier les caractéristiques de la décharge en changeant le gaz et en augmentant la distance interélectrode. Pour des valeurs entre 10^{16} et 10^{17} cm^{-3} , la densité électronique est plus élevée pour des gaz où l’énergie d’ionisation est plus basse. La densité électronique est plus basse lorsque la distance interélectrode est plus grande [24]. Aussi, la température d’excitation du tungstène, matériau utilisé pour les électrodes, et la température rotationnelle de l’OH et du C_2 , lorsque le gaz utilisé est formé de C, ne semblent pas dépendre de la composition du gaz et de la distance interélectrode [24]. Il est possible d’observer des différences dans la propagation de la décharge en changeant la permittivité du liquide. La figure 1.8 montre

ces différences. Généralement, plus que la différence de permittivité est élevée, plus la densité électronique, la source d'impact électronique et la densité de charge positive de la décharge auront une valeur élevée suivant l'interface Air/Liquide. Sinon, on verra les valeurs maximales des caractéristiques de la décharge se propager selon l'axe [25]. Ceci est dû à la discontinuité de la permittivité qui amplifie le champ électrique à la frontière de la bulle, et plus la différence de permittivité est grande, plus champ électrique à la surface de la bulle est amplifié.

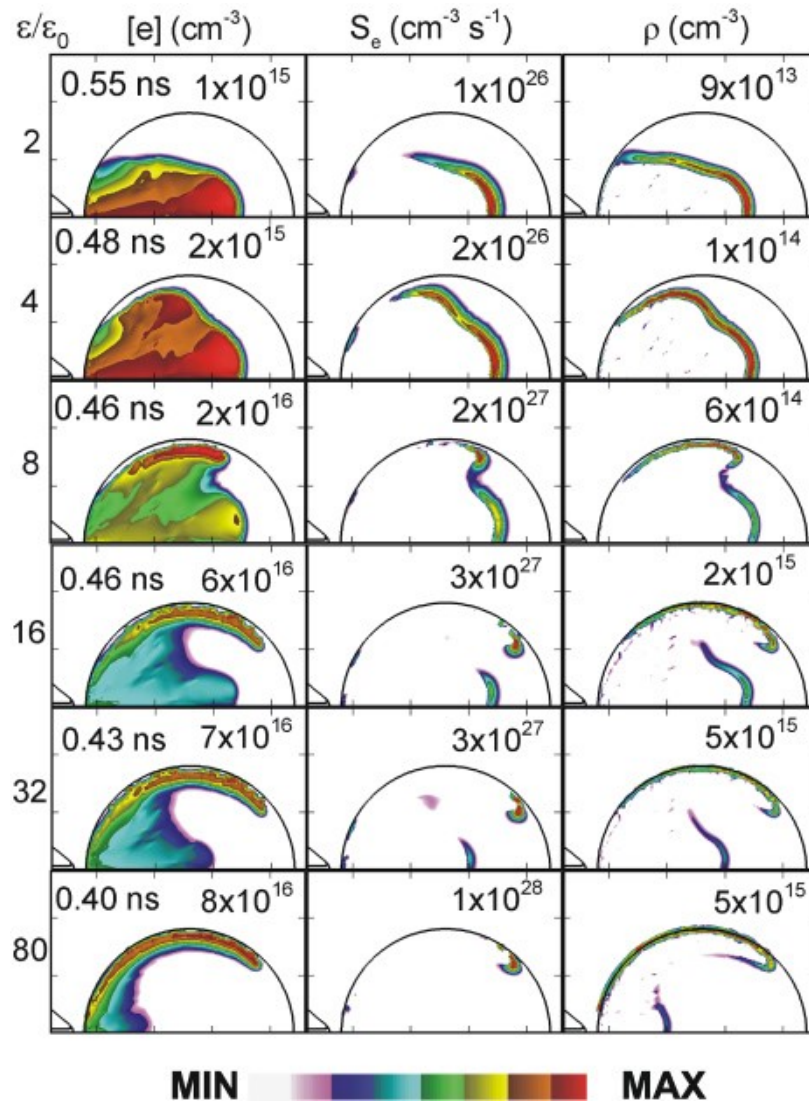


Figure 1.8 : Simulation de la propagation de la densité électronique ($[e]$), de la source d'impact électronique (S_e) et de la densité de charge positive (ρ). Le temps indiqué en ns est le moment de la simulation où l'image est prise et le nombre indiqué dans chaque case est la valeur maximale

de la caractéristique dans l'image. La permittivité relative ϵ/ϵ_0 du liquide augmente du haut vers le bas et la bulle est formé à partir de l'air ($\epsilon/\epsilon_0 = 1$) [25].

Un exemple d'émission à longue échelle d'un plasma formé dans une bulle de gaz est donné à la figure 1.9.

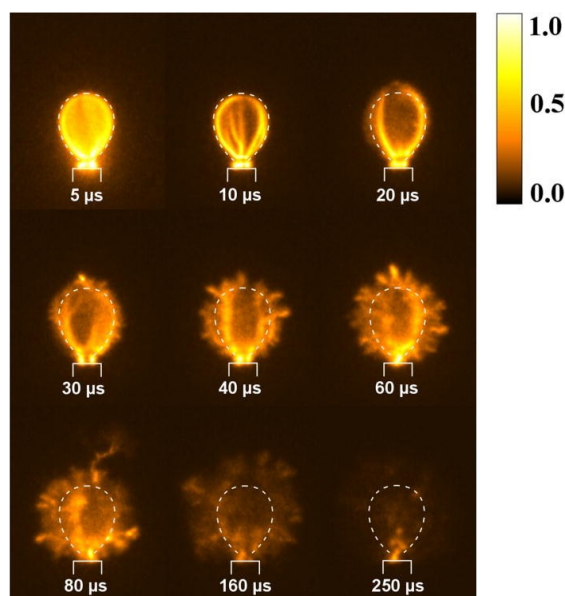


Figure 1.9 : Images de l'évolution d'un plasma impulsionnel dans une bulle d'air dans l'eau. La bulle est produite sur une aiguille ou la haute tension est appliquée. [26]

L'évolution de ce type de plasma se déroule en plusieurs phases. Tout d'abord, une décharge intense se produit dans les premières microsecondes. Cette décharge est causée par l'organisation des ions et des molécules dipolaires près de la surface de la bulle et par l'intensité du champ électrique. L'accumulation de charge sur la surface produit ainsi une décharge capacitive ($5 \mu s > t > 20 \mu s$). Par la suite, les électrons provenant de la pointe vont neutraliser les ions, et puis produire une accumulation de charge négative. Cette accumulation de charge négative va produire un moment où il n'y aura pas d'émission observée. Ce moment durera quelques centaines de nanosecondes. Par la suite, la chaleur à l'intérieur de la bulle va produire de la vapeur et environner la bulle. C'est à ce moment que les streamers vont commencer à se former ($t > 30 \mu s$). [26] Les valeurs attendues pour la température électronique varient entre 8 et 10 eV pour des plasmas de

densité de 10^{22} m^{-3} [27]. La température du gaz et la densité électronique dépendent de la composition du gaz, de la conductivité du liquide, de la puissance de la décharge, de la tension d'excitation et du volume de la bulle [10]. De cette façon, les espèces réactives sont produites dans la phase gazeuse et à l'interface bulle-liquide et sont diffusées dans le volume du liquide.

1.2.3 Plasma en phase gazeuse

L'interaction d'un plasma en phase gazeuse et un liquide est celle qui est étudiée dans ce mémoire, il sera donc décrit plus profondément que ceux introduits précédemment. Ainsi, il est approprié de définir deux types de couplage plasma-liquide. Plasma couplé directement avec un liquide est lorsque le liquide joue le rôle d'une électrode (anode ou cathode) dans le processus de formation du plasma. Cependant, un plasma indirectement couplé avec un liquide est lorsque le liquide ne joue pas un rôle d'électrode, mais il est l'objet à traiter par un plasma produit en amont [10].

1.2.3.2 Plasma en couplage indirect avec un liquide

Dans cette configuration, le plasma est généré indépendamment du liquide. Un exemple typique est un jet de plasma (figure 1.10). Bien que le liquide ne soit pas électriquement couplé avec le plasma, la présence du liquide modifie les propriétés du plasma à cause de l'évaporation et de l'injection des molécules du liquide. En bref, un jet du plasma est composé de deux électrodes entre lesquelles un gaz est soufflé. L'application du champ électrique aux électrodes ionise le gaz et produit un jet du plasma qui sera utilisé pour différentes applications, y compris le traitement du liquide.

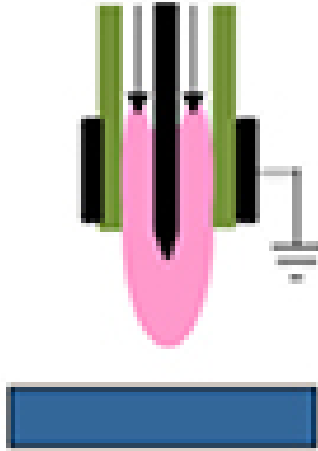


Figure 1.10 : Un jet du plasma à pression atmosphérique en contact avec la surface d'un liquide [1].

Différentes configurations de jet plasma ont été développées et plusieurs revues existent dans la littérature, par exemple [28]. L'un des avantages de cette configuration est de présélectionner les caractéristiques du plasma (composition, densité, température, etc.) avant de le faire interagir avec le liquide. Aussi, l'ajustement facile de la distance plasma-liquide, permet d'étudier l'influence de plusieurs zones du plasma (décharge, postdécharge, etc.) sur le liquide. Un exemple typique d'un jet du plasma TIAGO (Torche à Injection Axiale sur Guide d'Ondes) en contact avec l'eau, pour différentes distances est présenté à la figure 1.11 [29].

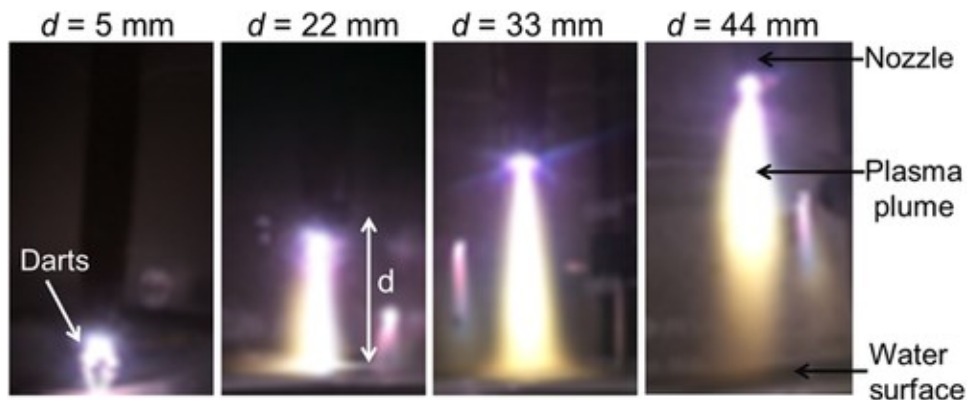


Figure 1.11 : Photo d'un plasma jet microonde produite à l'aide d'une Torche à Injection Axiale sur Guide d'Ondes (MWPJ-TIAGO) et est en contact avec l'eau pour différentes distances plasma-eau. [29]

Généralement, les propriétés de ce type de décharge dépendent de la composition du gaz injecté et de la puissance électrique injectée [28], mais la présence d'une surface d'eau change les propriétés du jet plasma. Par exemple, la présence d'un volume d'eau sous un jet plasma modifie la distribution de radicaux OH dans le plasma [30], comme montré à la figure 1.12. Cet effet est principalement relié à l'évaporation de l'eau.

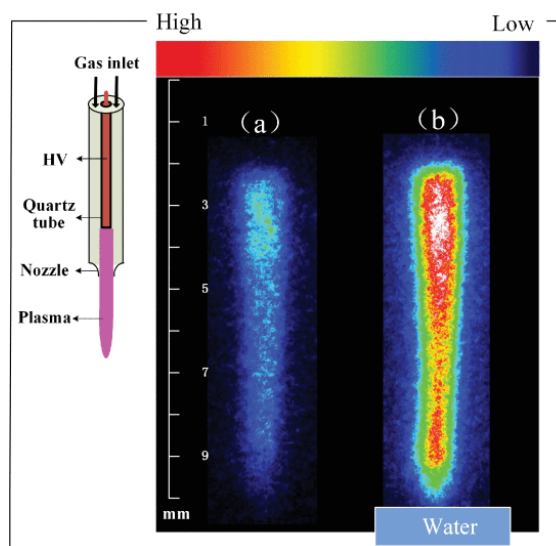


Figure 1.12 : Distribution 2D de radicaux OH par Fluorescence induite par laser (LIF). La figure a) présente la distribution de radicaux OH d'un plasma jet à pression atmosphérique à l'air libre, tandis que b) présente la distribution de radicaux OH d'un même plasma jet avec la présence d'un volume d'eau [30].

1.1.3.1 Plasma directement couplé avec un liquide

Comme mentionner précédemment, dans cette configuration, le liquide joue le rôle d'une électrode (anode ou cathode) dans le processus de formation du plasma. Pour bien comprendre ce rôle, quelques exemples de décharges sont abordés. Tout d'abord, une représentation d'un

dispositif typique pour produire un plasma directement couplé avec un liquide est montrée par la figure 1.13. Souvent une électrode pointe est soumise à haute tension tandis que la contre électrode est immergée dans le liquide. Si la polarité de la haute tension est positive, alors la pointe est considérée comme anode et le liquide comme cathode. Dans le cas inverse, si la polarité de la haute tension est négative, la pointe est alors considérée comme cathode et le liquide comme anode.

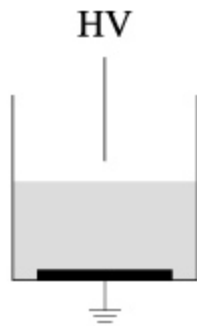


Figure 1.13 : une représentation d'un dispositif typique pour produire un plasma directement couplé avec un liquide. [10]

Le processus de formation de type plasma est relativement complexe, parce que l'électrode liquide est évolutive, comme elle peut changer des propriétés (composition, température, conductivité, acidité, etc.) et elle peut évaporer de la matière dans le plasma. Parmi plusieurs groupes de recherche, Bruggeman et al. ont réalisé beaucoup de progrès dans la description de ce type de décharge au cours de deux dernières décennies.

Dans le cas de l'eau (ou d'un liquide polaire, en général), l'application d'un champ électrique déforme la surface de l'eau et un cône se forme (Figure 1.14a) ; ce cône est le « cône de Taylor ». Comme ce cône est une réponse naturelle des molécules d'eau au champ électrique — polarisation, sa formation est indépendante de la direction du champ et donc de la polarité de l'électrode pointe. Ceci est bien démontré expérimentalement ; voir par exemple figure 1.14a et 1,14 c. Dans ce contexte, la distance entre la pointe et la surface de l'eau est d'une grande importance comme elle influence directement la valeur du champ électrique à la surface de l'eau. La formation du cône est donc plus importante à faible distance.



Figure 1.14 :(a) Cône de Taylor avant le claquage. (b) et (c) Cône de Taylor au claquage pour lorsque la pointe métallique a une polarité négative ou positive, dans l'ordre présenté. Dans le coin à droite, le temps par rapport au temps du claquage $t = 0$. Le temps d'ouverture de la caméra est de $15 \mu\text{s}$ [31]

Si l'intensité du champ est relativement grande, le milieu gazeux séparant la pointe et la surface de l'eau (c.-à-d. l'écart) peut subir un claquage et donc un plasma apparaît dans l'écart. Bien que l'initiation du plasma se produit de la même manière lorsque la distance est petite, la polarité de la pointe métallique a un effet sur le motif d'émission lumineuse dans l'écart lorsqu'il est au-delà de 3 mm. Les motifs d'émission lumineuse pour un plasma en courant continu pour la polarité négative et positive sont présentés à la figure 1.15. Premièrement, la colonne plasma de la décharge en polarité positive est d'abord plus lumineuse que la polarité négative. Deuxièmement, alors que pour la polarité négative de la pointe il y a absence de lumière, on voit que pour la polarité positive l'émission s'élargit pour former une structure filamentaire. Cette structure filamentaire est en contact avec la surface de l'eau. Pour la polarité négative, l'émission observée à la surface de l'eau semble former un disque, à grande échelle temporelle (ouverture de caméra à 20 ms). En réalité, le disque est en fait formé de points lumineux (ouverture de caméra à $100 \mu\text{s}$) [3]. L'émission lumineuse à la surface pour les deux échelles est montrée à la figure 1.16.

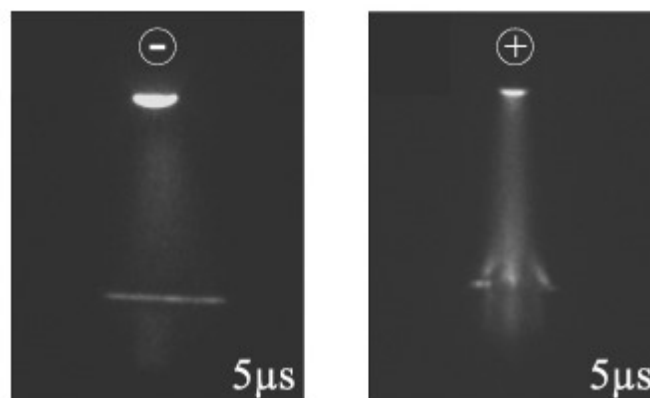


Figure 1.15 : Motif d'émission lumineuse dans l'écart pour de décharge en courant continu à 30,9 mA pour la polarité négative (à gauche) et positive (à droite) lorsque le temps d'ouverture de la caméra est de 5 μ s. L'écart est de 5 mm [3].

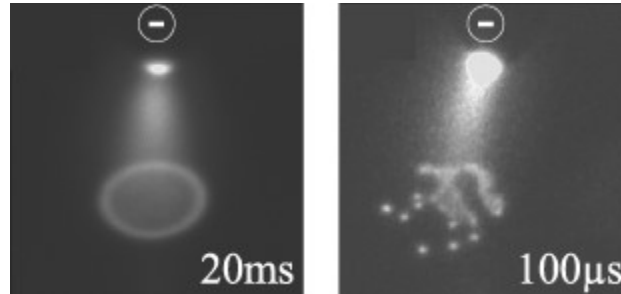


Figure 1.16 : Motif d'émission à la surface lorsque la pointe métallique est cathode. Le temps d'ouverture de la caméra est de 20 ms, à gauche, et de 100 μ s, à droite [3].

Si on s'intéresse alors à la composition du spectre lumineux d'une telle décharge, la figure 1.17 montre un exemple des excitations atomiques et moléculaires des espèces se retrouvant dans l'écart. Le spectre d'une décharge luminescente est généralement composé de la transition N_2 (C-B), qui correspond aux transitions vibrationnelles du N_2 se trouvant entre 290 et 500 nm. Il est aussi composé de la transition rotationnelle OH (A-X) se trouvant à 310 nm. On peut observer des transitions vibrationnelles du N_2^+ à 391 nm et à 420 nm, la transition rotationnelle du NO à 240 nm. Les transitions atomiques de H_α et de O_1 sont observées à 656 nm et à 777 nm. Avec une meilleure résolution, le calcul de la température du gaz se fait à partir de la température rotationnelle de certaines espèces, comme l'OH et le N_2 , et en faisant comme hypothèse que $T_{\text{gaz}} \approx T_{\text{Rot}} \approx T_{\text{Vib}}$. La température rotationnelle et du N_2 et de l'OH soit similaire. Cependant, dans le type de plasma que nous étudions, la température rotationnelle de l'OH n'est pas représentative de la température du gaz, lorsque le calcul se fait à la pression atmosphérique et dans un environnement contenant relativement beaucoup d'eau [32]. Par exemple, la température de gaz observé dans une décharge pulsée nanoseconde dans une atmosphère d'air en contact avec de l'eau se trouve entre 540 et 1300 K [33]. Pour la densité électronique, le calcul se fait à partir de la raie H_α , lorsque celle-ci est observable. Les calculs se font en utilisant l'élargissement de Stark, qui prend en compte les interactions entre les particules chargées dans l'élargissement spectral [34]. On retrouve des densités électroniques de l'ordre de $1 \times 10^{15} \text{ cm}^{-3}$ dans les décharges en contact avec les liquides [33].

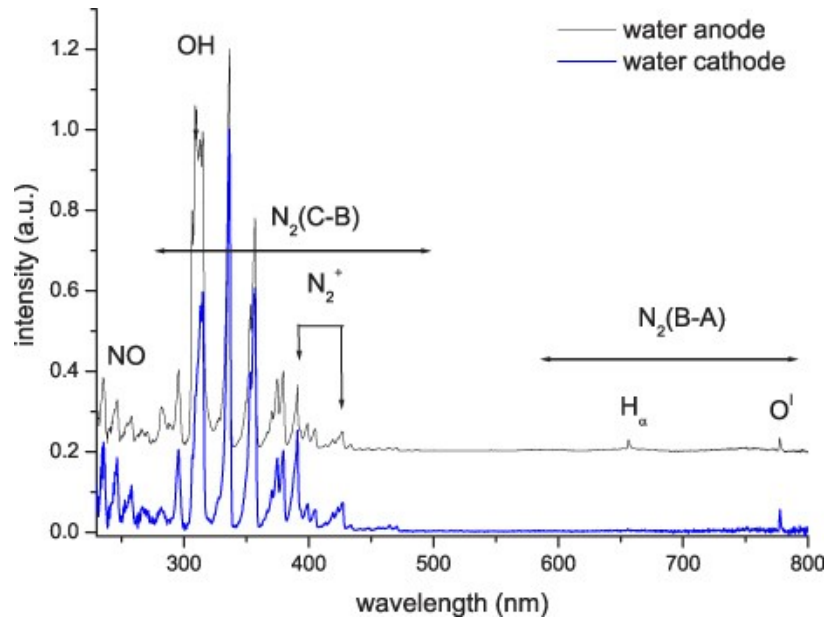


Figure 1.17 : Composition du spectre d'émission d'une décharge lumineuse près de l'eau.
 Une comparaison entre les polarités de l'eau, anode et cathode, est faite. [3]

La transition entre une décharge lumineuse et une décharge de type spark est d'ailleurs discutée dans un autre article [35]. La figure 1.18 montre cette transition avec les courbes de courant et de tension. Ainsi, la décharge lumineuse produit une légère montée de courant ($\approx 0,1$ A) avant que la décharge devienne de type spark, qui elle produit une montée de courant largement supérieure ($\approx 1,4$ A). Entre les deux décharges, les espèces ionisées durant la décharge lumineuse induisent des processus d'attachement et de recombinaison. Ces processus chauffent le gaz qui se trouve dans l'espace interélectrode, produisant aussi une augmentation du champ électrique et de la densité électronique. Finalement, le resserrement de la décharge lumineuse devient un canal restreint pour produire une décharge de type spark [36].

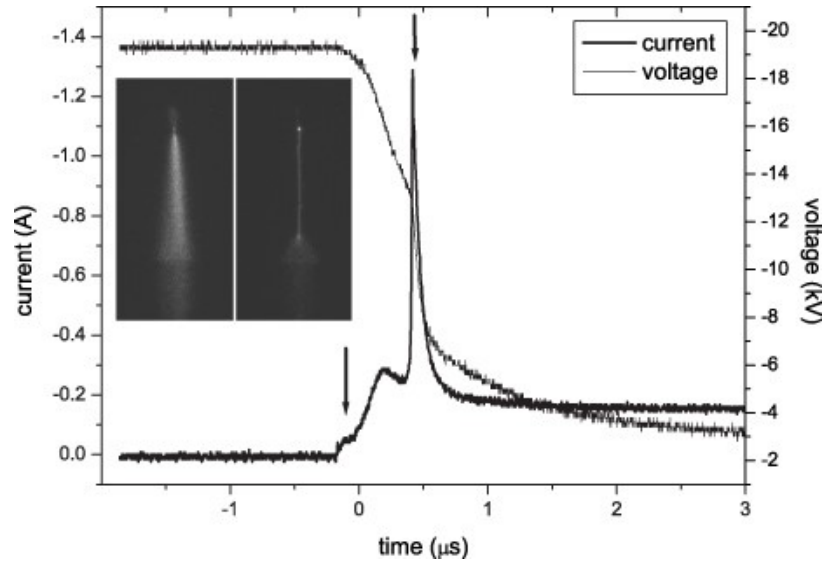


Figure 1.18 : Courbes de courant et de tension de la transition de la charge lumineuse vers la décharge spark lorsque la solution de NaCl a une conductivité de 100 $\mu\text{S}/\text{cm}$ est anode. La position temporelle des images est indiquée sur la figure, de gauche à droite. [35]

Ainsi, il est possible de comparer cette transition en changeant les propriétés du liquide, tel que la conductivité. La figure 1.19 montre la comparaison entre 3 conditions de conductivité.

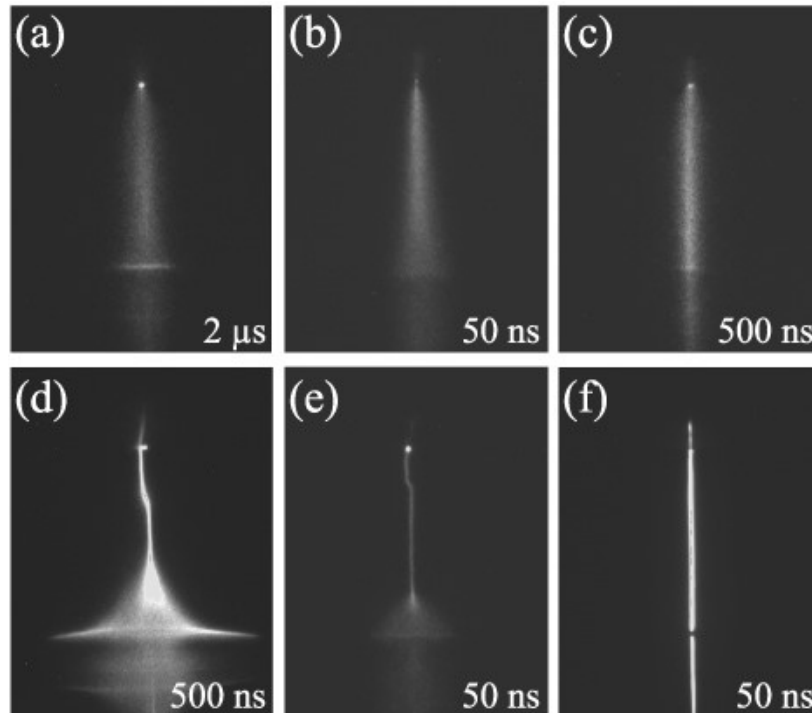


Figure 1.19 : Comparaison de la transition de la décharge lumineuse vers la décharge de type spark. Les figures (a) et (d) montrent la transition pour l'eau distillée. Les figures (b) et (e) pour une solution de NaCl une conductivité de 50 $\mu\text{S}/\text{cm}$. Les figures (c) et (f) pour une solution de NaCl avec une conductivité de 5000 $\mu\text{S}/\text{cm}$. Le temps d'ouverture de la caméra est indiqué en bas à droite de l'image [35]

L'effet de la conductivité sur la décharge est principalement de réduire la largeur de l'émission lumineuse de la décharge de type spark. En augmentant la conductivité, la largeur de la décharge de type spark diminue. Comme il n'y a pas d'électrons libres en liquide, les ions transportent le courant en liquide [37]. Ainsi, en augmentant la conductivité, on augmente aussi la densité de porteurs de charge dans le liquide. Cela fait en sorte que la surface de contact du plasma avec le liquide peut être plus petite parce que de la densité de courant dans le liquide peut être plus élevée pour la même valeur de champ électrique.

Il est aussi possible d'identifier les différentes zones d'une décharge lumineuse ; un exemple typique entre une décharge pointe et la surface de l'eau est présenté à la figure 1.20. De l'électrode vers le bas, on identifie l'espace sombre cathodique (CF), la lueur négative (NG), l'espace sombre de Faraday (FDS), la colonne positive (PC), et la lueur anodique (AG).

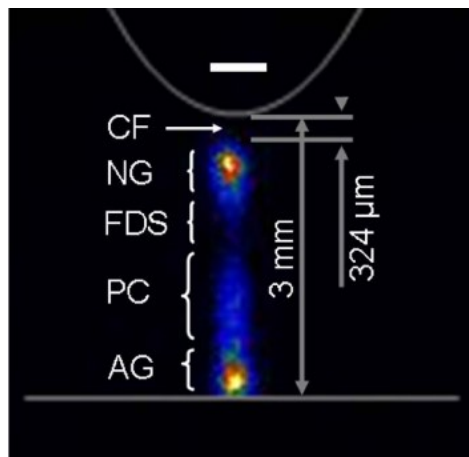
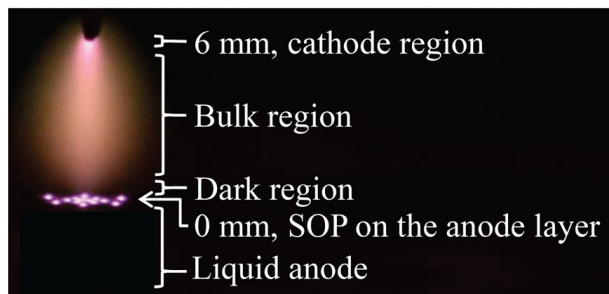
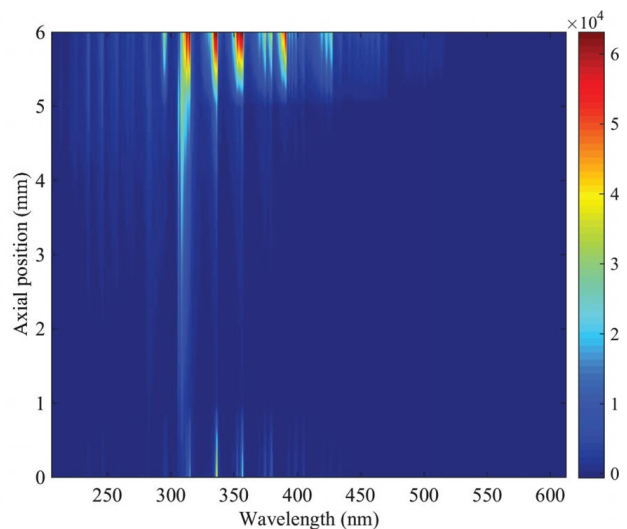


Figure 1.20 : Morphologie d'une décharge lumineuse soutenue à 1,25 mA et 1 kV lorsque l'eau est anode. L'espace interélectrode est de 3 mm. [3]

En ayant identifié la structure de la décharge lumineuse, il est possible de déterminer la composition du spectre à chaque point dans l'écart. Le spectre de l'émission lumineuse dans l'écart en fonction de la distance dans l'écart est présenté à la figure 1.21. Comme présenté à la figure 1.17, les bandes principalement observées sont : le système second positif N_2 ($C^3\Pi-B^3\Pi$), la transition OH ($A^2\Sigma^+ - X^2\Pi$) et le système NO ($A^2\Sigma^+ - X^2\Pi$). Le profil axial de chacune de ces raies est présenté à la Figure 1.22. À partir de ces figures, on voit que la transition OH (A-X) domine l'émission lumineuse dans la région de la colonne plasma, que l'émission est partagée entre le N_2 (C-B) et le OH (A-X) dans la région de la cathode et que l'émission près de la surface est dominée par le système second positif N_2 (C-B). L'émission de l' OH près de la cathode provient surtout de l'impact électronique de la vapeur d'eau dans l'air ambiant, et celui de la colonne plasma de la diffusion des radicaux OH près de la cathode et de l'excitation à partir du l'état fondamental de l' OH vers OH (A) par impact électronique. L'absence d'émission est due à la diminution de la concentration d'électrons libres au fur et à mesure que la distance à partir de l'électrode métallique augmente. Comme la concentration d'électrons est plus basse, il y a moins d'électrons pour exciter les différentes espèces, ce qui fait que l'émission provenant des différentes espèces diminue. Finalement, les motifs visibles à la surface le sont à cause de l'amplification du champ électrique à la surface par des vagues d'ionisation. Ce champ électrique accélère les électrons qui exciteront l'état N_2 (C) vers l'état N_2 (B) [4].



(a)



(b)

Figure 1.21 : (a) Image de l'émission lumineuse d'une décharge en courant continu lorsque la pointe métallique est cathode. (b) Spectre de l'émission lumineuse résolue spatialement selon l'axe de la pointe [4].

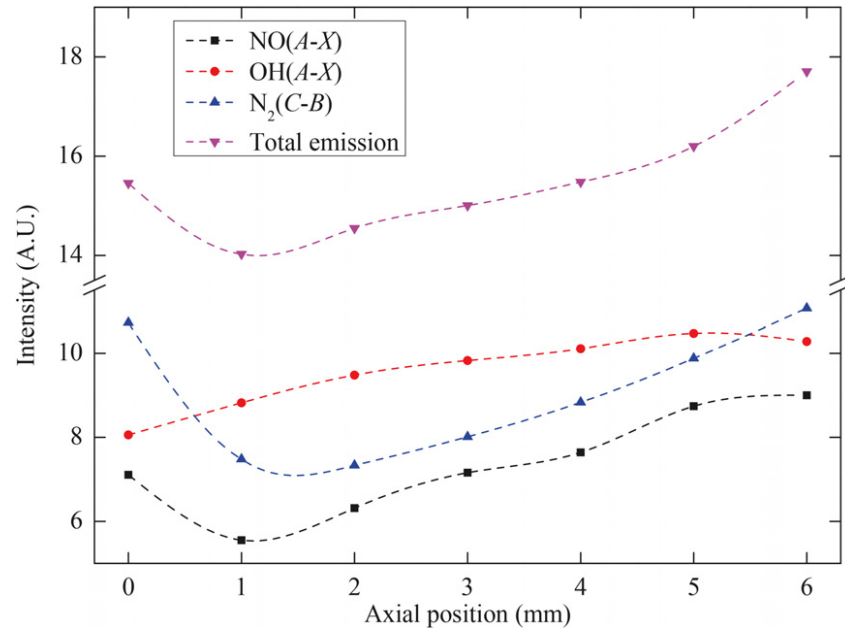


Figure 1.22 : Profil axial des raies OH (A-X) (309 nm), NO (A-X) (236,3 nm), N₂ (C-B) (337,1 nm) et l'émission totale avec l'intensité sur une échelle logarithmique [4].

Ainsi, les motifs à la surface de l'eau observés par [3] et par [4] dépendent des caractéristiques de la décharge et du liquide. Tout d'abord, la puissance est un facteur important. On observe tout d'abord que les motifs à la surface dépendent de l'intensité du courant, à la figure 1.23. Lorsque le courant est plus petit que 40 mA, le motif montre un disque et, lorsque le courant est suffisamment haut, un anneau entoure le disque. À partir de 50 mA, on voit que le disque et l'anneau se déforment en petit point. En changeant le courant pour différentes distances interélectrodes et en mesurant la tension de claquage, la figure 1.24 est obtenue. Ainsi, l'observation des différents motifs ne dépend pas du courant, mais de la puissance. Pour une distance donnée, la structure va d'un disque vers une structure en anneau vers un motif de points, alors que la puissance augmente. La distance est aussi un facteur important. Pour une distance donnée, il ne sera pas possible de former une structure en double anneau ($d < 5$ mm) ou en forme de multiples points ($d < 7$ mm).

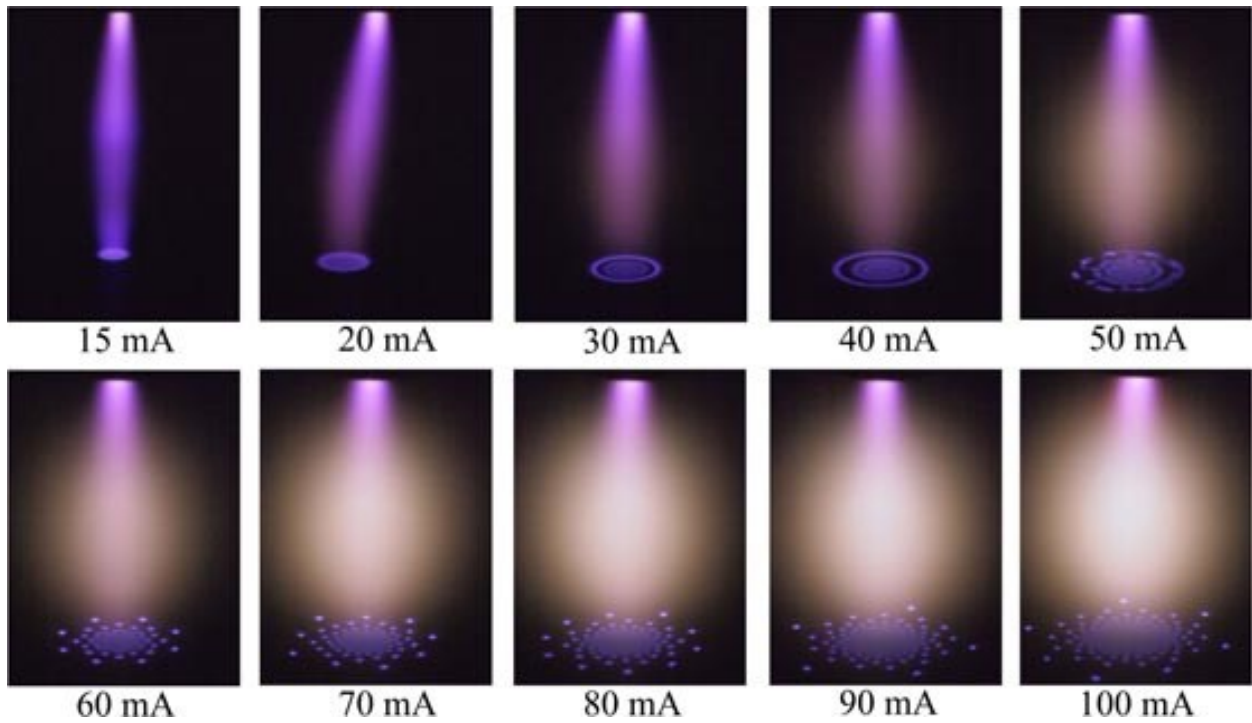


Figure 1.23 : Motif d'autoorganisation de l'émission anodique à la surface de l'eau lorsqu'elle est anode. La solution contient 1 % de NaCl. La distance interélectrodes est de 10 mm [38].

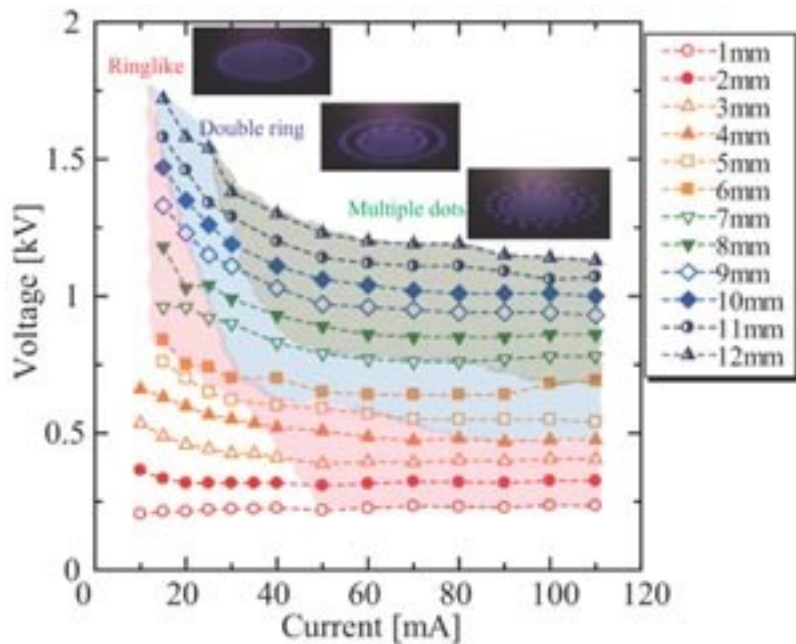


Figure 1.24 : Motif d'autoorganisation de l'émission anodique à la surface de l'eau en fonction de la distance et du courant et de la tension mesurée pour le même liquide qu'à la figure 1.23.

[38]

Il est aussi montré, dans le même article, qu'en changeant le gaz d'opération, les motifs changent à la surface [38]. La figure 1.25 montre comment le motif à la surface de l'eau est modifié lorsque la composition du gaz à la surface est modifiée. Plus un gaz est électronégatif, comme le O_2 , plus la densité d'électrons libre à la surface de l'eau est faible. Ainsi, il y a moins de collisions qui excitent les espèces près de la surface, ce qui forme les motifs [4].

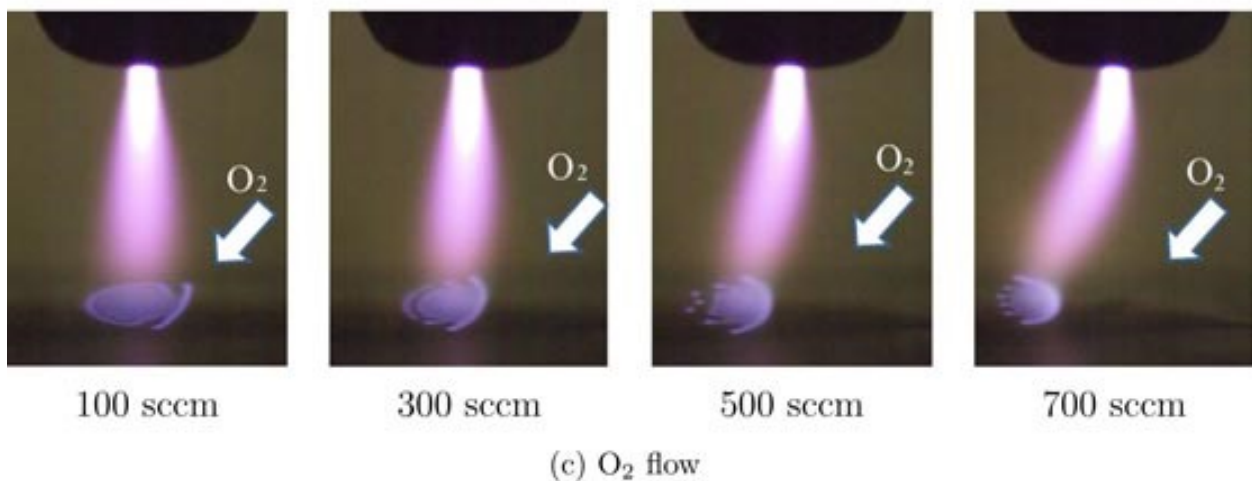
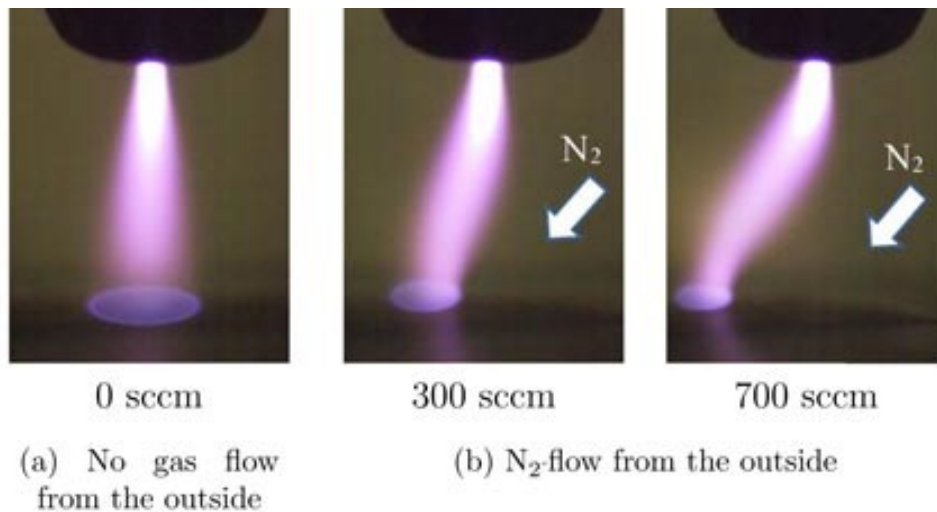


Figure 1.25 : Modification du motif à la surface de l'eau en fonction de la composition du gaz à la surface. Le flux de gaz est dirigé vers la surface, ce qui déplace le motif. (a) présente le motif sans flux de gaz (b) avec un flux de N_2 de 300 et 700 sccm et (c) avec un flux de O_2 de 100 à 700 sccm [38].

Les propriétés du liquide modifient les motifs à la surface. D'abord, la conductivité du liquide réduit le diamètre du motif, comme montré à la figure 1.26. On observe aussi que les motifs en

rayures, lorsque la conductivité du liquide est faible, deviennent des points plasma encerclant un cercle homogène quand la conductivité du liquide augmente.

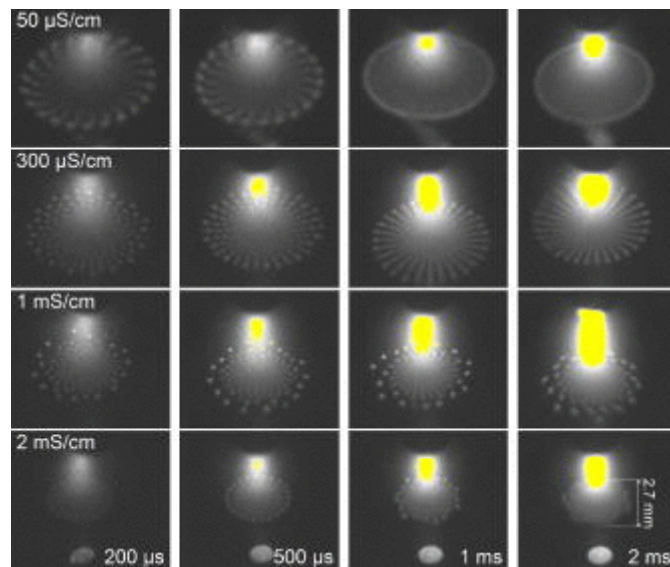


Figure 1.26 : Motifs à la surface de l'eau en fonction de la conductivité du liquide (du haut vers le bas) et en fonction de l'ouverture de la caméra (de gauche à droite). [39]

Le pH modifie aussi la forme du motif à la surface, comme montré à la figure 1.27 [6]. Lorsque pH est entre 1 et 4, le motif sur la surface forme des points plasma, et lorsque le pH est entre 5 et 7, le motif sur la surface ressemble à une roue d'engrenage.

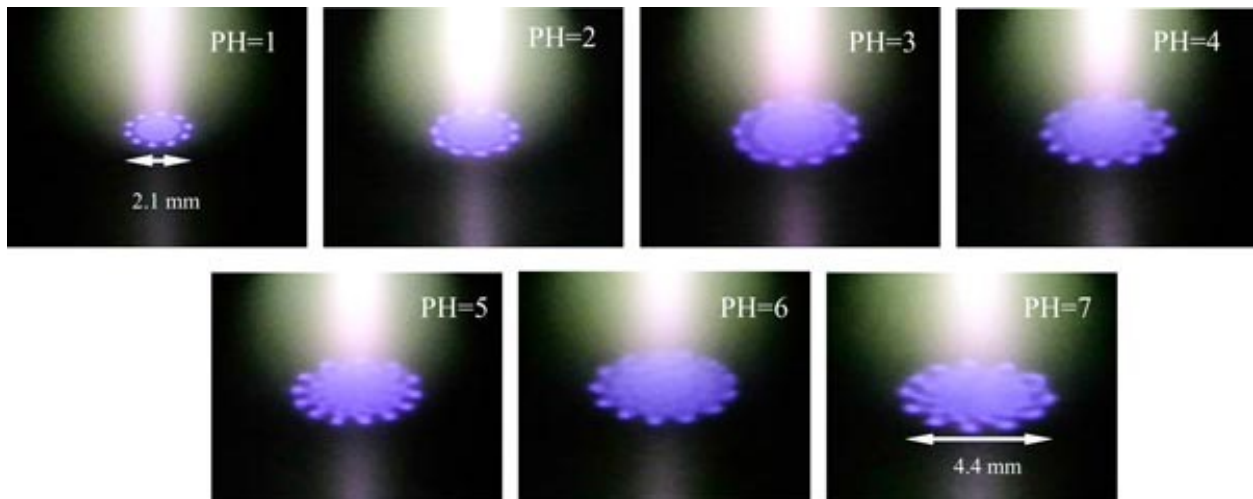


Figure 1.27 : Motif à la surface de l'eau d'une décharge en courant alternatif à une fréquence de 7 kHz. L'eau désionisée est acidifiée à partir du HNO_3 . [6]

Il faut quand même faire attention pour les modifications du motif à la surface de l'eau, puisque les tendances présentées ne sont pas des règles générales. La figure 1.28 montre que pour trois liquides avec la même conductivité et de la même nature, tous trois des acides, on obtient des motifs différents à la surface de l'eau. Ainsi, une meilleure compréhension de la formation de ces structures est à construire.

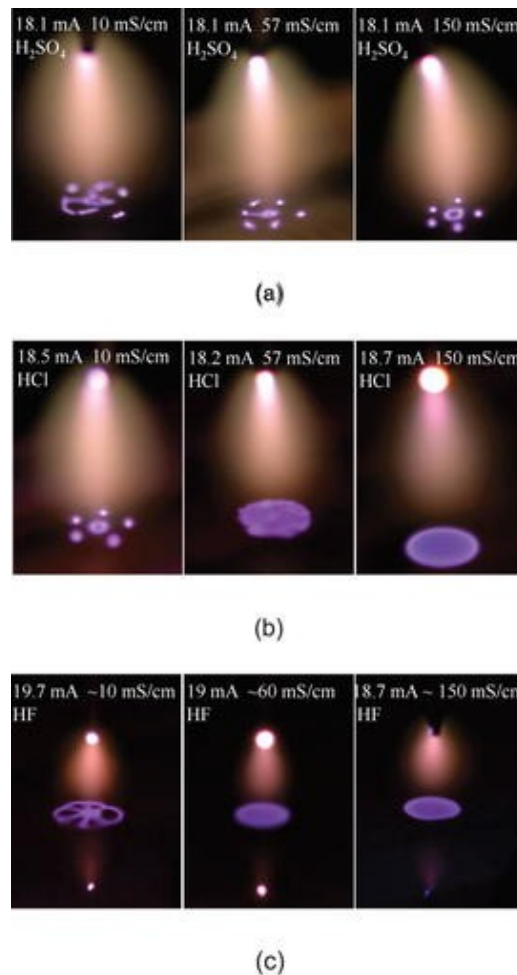


Figure 1.28 : Motif à la surface de l'eau d'une décharge lumineuse pour trois conductivités, 10 mS/cm, 57 mS/cm et 150 mS/cm, pour trois acides différents : (a) H₂SO₄ (b) HCl et (c) HF [32].

1.3 Application au traitement des eaux

Bien que le but principal de la maîtrise soit d'étudier les phénomènes fondamentaux de l'interaction plasma-liquide, il est important de garder une perspective d'application. Dans ce mémoire, nous avons choisi à étudier la dégradation des molécules organiques présentes dans l'eau. Pour cette fin, la molécule du méthylène bleu a été choisie ($C_{16}H_{18}ClN_3S$), figure 1.29.

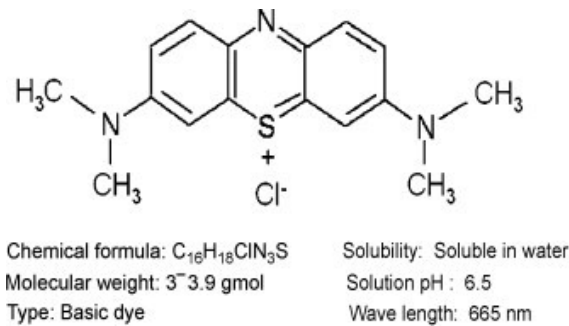


Figure 1.29 : Schéma moléculaire et propriétés chimiques du méthylène bleu. [40]

Généralement, la dégradation de cette molécule peut être suivie à travers la spectroscopie d'absorption UV-Visible et plus particulièrement en suivant l'absorption à 663 nm. Des spectres d'absorption typiques sont présentés à la figure 1.30. La diminution de l'intensité à 663 nm ainsi que son augmentation à ~ 300 nm sont la preuve que le procédé dégrade cette molécule (ici, c'est l'ozonation). Un mécanisme de dégradation détaillée de cette molécule est disponible dans la littérature, par exemple [41].

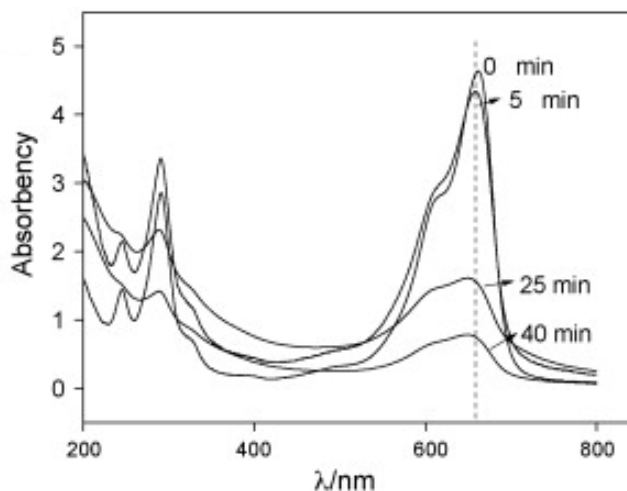
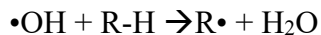


Figure 1.30 : Spectre d'absorption du méthylène bleu en solution en fonction du temps de traitement par ozonation [40].

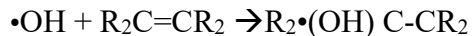
1.3.1 Méthodes d'oxydation avancées

Avant de présenter les différents travaux sur les plasmas qui ont été appliqués en remédiation environnementale, nous présentons brièvement les méthodes les plus utilisées dans le traitement des eaux. Ces procédés sont des procédés d'oxydation avancées (AOP), comme l'ozonation [40], la photocatalyse [41], la sonication [42] et les réactions de Fenton [43]. Le but de ces procédés est de produire une minéralisation totale (transformer les substances récalcitrantes en substances inorganiques) ou une minéralisation partielle (transformer les polluants en des substances biodégradables) [44]. Dans les processus AOP, l'oxydation peut être assurée par différentes espèces telles que les radicaux $\bullet\text{OH}$, l'ozone (O_3), HO_2 , et le peroxyde d'hydrogène. Ces espèces ont un potentiel d'oxydation de 2,85, 2,07, 1,70 et 1,68, dans l'ordre présenté. Les radicaux $\bullet\text{OH}$ sont en particulier très important dans un procédé AOP, puisqu'ils ont le meilleur potentiel d'oxydation et sont peu sélectifs dans le type de molécule attaqué [44]. En effet, les radicaux $\bullet\text{OH}$ viennent s'attaquer aux polluants organiques présents dans la solution. La manière dont ces radicaux attaquent les polluants dépend de la nature de la molécule, et cela peut se produire de trois manières différentes [45] :

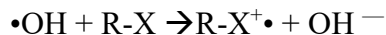
1. Abstraction d'hydrogène :



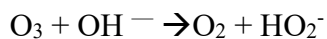
2. En s'ajoutant au polluant :

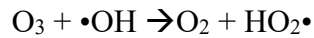
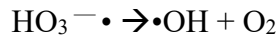
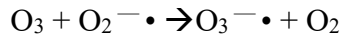
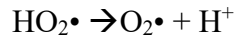
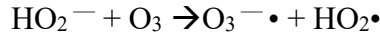


3. En transférant un électron non-pairé à d'autres substances telles que des carbonates :



Parmi les méthodes pour produire les radicaux $\bullet\text{OH}$ en liquide, on cite l'ozonation. Comme son nom l'indique, cette méthode utilise l'ozone pour décomposer l'eau et produire des radicaux $\bullet\text{OH}$. L'ozone est un gaz est généralement stable, mais lorsqu'il est en contact avec de l'eau, il est hautement instable et se décompose rapidement à travers ces réactions [46] :





Ces réactions peuvent être accélérées par l'ajout de peroxyde d'hydrogène et sont favorisées lorsque le pH de la solution est au-dessus de 5 [47]. Aussi, la présence de carbone activé stimule la production de radicaux $\cdot\text{OH}$ [40]. Il existe aussi des procédés basés sur la photocatalyse. Ce type de procédés utilisent l'activation de particules semi-conductrices telle que le TiO_2 par de photons UV pour décomposer les molécules d'eau et produire des radicaux $\cdot\text{OH}$ [41].

Ces deux méthodes font partie d'une multitude de procédés chimiques, ces deux procédés sont importants, puisqu'ils sont les constituants principaux du traitement de l'eau par plasma.

1.3.2 Traitement de l'eau par plasma

L'importance des plasmas pour le traitement des eaux usées est de trouver un procédé écologique pour éliminer les substances récalcitrantes dans les eaux usées. Les plasmas en contact avec les liquides sont d'excellents candidats, puisque la présence de l'eau dans l'environnement gazeux permet de produire des espèces hautement réactives telles que $\text{OH}\cdot$, O , O_3 , H , HO_2 et H_2O_2 [1,48]. La présence de O_2 , de N_2 et H_2O dans l'air permet la production d'espèces très réactives, tels que NO , O_2^* , N_2^* , N_2^+ , NH et plusieurs autres en plus des espèces réactives formées à partir de l'eau [49]. Ces espèces réactives azotées augmentent la concentration de peroxyde d'hydrogène et permettent la conversion de l'acide peroxonitrique en ions nitrites ($\text{ONO}_2\text{H}/\text{NO}_2$), une excellente réaction d'oxydation [50]. La figure 1.31 montre la répartition des espèces réactives pour une décharge pointe-plan.

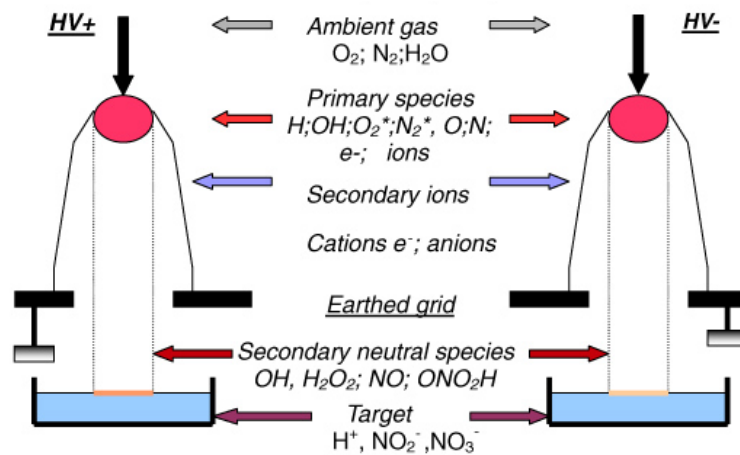


Figure 1.31 : Répartition des espèces réactives pour une décharge pointe-plan pour un plasma couplé directement avec l'eau dans l'air ambiant [50].

Même si, selon la figure 1.31, la polarité négative et la polarité positive d'une décharge en contact avec l'eau produisent les mêmes espèces, les concentrations peuvent être différentes. En effet, la décharge en polarité positive, qui produit une décharge de type spark, produira des concentrations plus élevées de H_2O_2 et de NO_3^- . Contrairement à la décharge positive, la décharge en polarité négative, qui produit une décharge lumineuse, produira des concentrations plus élevées de NO_3^- et de NO_2^- [49].

Ainsi, plusieurs paramètres peuvent influencer le traitement du liquide. Parmi ces paramètres, il y a le gaz d'opération (dont sa composition [51]), l'amplitude de la tension appliquée et la polarité de la tension appliquée qui influencent le plus l'efficacité du traitement. Le flux de gaz et le flux du liquide (si le dispositif utilisé permet de faire circuler le liquide pendant le traitement) sont des paramètres qui n'influencent pas significativement le traitement [52]. Il y a aussi l'ajout de gaz, tel que le O_2 et le O_3 , sous forme de bulles en liquide [53] et d'additifs, tel que le Fe pour former des réactions de Fenton [54], qui ont aussi été étudiées pour améliorer les procédés. L'ajout de bulles de gaz augmente considérablement l'efficacité du traitement en liquide, tandis que l'ajout de Fe ne l'augmente pas significativement.

Finalement, le rôle des espèces produites par le plasma qui participent au traitement des polluants dans les eaux usées et le rôle des paramètres qui influencent le traitement du liquide restent encore à être bien compris.

1.4 Objectifs du mémoire

L'objectif du mémoire est de développer un système expérimental pour caractériser l'interaction d'un plasma d'air directement couplé avec l'eau. Le plasma est produit par une décharge électrique en utilisant une source d'alimentation à courant alternatif (AC). La suite de ce mémoire est composée de deux chapitres, soient deux articles publiés dans des revues à comité de lecture.

Dans le chapitre 2 (article 1), nous présentons une caractérisation du plasma dans l'écart et à la surface de l'eau en utilisant l'imagerie résolue en espace et en temps. Dans le chapitre 3 (article 2), nous présentons une caractérisation électrique de la décharge AC d'air en contact avec l'eau. Selon la distance électrode-eau (écart), différents modes de décharges ont été étudiés en les caractérisant électriquement. Aussi, l'efficacité de chaque mode de décharge pour la dégradation du méthylène bleu (polluant organique modèle) a été évaluée.

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Chapitre 2 – Time and space-resolved imaging of an AC air discharge in-contact with water

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Time and space-resolved imaging of an AC air discharge in contact with water

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Résumé

De nombreux phénomènes physiques et chimiques sont impliqués dans les plasmas en contact avec les liquides. Ces phénomènes sont extrêmement sensibles à la source plasma et aux conditions expérimentales. Dans cette étude, nous investiguons la dynamique temporelle d'une décharge plasma produit dans l'air, soutenue par un courant alternatif AC, entre une électrode métallique et l'eau. Dépendant de la distance entre l'espace inter-électrode (d), la décharge subit une transition lorsque $d = 4.5$ mm. Lorsque $d < 4.5$ mm, une baisse de tension est observée durant les demi-périodes positives et négatives (i.e. lorsque l'eau est cathode et anode, respectivement). Lorsque $d > 4.5$ mm, la baisse de tension est observée seulement lors de la demi-période négative (i.e. lorsque l'eau est anode). Avant la transition et lorsque l'eau est cathode, l'émission du plasma dans l'espace inter-électrode est composée en deux parties : une émission en forme de cône près de la surface de l'eau et une émission en forme de cylindre dans l'espace inter-électrode. Lorsque l'eau est anode, une forte émission est observée à la pointe métallique et une émission en forme de disque est observée à la surface. Pour un $d > 4.5$ mm, après la transition, l'émission à la surface de l'eau est modifiée pour former un disque homogène au centre d'un anneau. L'évolution temporelle de l'émission dans l'espace inter-électrode et à la surface de l'eau est aussi discutée, et la relation entre la puissance injectée et la forme de l'émission plasma est décrite.

Mots-clés: Interface Plasma-Liquide, Décharge électrique, Imagerie résolue en temps, Structures Plasma.

Abstract

Numerous physical and chemical phenomena are involved in liquid plasmas. These phenomena are highly sensitive to the plasma source and to experimental conditions. In this study, we investigate the temporal dynamics of an AC-sustained plasma produced in air by a discharge between a pin electrode and water. Depending on the gap distance (d), a discharge transition is observed at $d = 4.5$ mm. At $d < 4.5$ mm, voltage drop is observed during both positive and negative half-periods (i.e., when water is cathode and anode, respectively). Meanwhile, at $d > 4.5$ mm, voltage drop is observed only during the negative half-period (i.e., when water is anode). Before transition and when water is cathode, the plasma emission in the gap space consists of two components: a conical-like emission at the water surface and a cylindrical-like in the gap. When water is anode, strong emission is observed at the electrode pin, along with a disc-like emission at the water surface. Increasing d beyond 4.5 mm (i.e., after transition) modifies the emission structure at the water surface, forming an inner homogeneous spot at the center of an outer ring. The temporal evolution of the emission in the gap and at the water surface is also discussed, and its relationship with the injected power is assessed.

Keywords: Plasma-liquid interface, Electrical discharge, Time resolved imaging, Plasma structuration.

2.1 Introduction

Non-thermal atmospheric pressure plasmas, such as plasma jets [1-4] and dielectric barrier discharges [5, 6], have been extensively studied during the past century. In principle, such plasmas can be sustained in various regimes, such as streamers [7], spark [8], corona [9], and glow [10], among others [11], and they are used in numerous applications, including surface processing, thin film deposition, and biomedicine [4, 5]. When coupled with liquids, non-thermal plasmas efficiently produce reactive species, and so, they can be used for water treatment [6, 12], liquid fuel reforming [13], sterilization [14], and nanomaterial synthesis [15].

Plasmas may be generated inside the liquid medium or in the gaseous medium in-contact with liquid [16]. In the latter case, the plasma and the liquid can be coupled directly or indirectly. Indirectly coupled plasmas such as plasma jets in-contact with liquid are independent of the liquid medium [2, 17, 18]; however, their dynamics and properties are strongly influenced by the liquid [19]. Meanwhile, directly coupled plasmas are electrically connected to the liquid, which is considered as an electrode in the system [20, 21]. Both types of coupling are characterized by complex interactions at the liquid surface [22, 23], and they involve numerous phenomena (ionization, diffusion, dissociation, evaporation, etc.) that can simultaneously occur on a relatively short time scale (around nanoseconds). In this study, we only consider directly coupled plasmas in contact with liquid.

Considering the advanced oxidation processes triggered by plasmas in-contact with water, the fundamental mechanisms and applications of these plasmas have been researched in numerous studies, particularly in terms of their potential in wastewater treatment [12]. In general, such plasmas can effectively degrade pollutants in water by generating various reactive species at the water surface and in the bulk volume [6]. The

efficiency of the treatment process (i.e., degradation efficiency) is thus dependent on the different factors affecting the degradation reactions [24], including the plasma properties. In the case of plasmas in-contact with water, these properties strongly depend on the electrical excitation source. In DC regime [22, 25-27], water may be considered as either cathode or anode, depending on voltage polarity. Meanwhile, when an AC source is used, the water polarity continuously alternates between anode and cathode [20, 28-30]. This induces temporal variations in the discharge within the same cycle and between different cycles, due to the modification of water properties, such as acidity, conductivity, and temperature. Therefore, the repetition rate in AC regime is an important parameter that significantly influences discharge dynamics due to the lasting effects of long-lifetime energetic species, such as metastable compounds and dimers [31].

To investigate plasma-water interactions, researchers often rely on the analysis of plasma behavior at the water surface where emission structuration is observed [22, 30, 32, 33]. Depending on the discharge conditions (DC, AC, gas composition, etc.), various emission structures are identified, including dots and rings, among others. The fundamental analysis of these emission patterns is of great importance due to their effect on the local production and transport of reactive species. The mechanisms involved in the structuration process are not well understood; however, it has been established that oxygen species [34], injected power [30, 32], water polarity [35], and other water properties (composition, acidity, conductivity...) [36] play an essential role in this process.

Previously, we had studied the influence of gap distance (distance between electrode tip and water surface) on the electrical characteristics of an AC air discharge in-contact with water and on the degradation efficiency of methylene blue dye [20]. Herein,

we further investigate this type of discharge by analyzing the plasma emission dynamics in the gap and at the water surface during positive and negative half periods.

2.2 Experimental setup

Figure 2.1 presents a scheme of the experimental setup used in this study. The discharge is sustained in ambient air by applying an AC high voltage between a pin electrode and water. The pin electrode is made of tungsten (diameter = 2 mm, from Goodfellow), and its tip is mechanically polished to a curvature radius of $\sim 50 \mu\text{m}$. The stainless-steel counter electrode (diameter = 15 mm, thickness = 6.5 mm) is placed at the bottom of a cylindrical quartz cell filled with 50 mL of deionized water (initial conductivity $\sim 5 \mu\text{S/cm}$). A micrometer positioning system is used to adjust the air gap distance (d) between electrode tip and water surface from 0.5 to 9 mm.

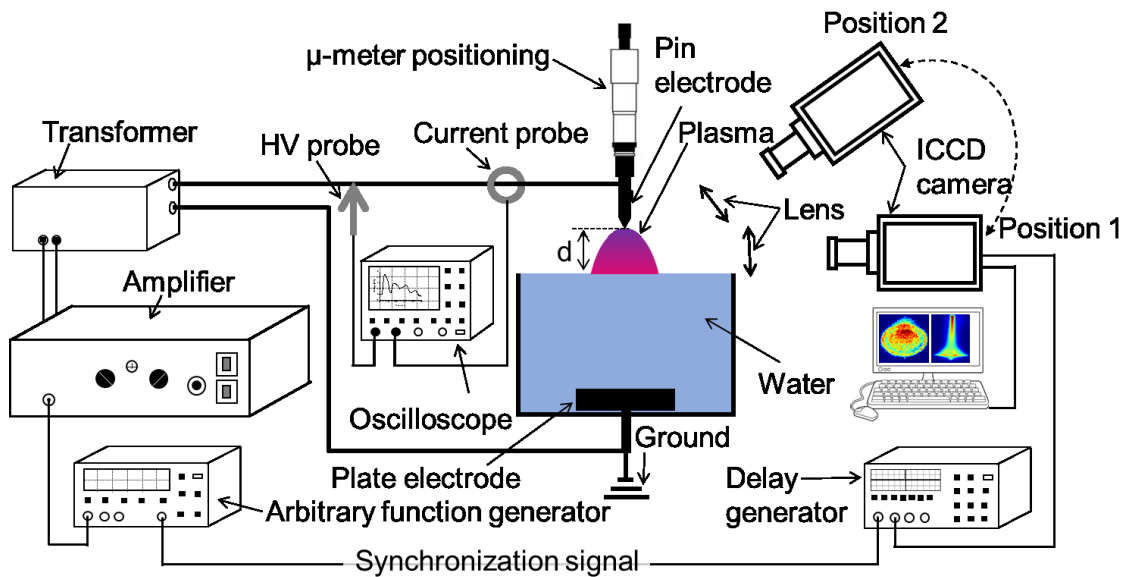


Figure 2.1 -Scheme of the experimental setup.

Both conductivity and acidity of water increase with the plasma processing time. In this study, the experiments are conducted between 5 and 10 minutes of processing, where

water acidity and conductivity are in the range of 2.5-3 pH and 100-300 $\mu\text{S}/\text{cm}$ [20], respectively.

The plasma is generated in ambient air by applying a high voltage sinusoidal AC at a frequency of 10 kHz and a magnitude ($V_{\text{peak-to-peak}}$) of 10 kV. This waveform is predefined and produced using a waveform generator (HP Agilent 33120A) coupled to a linear power amplifier (Crest Audio model 4000) and a transformer (Montoux 600 VA, 60 V/9 kV). The electrical characteristics (voltage (V), current (I), injected charge, energy, and power) of the discharge under various conditions are also investigated. V is measured at the pin using a Tektronix probe (P6015A), whereas I is measured using a Pearson coil (P2877). I and V waveforms are acquired using a Tektronix oscilloscope (DPO5420B), and they are averaged over 16 events. The injected charge and energy were calculated by time integration of the current ($\int I(t)dt$) and of the power ($\int V(t)I(t)dt$), respectively.

Plasma emission dynamics is investigated using an ICCD camera (Andor Technologies DH520 18F) that may be mounted horizontally (i.e., position 1 in Figure 2.1) or obliquely (at 45° angle from horizontal, i.e., position 2 in Figure 2.1) in order to analyze the gap space or the water surface, respectively. We placed a 2-inch convergent lens between the discharge and the camera to magnify the imaged zones. A delay generator (Quantum Composers Plus 9518 Pulse Generator) is used to ensure synchronization and to control the delay time between the camera and the voltage waveform.

2.3 Results

In this section, we examine the electrical characteristics of the discharge, and the behavior of the plasma emission under varying conditions of gap distance and water polarity (cathode or anode). Subsequently, we present the half-period (50 μs) integrated ICCD images of the plasma in the gap space as well as at water surface. Finally, we analyze the temporal evolution (period of 100 μs) of the plasma using ICCD images integrated over 5 or 1 μs . Note that the ICCD images are shown in a false color scale degraded from blue (minimum) to red (maximum). Because the emission intensity may significantly change from a condition to another, we chose to provide the intensity in percentage to make the comparison as fruitful as possible. While the lowest intensity was common (0%), the highest intensity (100%) was observed for a discharge integrated during the first half-period (50 μs) at $d = 0.5$ mm. The intensity of every ICCD image presented here is thus provided in percentage.

2.3.1 Time-averaged characterization of AC air discharge in contact with water

Discharges at water surface produce a system that is spatiotemporally dynamics. Although numerous studies have reported on these discharges, it is still unclear if the discharge is glow (or glow-like) or filamentary. This is because of the many involved factors and parameters, that some of them are controllable but others are not. In this context and based on the available reports (also see the Discussion), it becomes crucial to address (at least qualitatively) the influence of the main controllable parameters. Here, we chose to study the influence of the gap distance on an AC air discharge in contact with water, while keeping the other parameters unchanged. The discharge is characterized electrically, by

measuring I-V waveforms and by calculating its injected charge, energy, and power, and optically, by imaging the plasma emission in the gap space as well as at water surface. As detailed below, the increase of the gap distance from 0.5 to 9 mm highlights a transition in the discharge behavior at 4.5 mm that has a clear signature electrically and optically. These latter characteristics for discharges before and after the transition are thoroughly investigated and the results are detailed hereafter.

2.3.1.1 Water polarity: Cathode

The analyses performed at gap distances varying between 0.5 and 9 mm highlight a transition that occurs at $d = 4.5$ mm, as evidenced by the electrical characteristics, the plasma emission, and the discharge sound. As shown in Figure 2.2a-b, at $d = 1.5$ and 3.5 mm, i.e., before the transition, the voltage increases from 0 to a maximum value (breakdown voltage), then it rapidly decreases to 1.5 kV followed by a slow decrease to 0 kV. As expected, the breakdown voltage increases with d (it is ~ 2.5 kV at $d = 1.5$ mm and ~ 3.2 kV at $d = 3.5$ mm). As for the corresponding current waveforms, they exhibit a rapid increase synchronized with the voltage drop. At $d = 1.5$ and 3.5 mm, the peak current values are ~ 45 and ~ 70 mA, respectively. The similarity between the electrical characteristics recorded at gap distances less than 4.5 mm indicate that before the transition, both discharge ignition and steady state are independent of d .

At $d = 7$ mm, i.e., after the transition, no clear voltage drop is observed, as shown in Figure 2.2c. Moreover, no current peak can be identified at this gap distance, and the waveform is similar to that recorded without discharge (i.e., capacitive current). This is consistent with the observations of Zheng *et al.* [37] for an AC discharge in contact with tap water ($d = 6$ mm and frequency = 7 kHz).

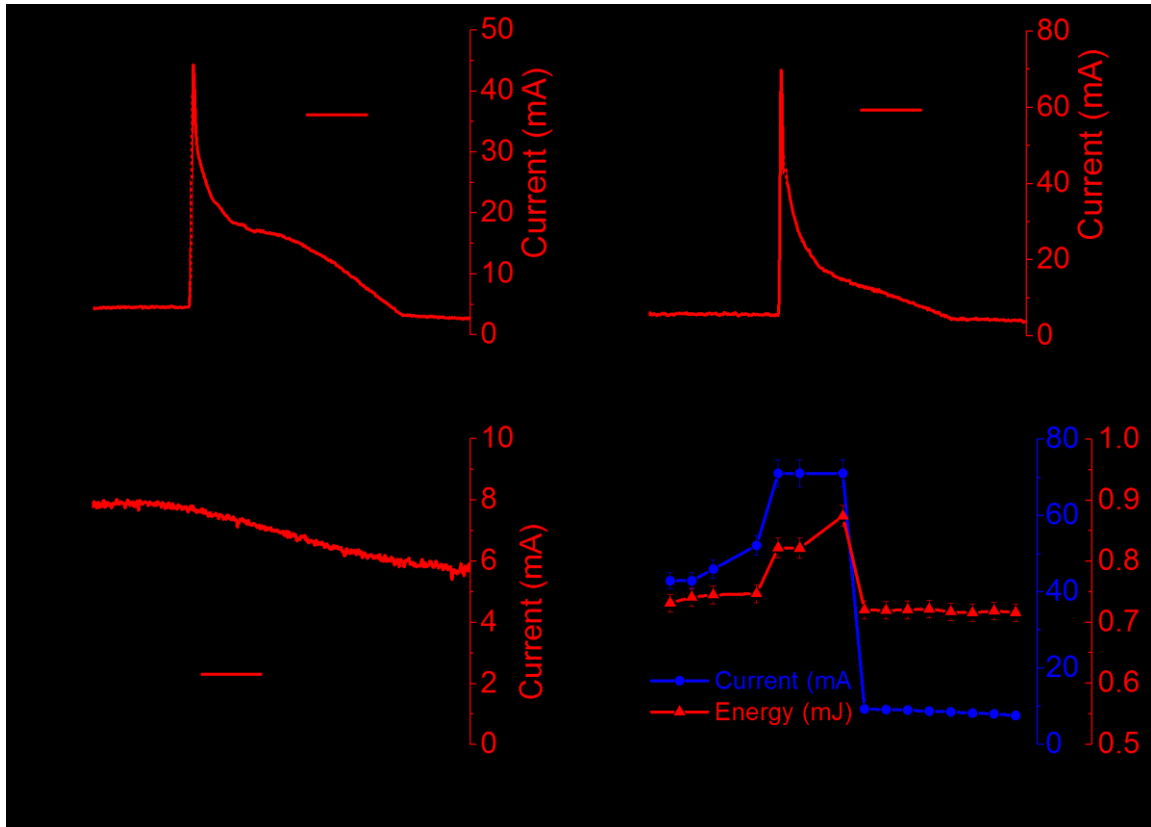


Figure 2.2. Voltage and current waveforms recorded at a) $d = 1.5$ mm, b) $d = 3.5$ mm, and c) $d = 7$ mm during the first half-period (i.e., water as cathode). d) Variation of the injected charge, current peak, and energy as a function of gap distance.

Figure 2.2d presents variations in the current peak, injected charge, and energy of the plasma as a function of d . The presented profiles show that the injected charge slightly decreases as d is increased from 0.5 to 4.5 mm. The decrease is steep ($\sim 0.1 \mu\text{C}$) between 4.5 and 5 mm due to a transition in the discharge behavior. Beyond 5 mm, the injected charge exhibits a quasilinear decrease until it reaches $\sim 0.35 \mu\text{C}$ at $d = 8.5$ mm. As for the current peak, it significantly increases from ~ 40 to 70 mA as d is increased from 0.5 to 4.5 mm, then it sharply decreases to 10 mA at $d = 5$ mm. The current peak value (~ 9 mA) does not appreciably change beyond 5 mm of gap distance. Finally, increasing d from 0.5 to 4.5

mm induces an energy increase in the discharge from ~ 0.7 to ~ 0.9 mJ. Between 4.5 and 5 mm, the energy decreases sharply to 0.7 mJ remaining stable beyond.

Based on the ICCD images illustrated in Figure 2.3a ($0.5 < d < 4.5$ mm, integrated during $50 \mu\text{s}$, i.e., the whole half-period when water is cathode), the shortest distance (0.5 mm) yields the highest intensity (100%) of plasma emission at the electrode tip. It should be noted that the maximum intensity of emission in each image is normalized independently. This intensity decreases to 40% at $d = 4.5$ mm. The dependence of the maximum intensity on d is given in Supplementary material (Figure S1). The spatial emission of the discharge acquired at $d = 0.5$ mm is rather continuous with a hot spot at the anode tip. Away from the tip, the plasma emission expands till it reaches the water surface, and its intensity decreases. Such an expansion at the water cathode surface was previously reported, and it is associated with the spread of charges in this area [25, 30]. Figure 2.3b depicts the edge of plasma emission profiles determined using the threshold method (this method consists of measuring the radius of emission, that approximately corresponds to the transition between the green and the blue region, for each pixel in the gap distance). Although only the right edges are presented, the left ones can be inferred, since the profiles are axisymmetric. Based on the obtained results, the plasma column widens with increasing gap distance, and the emission profile shape is altered from quasi-conical at $d = 0.5$ -1.5 mm to Witch's-hat at $d = 2.5$ -4.5 mm. In fact, it may be assumed that the plasma emission consists of two components: a conical-like emission with a broad base at the water cathode surface and a cylindrical-like emission connecting the top of the cone to the anode tip. At $d = 0.5$ and 1 mm, the plasma-edge profiles are dominated by the conical component; however, at $d \geq 1.5$ mm, the conical and cylindrical components are distinguishable. The

nearly constant slope of the conical component indicates that the base of the plasma at the water surface (length of $\sim 2 \times 0.6$ mm and height of ~ 1 mm) is not significantly affected by gap distance.

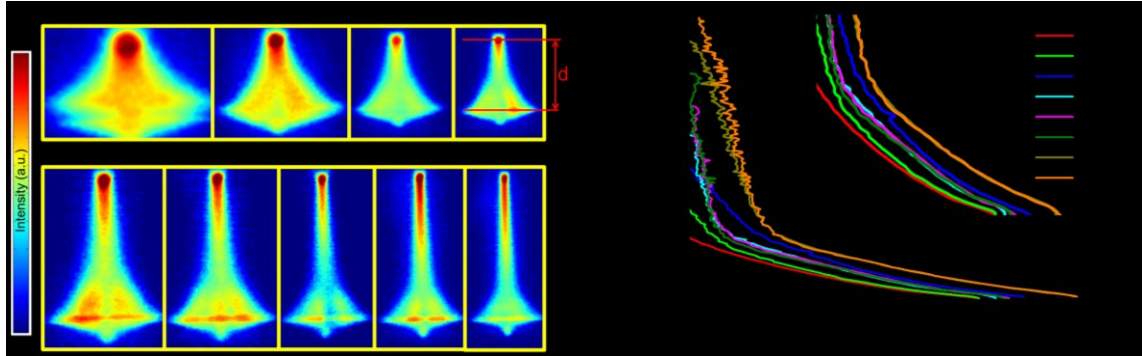


Figure 2.3. a) ICCD images (integrated during the $50 \mu\text{s}$ when water is cathode) of the plasma column emission recorded under various gap distance in the range of 0.5 - 4.5 mm; each image is normalized to a maximum value that is shown in supplementary Figure S1. b) The plasma-edge emission profiles determined using the threshold method.

As mentioned previously, increasing d beyond 4.5 mm induces a transition in the discharge behavior. Figure 2.4 presents the ICCD plasma images recorded at $d > 4.5$ mm and shows that under these conditions, the emission mainly concentrates over distinct zones. Note that the global intensity of plasma emission ($d > 4.5$ mm) is relatively low ($\sim 7\%$), compared to the maximum emission (100%) observed at $d = 0.5$ mm. At the anode tip, the emission is strong and localized. The adjacent zone is dark, and its length increases with increasing d . The dark zone is followed by a bright one that occupies a major part of the gap. The plasma emission in this zone has a divergent geometry, probably due to the non-homogeneous electric field configuration (pin-to-plate), and the emission intensity seems to be high at $d = 7$ and 8 mm, despite the fact that the scale of intensity (from 0 to 7%) could make insignificant changes (e.g., reproducibility) clearly visible. At longer gap

distances, this emission becomes off-axis (see the image recorded at $d = 9$ mm where the dashed white line indicates the electrode axis). A second dark zone precedes a final bright spot at the water cathode surface. The dimensions of this spot are seemingly independent of d .

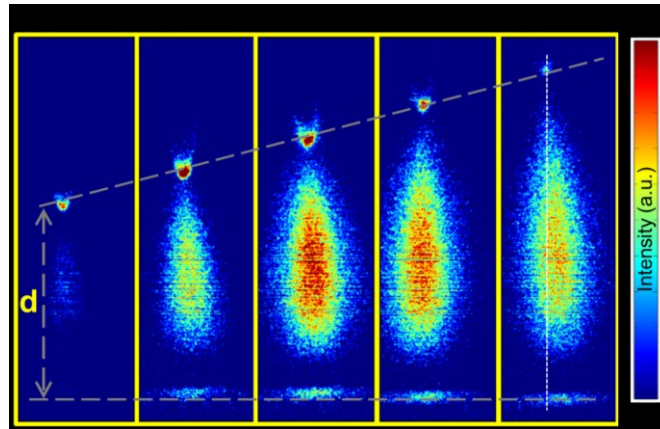


Figure 2.4. ICCD images (integrated during the $50 \mu\text{s}$ when water is cathode) of the plasma column emission recorded under various gap distances in the range of 5-9 mm. The color scale is common for all the images and ranges from 0 to 7%.

2.3.1.2 Water polarity: Anode

The electrical characteristics of the discharge were also recorded during the second half-period, i.e., the $50 \mu\text{s}$ when water acts as anode. The results illustrated in Figure 2.5 show that at $d = 1.5$ mm, the voltage profile only slightly deviates from sinusoidal behavior; however, the voltage values are significantly attenuated (maximum -1.5 kV vs. -5 kV; this latter corresponds to V_{peak}). The current waveform is similar to that of voltage, and the peak value of ~ -15 mA. Unlike the electrical characteristic recorded at $d = 1.5$ mm under cathode water polarity, the corresponding profiles measured during the second half-period do not exhibit a voltage drop or a sharp current peak. The water anode profiles measured

at $d = 3.5$ mm are similar to those determined at $d = 1.5$ mm, but with higher voltage amplitudes (maximum ~ -1.8 kV). Finally, at $d = 7$ mm, i.e., after the transition, the current and voltage waveforms recorded under water anode polarity are similar to those determined under cathode polarity, except for the voltage-drop and current peak values. Here, one measures a voltage drop of ~ 0.8 kV and a current peak of ~ -18 mA. The voltage drop observed in this condition may be attributed to the lack of breakdown in the first half-period (Figures 2.2c and 2.4), where the accumulated charges on water surface seems to be insignificant to facilitate the discharge occurrence through, e.g., memory effect phenomenon.

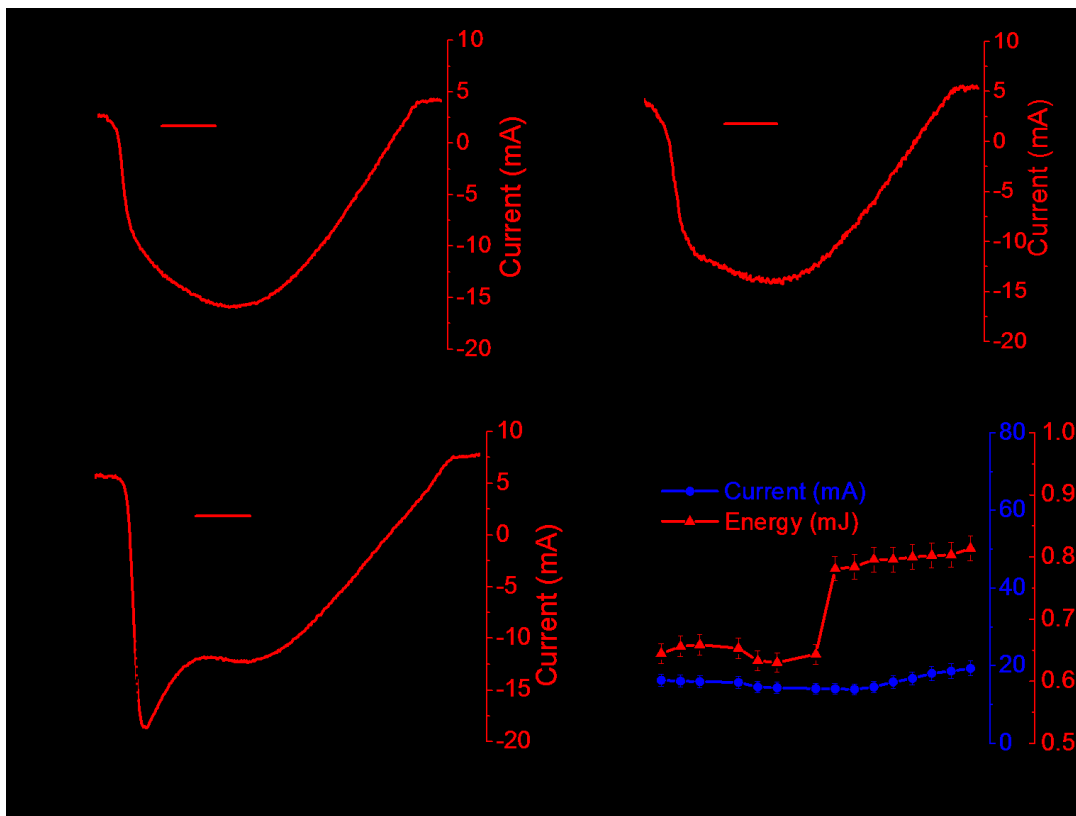


Figure 2.5. Voltage and current waveforms recorded at a) $d = 1.5$ mm, b) $d = 3.5$ mm, and c) $d = 7$ mm during the second half-period (i.e., water as anode). d) Variation of the injected charge, current peak, and energy as a function of the gap distance.

Figure 2.5d presents variations in the current peak, the injected charge, and the energy in the plasma as a function of d . The injected charge decreases by $\sim 0.08 \mu\text{C}$ (80 nC) as d is increased from 0.5 to 4.5 mm. Between 4.5 and 5 mm, sharply increases by ~ 70 nC due to a transition in the discharge behavior. Further increasing d beyond 5 mm results in a quasilinear decrease of the injected charge until it reaches $\sim 0.4 \mu\text{C}$ at $d = 8.5$ mm. As for the electrical current, its peak value (~ 15 -20 mA) is practically independent of d in the range of 0.5-8.5 mm. Finally, the energy is ~ 0.65 mJ in the gap distance range of 0.5-4.5 mm and ~ 0.8 mJ in the range of 4.5-8.5 mm.

The ICCD images (integrated during the $50 \mu\text{s}$ when water is anode) as a function of d are presented in Figure 2.6. At shorter distances (0.5 mm), the intensity is relatively low (40%), while the highest intensity (90%) is observed at $d = 4.5$ mm. Such an increase in intensity cannot be readily explained based on the electrical characteristics acquired during this second half-period, but it does when coupled with those acquired during the first half-period (Figure 2.2). Indeed, the increase of d is accompanied by an increase of the breakdown voltage and current peak, i.e., a power peak. This peak of power can significantly heat the electrode tip and makes the emission of electrons (once the pin polarity becomes cathode) as well as of the plasma relatively high. Although this explanation requires further investigations (e.g., by changing the material of the pin), we note that the electrode pin becomes orange red, as observed by a necked eye during experiments. Here also, we note that the maximum intensity of emission in each image is normalized independently. The dependence of the maximum intensity on d (in the range 0.5-4.5 mm) is given in Supplementary material (Figure S2). However, for larger gaps ($5 < d < 9$ mm), the maximum intensity is fixed at 80%.

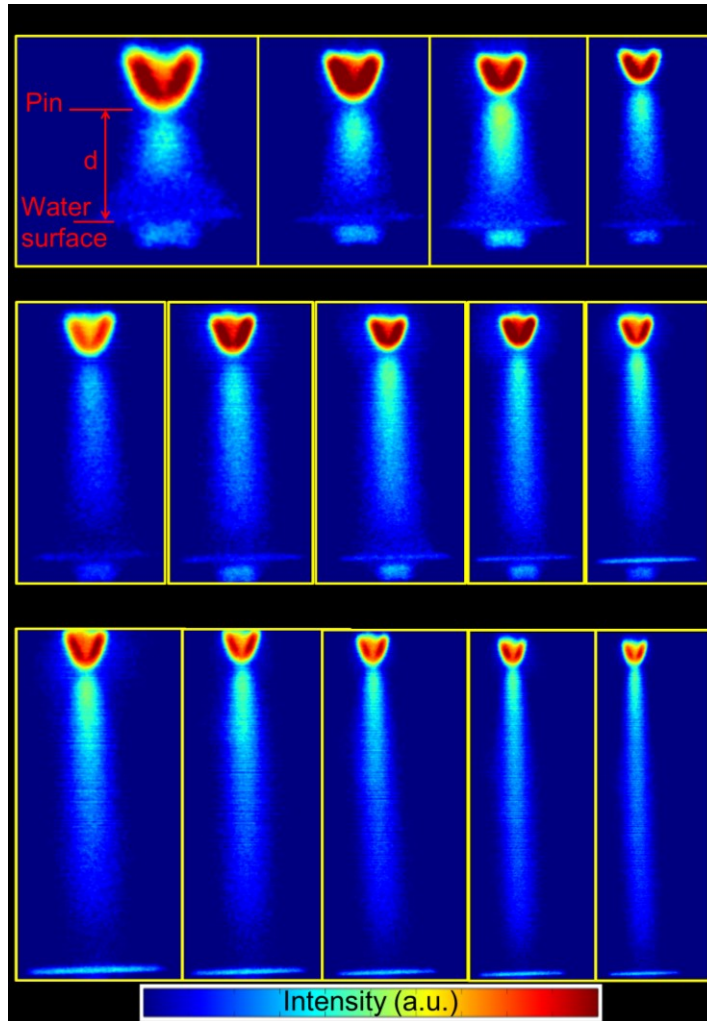


Figure 2.6. ICCD images (integrated over $50 \mu\text{s}$ when water is anode) of the plasma column emission recorded under various gap distances in the range of a) 0.5 - 4.5 mm and b) 5-9 mm. Each image in a) is normalized to a maximum value that is shown in supplementary Figure S2, while images in b) have a common scale that ranges from 0 to 80%.

Overall, the ICCD images show that the emission intensity at the cathode pin is relatively high (cathode spot) compared to that in the gap or at the water surface. At $d \leq 1.5 \text{ mm}$, the plasma emission has a conical shape and looks rather continuous in the gap, despite a significant variation in intensity. In the range of 2-9 mm, the plasma emission is

well developed in the gap with an almost constant diameter. Moreover, a dark zone appears above the bright spot at the water anode surface.

2.3.1.3 Plasma emission at the water surface

The plasma imaging in the gap space reveals a localized emission at the water surface. The morphology of the emission at the water surface is investigated with the ICCD camera oriented at 45° angle with the horizontal. Figure 2.7 depicts the images of plasma emission at the water surface under cathode water polarity. In the range of 0.5-4.5 mm (the maximum intensity is 20%), the plasma is filamentary, and its intensity decreases by increasing the gap distance. Between 4.5 and 5 mm, i.e., during the transition, the emission intensity exhibits a sharp decrease until practically no emission can be observed on the same intensity scale (20%) (see the inset in Figure 2.7 at $d = 5$ mm). However, upon adjusting the maximum intensity to 1%, a large homogeneous disc-like emission becomes evident, as shown in Figure 2.7. Further increasing d to 9 mm results in a strong intensity decrease until the emission is too low to be detected at $d > 9$ mm (i.e., the plasma extinguishes).

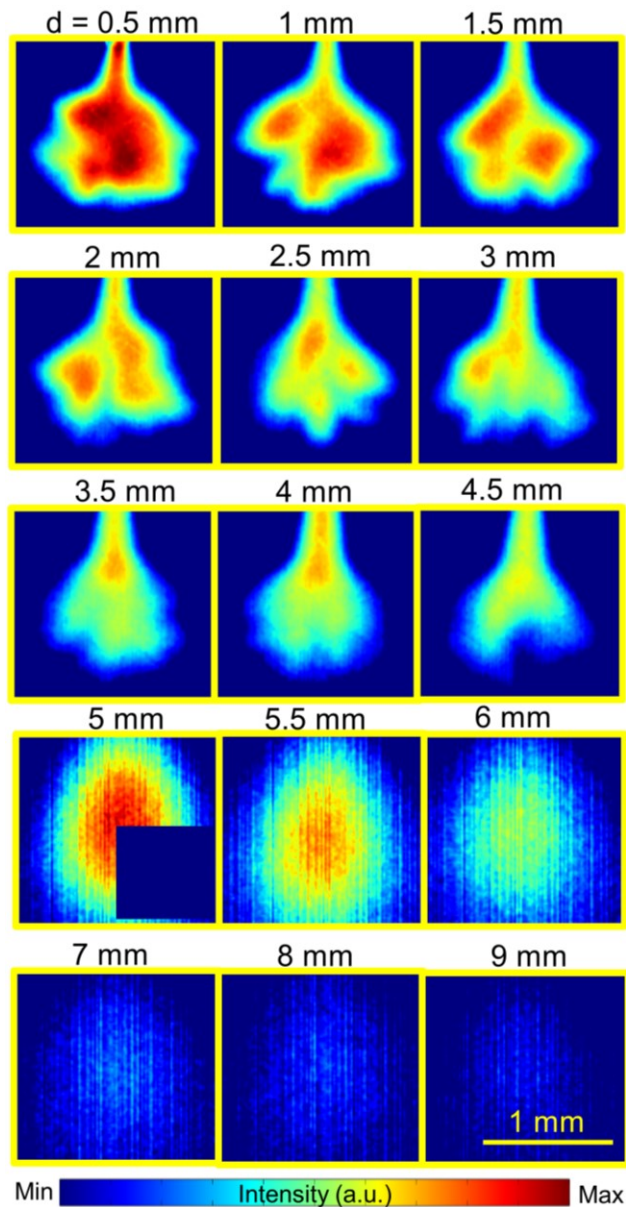


Figure 2.7. ICCD images (integrated during the $50 \mu\text{s}$ when water is cathode) of the plasma emission at the water surface recorded under gap distances in the range of 0.5 - 9 mm. The maximum intensity is 20% and 1% for images recorded at $0.5 < d < 4.5 \text{ mm}$ and $5 < d < 9 \text{ mm}$, respectively. The inset at $d = 5 \text{ mm}$ shows the same image at maximum intensity of 20%.

The ICCD images in Figure 2.8a show that the plasma emission under water anode conditions behaves completely differently than that observed when water is cathode.

Indeed, the plasma is more homogeneous with a disc-like shape during this second half-period (water is anode). At $d = 0.5$ mm, the disc-like emission has low intensity and is superimposed to the plasma column above the water surface (the emission from the column and/or the tip are visible). As d increases to 4 mm, the intensity of the disc-like emission increases, while that of the column decreases. At $d = 4.5$ mm, the emission becomes structured, and the initially homogeneous disc breaks down into a smaller disc surrounded by a ring. When d is increased beyond 4.5 mm, the plasma emission maintains its structure, with the outer ring further separating from the inner disc. For comparison purposes, the horizontal profiles of plasma emission at the water surface were extracted and plotted. As shown in Figure 2.8b, increasing d between 0.5 and 2 mm enhances the development of the disc emission (slight increase in diameter); however, beyond 2 mm, the diameter of the total emission does not significantly change. For $d \geq 4$ mm, it is possible to distinguish between the outer ring and the inner disc emissions. At $d = 9$ mm, further breakdown in the emission structure is noticed, wherein the inner disc decomposes into another ring. However, the spatial resolution is not good enough to be more specific about this observation.

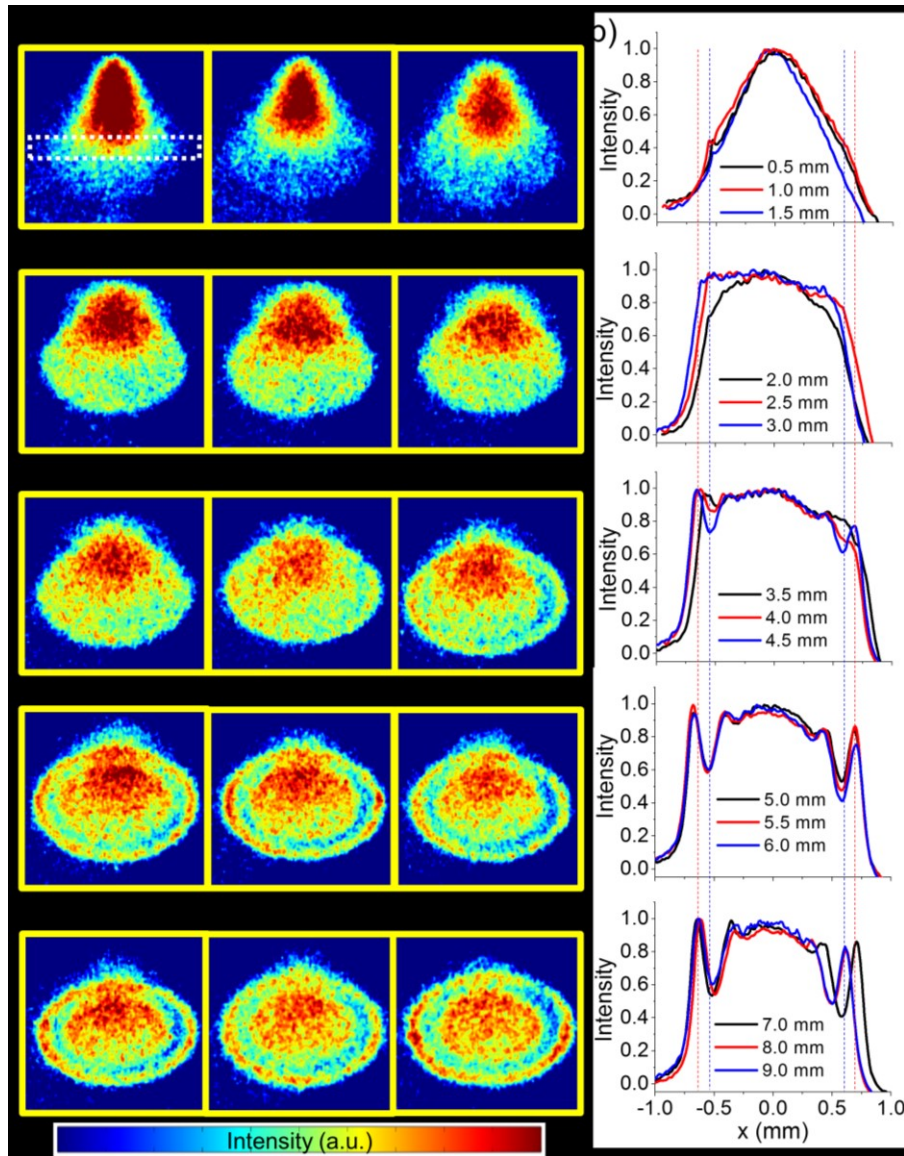


Figure 2.8. a) ICCD images (integrated during the $50 \mu\text{s}$ when water is anode) of the plasma emission at the water surface recorded under various gap distances in the range of 0.5 - 9 mm (the maximum intensity is 40%). b) Normalized horizontal profiles extracted from the ICCD images (specifically, the area marked by a white-dashed rectangle in the $d = 0.5 \text{ mm}$ image).

2.3.2 Time resolved imaging of AC air discharge in contact with water

In this section, we present and discuss the temporal evolution of the discharge under anode and cathode polarities of water and at $d = 3$ and 5 mm (i.e., before and after the transition in discharge behavior).

The ICCD images (integrated over a period of $5 \mu\text{s}$) in Figure 2.9 show that when water is cathode (time between 0 and $50 \mu\text{s}$) and $d = 3$ mm, no plasma emission occurs before the voltage drop (~ 3.5 kV at $17.5 \mu\text{s}$). Once the drop is attained, a strong non-homogeneous emission is detected in the entire gap. As mentioned previously, two components of the plasma can be discerned, namely, column and cone-like emission. After $5 \mu\text{s}$ of strong emission, the intensity significantly decreases until emission vanishes at $40 \mu\text{s}$. Emission at the water surface is also concurrent with the voltage drop, and its intensity decreases with time until $40 \mu\text{s}$ where it also vanishes.

When the water polarity is switched to anode (time between 50 and $100 \mu\text{s}$), the plasma emission is instantaneously reinitiated in the gap, as well as at the water surface. It is worth noting that the emission distribution along the gap, beyond the tip, is rather homogeneous. This is also valid for the emission at the water surface, where a homogeneous disc-like plasma is observed. With time, the global morphology of the plasma in the gap space does not significantly change, but its intensity keeps on increasing up to $85 \mu\text{s}$. However, at the water surface, the intensity remains almost the same, the disc diameter increases during the first $15 \mu\text{s}$, and a ring is formed between 75 and $85 \mu\text{s}$. Beyond $85 \mu\text{s}$, the plasma emission intensity in the gap, as well as at the water surface, decreases appreciably, with only minor emission observed at the cathode tip.

As shown in Figure 2.9, I - V waveforms are superimposed with the ICCD images in order to provide a better understanding of plasma emission temporal variation. To account for both electrical characteristics at the same time, the power was plotted in the same graph. Interestingly, the data show that plasma emission occurs at powers greater than ~ 15 W. Under cathode water polarity conditions, a power peak of ~ 250 W takes place simultaneously with the voltage drop and with the observation of high plasma emission intensity. Thereafter, the power rapidly decreases to less than 15 W at $t > 30 \mu\text{s}$, which matches the evolution of plasma intensity. The lack of a voltage-drop and current peak in the case of anode water polarity renders the power almost constant (15-20 W) between 55 and 80 μs , the time period during which the plasma emission is relatively high. Based on these results, it may be concluded that power and emission are correlated, and that the minimum power needed for plasma emission in the gap is ~ 15 W. Zheng et al. [37] have also suggested that the two parameters are related to each other, and they even established a mapping that links discharge power to discharge shape (further discussion can be found below).

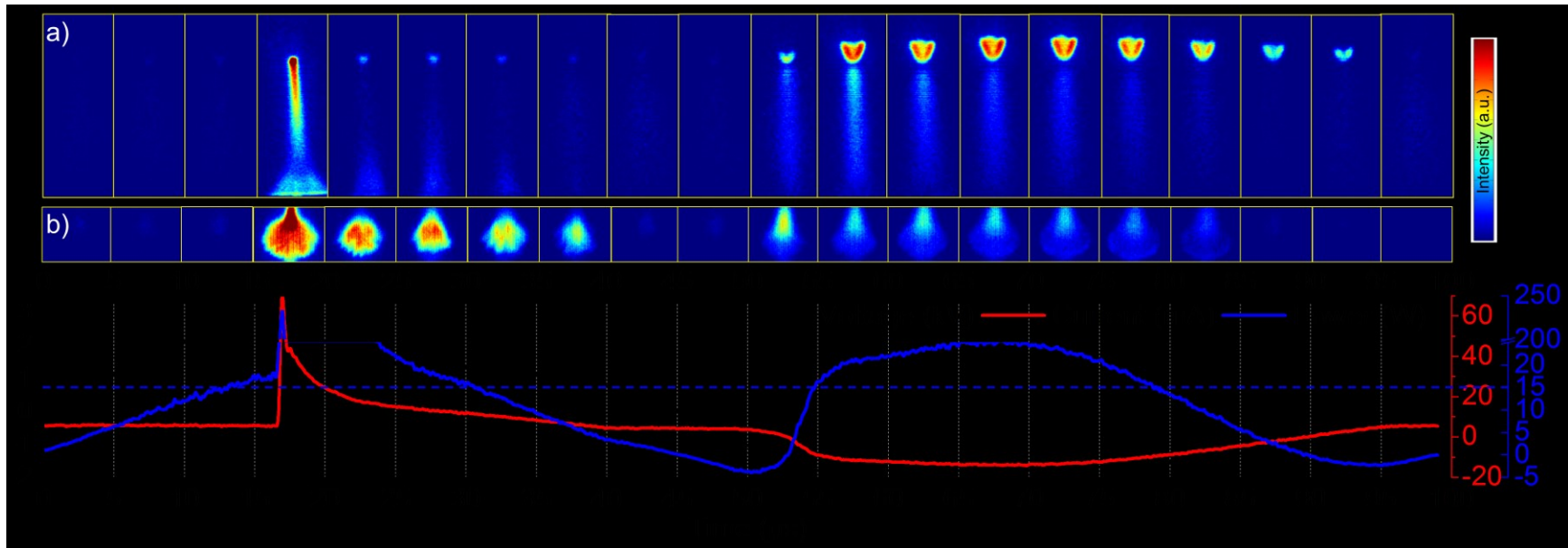


Figure 2.9. ICCD images (integrated during $5 \mu\text{s}$) showing the temporal evolution of the plasma a) in the gap (maximum intensity is 50%) and b) at the water surface (maximum intensity is 15%) over a whole period for $d = 3 \text{ mm}$. c) Electrical characteristics (voltage, current, and power) corresponding to the ICCD images.

The temporal evolution of plasma emission was also studied at $d = 5$ mm. The resulting ICCD images (integrated over a period of $5 \mu\text{s}$) depicted in Figure 2.10 show that when water is cathode, emission is observed very early on at the anode tip. With time, the intensity of this emission increases. As for the minor emission observed in the gap between 10 and $15 \mu\text{s}$, its intensity, length, and width increase with the time. Surprisingly, the plasma does not extinguish at the end of the first half-period, unlike the emission detected at $d = 3$ mm. Instead, the plasma column keeps on expanding and increasing in intensity until it fills the entire gap. At the water surface (Figure 2.10b), the situation is very similar, with a minor emission observed at 10- $15 \mu\text{s}$, and stronger emissions being detected later. The emission intensity keeps on increasing with time until a homogeneous disc-like structure is attained at the end of the first half-period. Analysis of the electrical characteristic profiles (voltage, current, and power) presented in Figure 2.10c shows that emission in the gap is generally associated with a power threshold of 15-20 W. However, at $\sim 40 \mu\text{s}$, the emission intensity continues to increase despite nil power. This suggests that another physical phenomenon is implicated in maintaining the plasma at this time, e.g., the release of charges accumulated at the water surface. Similarly, during the last $5 \mu\text{s}$ in the half-period, the power is -10 W (negative power because the voltage is negative and the current is positive) and yet, the emission intensity is high and fills the whole gap, probably due to the pending switch in voltage polarity.

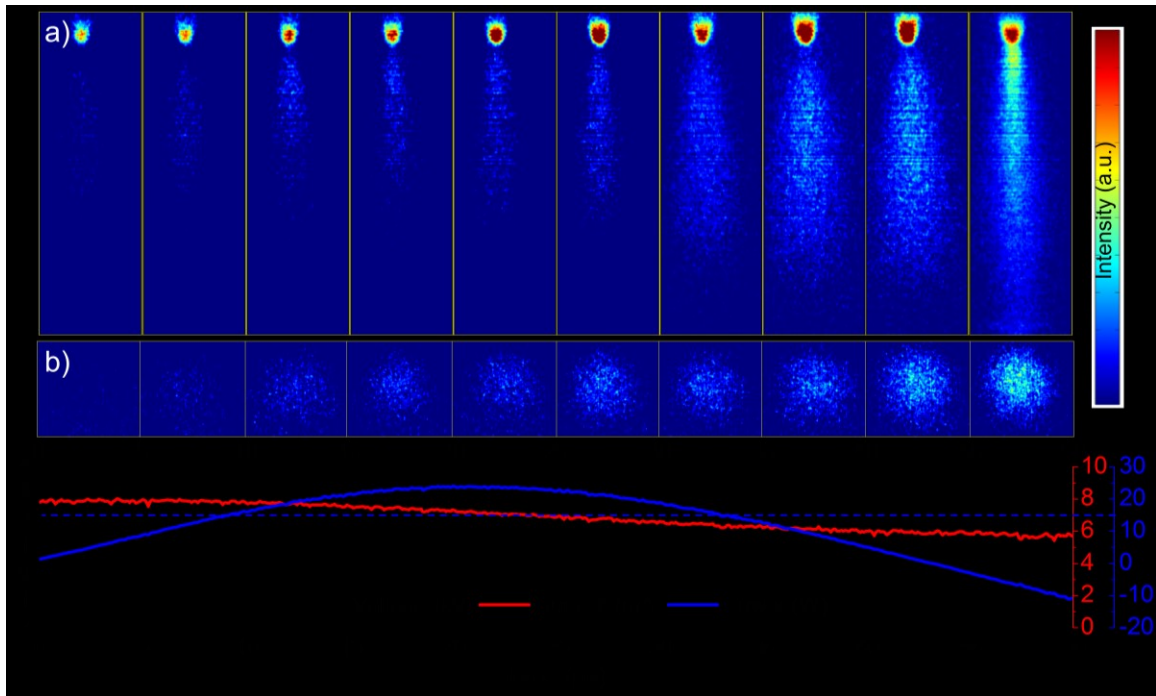


Figure 2.10. ICCD images (integrated during $5 \mu\text{s}$) showing the temporal evolution of the plasma a) in the gap (maximum intensity is 7%) and b) at the water surface (maximum intensity is 7%) during the first half-period (when water is cathode) for $d = 5 \text{ mm}$. c) Electrical characteristics (voltage, current, and power) corresponding to the ICCD images.

As shown in Figure 2.11, when the water is anode and $d = 5 \text{ mm}$, the emission in the gap is strong at the beginning due to the early switch in polarity towards the end of the first half-period. Between 50 and $80 \mu\text{s}$, the emission intensity in the gap remains high; however, it significantly decreases beyond $80 \mu\text{s}$. The threshold power associated with this emission is $\sim 15 \text{ W}$. Strong plasma emission is also observed at the water surface (Figure 2.11b) during the first $5 \mu\text{s}$ (50 - $55 \mu\text{s}$), when a power peak of $\sim 45 \text{ W}$ appears. The morphology of the emission at this time is not well defined, as it is neither filamentary nor disc-like. After the first five microseconds, the emission intensity of the plasma significantly decreases, and it begins to take the shape of a homogeneous disc. This disc

breaks down into an outer ring and a smaller inner disc in the time between 65 and 70 μs , with a slight increase in intensity. Interestingly, the outer diameter of the ring is practically the same as that of the original disc. Beyond 70 μs , the emission intensity gradually decreases, and a second breakdown of the inner disc is detected at 85-90 μs , despite the relatively low intensity. At 90-95 μs , the emission of the outer ring looks discontinuous, and it significantly decreases during the last 5 μs in the time period. The analysis of electrical characteristics corresponding to plasma emission at the water surface confirms the correlation between power and intensity. Between 65 and 70 μs , a second power peak is distinguished. Although this peak is relatively small compared to that observed at ~ 53 μs , it is clearly concurrent with an increase in emission intensity above the surface.

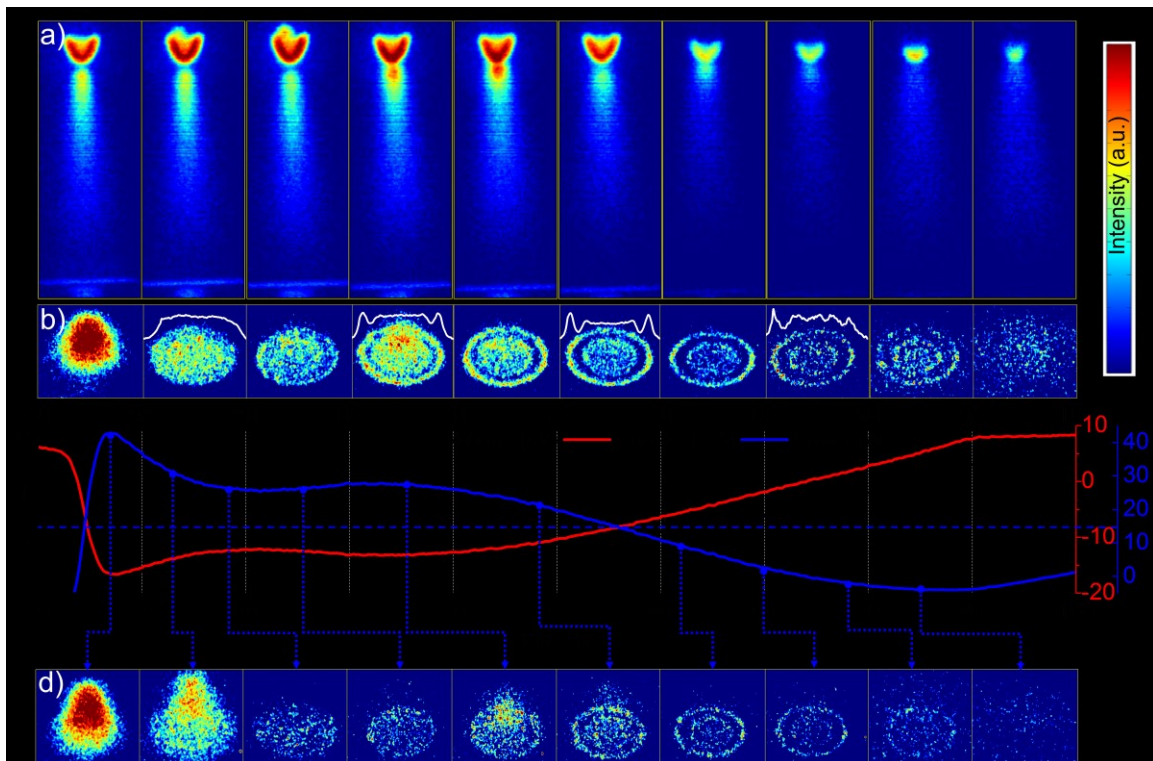


Figure 2.11. ICCD images (integrated during 5 μs) showing the temporal evolution of the plasma a) in the gap (maximum intensity is 35%) and b) at the water surface (maximum intensity is 20%) during the second half-period (when water is anode) for $d =$

5 mm; the white lines superimposed to the images are the horizontal profiles. c) Electrical characteristics (voltage, current, and power) corresponding to the ICCD images. d) 1- μ s-integrated ICCD images of the plasma at the water surface (maximum intensity is 10%) acquired at specific times during the half-period.

To enhance the temporal resolution of the acquired ICCD images, the acquisition time was reduced to 1 μ s, as shown in Figure 2.11d. Despite the relatively low intensity of these images, it is possible to identify some transitions of interest. For instance, beyond the first power peak, the emission disc becomes more clearly defined, and the intensity above it decreases. Similarly, the intensity and reillumination above the disc increase during the second power peak. Unfortunately, it is not possible to confirm whether or not the ring is composed of discrete spots.

2.4 Discussion

Numerous studies have investigated the morphology of plasma emission at the water surface or in the gap between the electrode and water. The results obtained using a DC excitation source show that the emission dynamics is time independent over short timescale (few minutes), and that temporal variations in water properties, such as conductivity, acidity, and temperature, can be neglected. To understand the influence of water polarity, Bruggeman et al. [35] studied the electrical and optical characteristics of an air discharge between a metal pin and tap water under both, water anode and water cathode conditions. Their results indicate that when water is cathode, the plasma is filamentary at the water surface. However, under water anode conditions, the discharge is glow, and the plasma is diffuse. Zhang et al. [36] investigated the structure and properties of an air discharge in contact with various electrolytes (water with HCl, HF, or H₂SO₄), and they

always observed a dark zone above the electrolyte surface, irrespective of its nature. The observations of Zhang et al. [36] are consistent with those of Liu et al. [30], as well as with the ICCD images recorded herein under anode water polarity conditions. According to Miao et al. [32], plasmas generated using a DC source and anode water generally have a conical (umbrella-like) shape. However, this morphology depends on various experimental parameters, including air gap distance, cathode dimension, and water conductivity. For example, an increase in the electrical current (from 0.8 to 2.5 mA), a decrease in electrical conductivity (from ~ 37 to ~ 3 $\mu\text{S}/\text{cm}$), or a decrease of the cathode diameter (from 7 to 2 mm), ultimately reduces the plasma-umbrella diameter and shifts the structure from hollow to filled. At this stage, it is clear that the morphology and properties (not investigated here, but related studies can be found in [28], [35]–[37]) of the plasma are highly sensitive to numerous controlled (e.g., voltage-current, electrode geometry, gap distance, etc.) and uncontrolled parameters (e.g., local conductivity, local temperature, time evolution, etc.).

In this study, the electrical characteristics are kept unchanged, and the measurements are performed over a relatively short period of time in order to limit the temporal evolution of the discharge. This ensures that all variations in plasma morphology observed herein are attributed solely to changes in gap distance and water polarity. The data determined using AC discharge at 10 kHz can be directly compared to the DC emission morphology reported by Bruggeman et al. [35] in each half period. This is due to the fact that a half period of 50 μs is long enough to reach a stationary state of the discharge. Similarly, we can assume that for long half periods, the properties (composition, temperature, density, etc.) of AC plasmas are comparable to those of DC plasma. To validate this hypothesis, we calculated the temperatures and electron density of the AC

plasma investigated herein (data not shown here) and found that the values agree well with those reported in the literature for DC plasmas (electron density of $\sim 10^{14} \text{ cm}^{-3}$, gas temperature of $\sim 3000 \text{ K}$, and electron temperature of $\sim 0.5 \text{ eV}$). On the other hand, as shown by Miao et al. [32], emission plasma morphology is strongly sensitive to experimental parameters, but the plasma shape obtained here is always filled-like when water is anode. Furthermore, our data highlights a transition in discharge behavior at $d = 4.5 \text{ mm}$ and a structuration of the emission at the water surface for $d \geq 4.5 \text{ mm}$. Such a structuration has not been reported by Miao et al. [32]; however, they were observed by Bruggeman et al. [35] for discharge currents $< 20 \text{ mA}$. The inconsistencies between plasma emission morphologies reported in different studies may thus be attributed to variations in the electrical current (1-3 mA in [32], 5-30 mA in [35], and 15-20 mA in this study).

In AC discharge mode, the voltage and current change simultaneously, and the water polarity alternates. Therefore, in order to fully understand the dynamics of this discharge, it is necessary to study its temporal evolution. Few studies are available in the literature regarding the dynamics of AC plasma emission in the gap and at the water surface. In one of these studies, Liu et al. [30] used a setup very similar to our own to analyze plasma behaviour in the gap at different moments within the period. By manipulating the discharge conditions, the authors were able to sustain it before the transition, where voltage breakdown is observed during the two half periods (similar to the $d < 4.5 \text{ mm}$ case in our study). The resulting variations in plasma emission intensity are similar to those reported herein for gap distances in the range of 2-4.5 mm (typical case is shown in Figure 2.9). During the positive half cycle (water as cathode), Liu et al. observed bright emission, identified as anode glow, close to the tip, as well as a bright layer,

identified as negative glow, near the water surface. Meanwhile, during the negative half cycle (water as anode), only the bright zone at the tip was detected. Similar observations are recorded herein for $d < 4.5$ mm; however, when d exceeds 4.5 mm, the plasma emission in the positive half-period is strongly reduced, while that in the negative half-period remains high. Moreover, a bright structured emission zone appears at the water surface when water is anode and d is greater than 4.5 mm (Figure 2.11). Such behavior has also been observed by Zheng et al. [37] who show that the morphology plasma emission at the water surface is strongly affected by experimental conditions. To represent the correlations between plasma structure and various discharge parameters, the authors established a mapping that depicts the effects of power, frequency, and gap distance in the ranges of 5-35 W, 5-14 kHz, and 4-11 mm, respectively. Our data partially fits this map, with some inconsistencies that may be attributed to the author's use of averaged power along a period and 40-ms-integrated plasma patterns at the water surface (i.e., over many periods). This confirms the importance of temporal evolution data (integration time of 1 and 5 μ s) in establishing a correlation between plasma structure at the water surface and instantaneous power. Based on our results, the plasma structure does indeed change with time, and it takes the shape of a homogeneous disc at high instantaneous power (~ 45 W, Figure 2.11). This disc may break into single-or double-ring-like structures, depending on the gap distance.

To further assess the influence of power, the plasma pattern at the water surface was monitored at lower frequency (5 kHz). The ICCD images recorded at an integration time of 100 μ s show that when water is anode and d is less than 6 mm, the emission at the water surface takes the shape of a homogeneous disc (Figure 2.12), similar to the one

observed at 10 kHz. Beyond 6 mm, the plasma becomes structured, with peripherals that depend on d and, thus, on power. At $d = 6$ mm (~ 30 W of power), the structure is flower-like, and at 7 mm (~ 32 W of power), spots appear at the edge of this structure. When d is further increased to $d = 8$ mm (~ 33 W of power), the flower-like morphology disappears and only the spots remain. At $d = 9$ mm (~ 34 W of power), the spots are replaced by a ring-like structure, similar to the one observed at 10 kHz. This structure is maintained at $d \geq 10$ mm, but its radius decreases, despite the slight increase in power.

As mentioned earlier, the global plasma emission is actually the sum of two components; one in the gap and the other at the water surface. Increasing d modifies the power distribution between these two components, thereby changing the plasma structure at the surface. However, this change is different than that proposed by Zheng et al. [37]. Previous reports confirm that a DC-sustained discharge usually leads to the formation of dots, ring-like, and homogeneous disc-like structures at high (~ 27 W), intermediate (~ 15 W), and low (10 W) power, respectively [35, 36]. Therefore, the use of total discharge power to explain changes in plasma morphology at the water surface under varying gap distances is misleading. Even when d is kept constant, the temporal evolution of the discharge may also influence the percentage of power consumed in the gap and at surface.

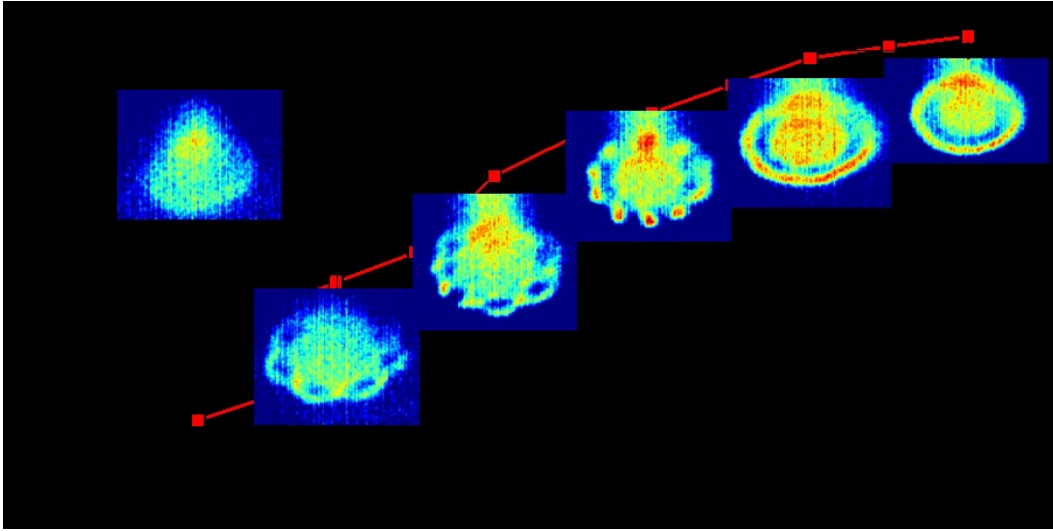


Figure 2.12. *The evolution of power as a function of the gap distance for a discharge generated at 5 kHz. The ICCD images (integrated during 100 μ s, i.e., half-period when water is anode) show the corresponding structures of the plasma at the water surface.*

These findings, along with those reported in the literature, confirm that discharges generated under the conditions investigated herein are highly sensitive to external parameters, including those not investigated here such as solution acidity, conductivity, and temperature. Also, water surface may be deformed under the action of an electric field, especially during discharge ignition, which could influence the whole discharge dynamics. Water evaporation is another important factor that its influence on the discharge should be addressed, e.g., by investigating the discharge behavior at the surface of a water-controlled temperature. Despite the simplicity and applicability of these discharges in various fields, their dynamics and dependence on various operating conditions remain unclear.

2.5 Conclusion

This study investigates the spatiotemporal dynamics of plasma emission in the gap between an electrode and water, as well as at the water surface. Specifically, the effects of gap distance (d) and water polarity on the morphology of AC-sustained plasma are investigated. Depending on d , a transition in discharge behavior is observed at $d = 4.5$ mm. At $d < 4.5$ mm, the discharge is characterized by voltage drop during the positive and negative half-periods, i.e., when water is cathode and anode, respectively, while at $d > 4.5$ mm, the discharge exhibits voltage breakdown only when water is anode. When d is shorter than 4.5 mm and the water polarity is cathode, the plasma emission in the gap consists of two components: a conical-like structure at the water surface and a cylindrical-like one connecting the top of the cone to the electrode pin. Meanwhile, when water is anode, strong plasma emission is observed at the electrode pin and a disc-like structure appears at the water surface at $d < 4.5$ mm. Increasing the gap distance beyond 4.5 mm induces plasma structuration at the water surface, wherein a ring centered by a homogeneous disk is detected. The temporal evolution of the plasma in the gap and at the water surface is also analyzed, and a relationship between plasma structuration and instantaneous injected power is proposed.

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Chapitre 3 – Characterization of various air plasma discharge modes in contact with water and their effect on the degradation of reactive dyes

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ORIGINAL PAPER



Characterization of Various Air Plasma Discharge Modes in Contact with Water and Their Effect on the Degradation of Reactive Dyes

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Résumé

Les plasmas en ou en-contact avec les liquides sont des technologies qui ont un grand potentiel pour des applications de traitement des liquides. La production d'espèces hautement réactives rend les plasmas efficaces pour l'élimination de polluants qui sont difficiles à éliminer lors de l'utilisation de méthodes conventionnelles. Dans cette étude, nous investiguons un plasma d'air en contact avec l'eau produit par un signal d'excitation électrique en courant alternatif AC, générant 5 modes de décharges. Les mode 1, 2 et 3 sont produits à une distance inter-électrode de 1, 3 et 5 mm, respectivement, en utilisant un signal sinusoïdal de fréquence 10 kHz et une amplitude de tension 5 kV. La polarité de l'eau alterne entre cathode et anode dans les modes 1 et 2, tandis que pendant le mode 3 l'eau est seulement anode. Le mode 4 est similaire au mode 1, mais avec un signal sinusoïdal de fréquence 5 kHz. Le mode 5 est similaire au mode 3, mais sans la montée en tension précédant la décharge lorsque l'eau est anode. Les caractéristiques électriques de chacun des modes de décharge sont présentées en détail, et les variations des propriétés de l'eau, telles que l'acidité et la conductivité, sont discutées. L'effet du mode de décharge sur le taux de dégradation du méthylène bleu (MB), un polluant standard, est aussi étudié. Les modes 1, 2 et 4 montrent une efficacité comparable de dégradation du MB, indiquant que le taux de dégradation ne dépend ni de la distance inter-électrode ni du nombre de décharges. La différence entre l'efficacité obtenues entre les modes 3 et 5 suggère un effet substantiel du champ électrique appliqué entre deux décharges successives.

Mots-clés: interface plasma-eau; mode de décharge; traitement de l'eau; dégradation du méthylène bleu.

Abstract

Plasma in or in-contact with liquid is an emerging technology that has high potential for use in liquid treatment applications. Due to the simultaneous production of highly reactive species, plasmas can efficiently eliminate pollutants that are difficult to remove using conventional methods. In this study, we investigate an AC-driven air plasma in contact with water, generated using five discharge modes. Modes 1, 2, and 3 are run at air-gap distance of 1, 3, and 3.5 mm, respectively, at a repetition rate of 10 kHz (sinusoidal waveform). Water polarity alternates between cathode and anode in modes 1 and 2, whereas mode 3 produces anode polarity only. Mode 4 is similar to mode 1, but with a repetition frequency of 5 kHz, while mode 5 is similar to mode 3, but without the high-voltage preceding discharge when water is anode. The electrical characteristics of each discharge mode are presented in detail, and variations in water properties (namely water acidity and conductivity) are also discussed. The effect of discharge mode on the degradation rate of methylene blue (MB), a standard pollutant, is also investigated. Modes 1, 2, and 4 exhibit comparable MB degradation efficiencies, indicating insignificant dependence neither on air-gap distance or number of discharges. The difference between the efficiencies obtained using modes 3 and 5 suggests a substantial effect of the electric field applied between two successive discharges.

Keywords: plasma-water interface; discharge mode; water treatment; methylene blue degradation.

3.1 Introduction

Water treatment is a research field that has been investigated from various angles and by different disciplines, physics, chemistry, biology, and engineering. Studies concerning this subject have been very useful in developing and advancing water treatment plants and technologies. However, despite substantial efforts, it is still difficult to eliminate certain pollutants from wastewater (see *e.g.*, Reference [1] and references therein), particularly those originating from highly-persistent organic industrial rejections (*i.e.* pharmaceutical residual, drugs, pesticides, herbicides, hormones, microbiological pollutants, nanomaterials, etc.).

The water treatment procedure typically comprises multiple physico-chemical treatment cycles [2] followed by various advanced oxidation processes (AOPs) that are specifically designed to remove persistent residual pollutants. Although providing an exhaustive list of AOPs is beyond the scope of this paper, we briefly mention a few of the methods commonly used for water treatment. Ozonation is the most well-known AOP, and it consists of adding O₃ molecules to water in order to produce oxidative species in the medium [3]. Sonication is another AOP that relies on ultrasonic cavitation to dissociate water into H and ·OH (hydroxyl radical) under high temperatures and pressures [4]. To enhance the treatment efficiency of sonication, it is coupled to catalysis: sono-catalytic process [4]. UV radiation and semiconductor materials may also be used to produce oxidative species for water dissociation in a method known as photo-catalysis [5]. Another process used to generate oxidative species in water is the reaction of ferrous iron (Fe²⁺) with hydrogen peroxide (H₂O₂): $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$ [6]. It is worth noting that AOPs can be operated either separately or in combined mode. However, combining multiple processes increases the cost of treatment. In this context, the development of efficient processes at relatively low cost remains a major scientific challenge.

Plasmas simultaneously produce multiple oxidative species, and so, they have been proposed as suitable alternatives or complementary techniques to AOPs [7]. Indeed, the dissociation of water by plasma leads to the generation of highly reactive species such as $\cdot\text{OH}$, O , O_3 , H , HO_2 , and H_2O_2 [8], [9]. Additional reactive species, such as NO , NH , N , N_2^+ , and HNO_3 [12], are produced by plasmas in-contact with water [10] or in air bubbles in water [11]). Depending on the experimental conditions, UV/VUV radiation and shock waves may also be generated [8], [9], and they too can contribute to the degradation of pollutants in water. Considering that, in addition to the generation of reactive species, plasma-based processes are environment-friendly and do not require the addition of chemicals (H_2O_2 , HCl , O_3 , etc.) [12], [13].

To produce plasma in- and in-contact with water, numerous configurations have been proposed [7]. In this study, we use a pin-to-water configuration to create an electrical discharge in-air that is in-contact with water. Although several studies have been conducted regarding this configuration [14]–[19], the influence of electrical excitation waveforms on plasma-water interactions is rarely evaluated and not well understood. In this study, we investigate this parameter under five different conditions that lead to various discharge modes. These discharge modes are obtained by a slight modification of the air-gap distance, but their influence on the discharge and on water is not known. Here, we report the electrical characteristics of each discharge mode by measuring the temporal evolution of the voltage, current, charge, and energy. We also report the variations in water properties (namely water acidity and conductivity) encountered in each discharge mode. The efficiency of each discharge mode in degrading a standard pollutant (methylene blue, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) is determined.

3.2 Experimental setup and discharge modes

3.2.1 Experimental Setup

The experimental setup is schematically presented in Figure 3.1a. The plasma is produced in air by applying high-voltage between a pin electrode and the surface of water. The pin electrode consists of a tungsten rod, 2 mm in diameter, with a polished tip allowing for a curvature radius of $\sim 50 \mu\text{m}$. The pin-water distance (*i.e.*, air gap distance, d) is controlled using a micrometer positioning system. On the other hand, the counter electrode is composed of a stainless-steel plate (diameter = 15 mm, thickness = 6.5 mm) that is placed at the bottom of a cylindrical quartz cell filled with 50 mL of deionized water (initial water conductivity $\sim 5 \mu\text{S/cm}$). Water containing methylene blue (MB) solution is prepared by dissolving 200 ± 1 mg of MB powder (Sigma Aldrich, M9140-100G) in 500 mL of deionized water, then diluting to a final MB concentration of 10 mg/L.

The high voltage is generated using an adapted power supply. The waveform's amplitude and frequency are provided by an arbitrary function generator (Agilent, 33220A), and are amplified using an electrical current amplifier (Crest-Audio, CC-4000) coupled with a transformer (Montoux, 600VA 60V/9 kV). The current-voltage characteristics (I-V) are simultaneously measured using a current coil (Pearson, P2877) and a high-voltage probe (Tektronix, P6015A), both of which are connected to an oscilloscope (Tektronix, DPO5420B). Note that I-V waveforms are averaged over 16 events, and the discharge characteristics, such as the injected charge and energy, are averaged over 4 experiments. The electrical conditions that correspond to the various discharge modes investigated in this study are detailed in the next section (Section 2.2).

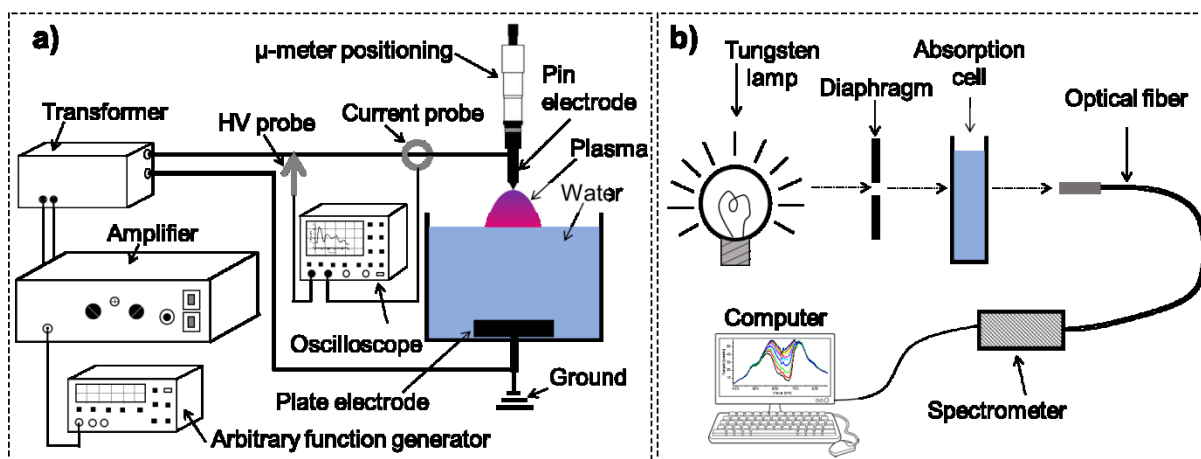


Figure 3.1. a) Schematic of the experimental setup used to generate electrical discharge in-air that is in-contact with water. b) Schematic of the absorption setup used to monitor the degradation of MB.

The absorption setup used to monitor the degradation of MB is depicted in Figure 3.1b. Samples are filled in a rectangular cell that has an absorption length of 11 mm and is positioned between a lamp and an optical fiber. A 60 W tungsten lamp is used as a source of continuous radiation in the range of 400-1000 nm. Absorption spectra are acquired in the range of 330-850 nm with using a UV/Vis spectrometer (Avantes, AvaSpec 2084-USB2). Note that, this (homemade) absorption setup is calibrated using standard MB solutions with concentrations ranging between 0.005 and 15 mg/L, and each presented data results from averaging 4 experiments. Water acidity (pH) and conductivity are measured using a pH meter (VWR, SB20 pH Meter Symphony) and conductivity meter (Cole-Parker Instrument, 19101-10 Digital Conductivity Meter), respectively.

3.2.1 Electrical Waveforms and Discharge Modes

As the main goal of this paper is to investigate the influence of the discharge mode on MB degradation, Figure 3.2 presents typical I-V characteristics of each mode (in deionized water) after 2.5 and 30 minutes of plasma processing.

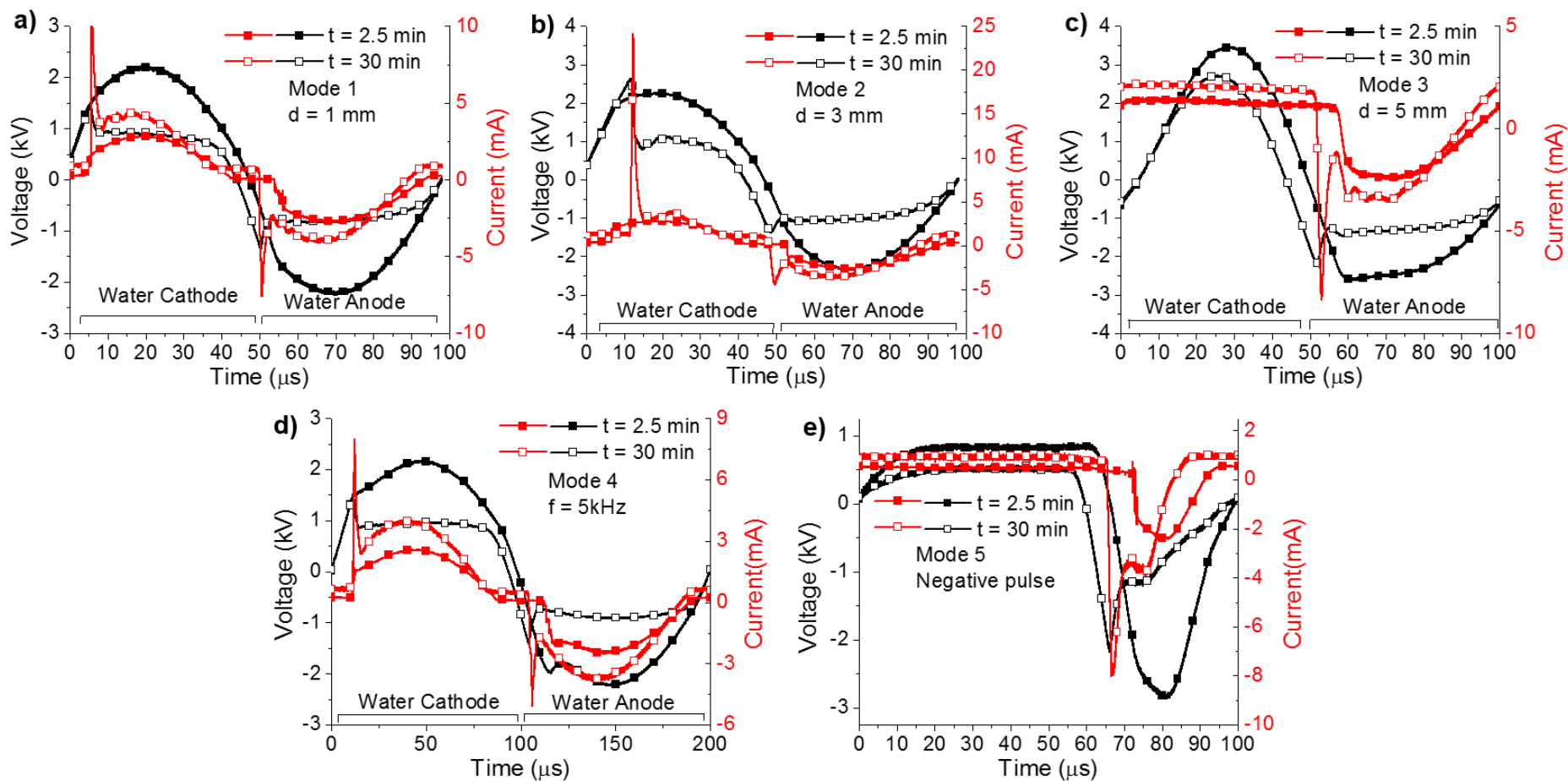


Figure 3.2. Current-voltage (I - V) characteristics of the various discharge modes: a) Mode 1, b) Mode 2, c) Mode 3, d) Mode 4, and e) Mode 5.

Mode 1 (Figure 3.2a) is achieved through the application of a sinusoidal high-voltage ($V_{\text{pk-pk}} = 10 \text{ kV}$), at frequency = 10 kHz and $d = 1 \text{ mm}$. As the voltage is sinusoidal, the water alternates between cathode and anode every 50 μs . The properties of the discharge (and its corresponding I-V) change with time due to changes in the liquid properties during plasma processing. Typical I-V characteristics for mode 1, at $t = 2.5 \text{ min}$ and $t = 30 \text{ min}$, are presented in Figure 3.2a. Note that before discharge, $V_{\text{pk-pk}}$ is close to 10 kV and the current is only a few microamperes (this current, known as displacement current, is evaluated when the discharge is off) and has been neglected. The discharge starts in a filamentary mode (data not shown) that lasts for several seconds. After that, a visually homogenous plasma is observed. At $t = 2.5 \text{ min}$, no significant drop in voltage is recorded, however, the overall waveform is attenuated (the measured $V_{\text{pk-pk}}$ is 5 kV instead of 10 kV). The associated current waveform remains almost sinusoidal (with slight deformation), with maximum value close to 2.5 mA. At $t = 30 \text{ min}$, the voltage drops significantly (from ~ 1.5 to 1 kV for both water polarities), while the current increases. In fact, departure from sinusoidal-like waveform is observed after ~ 4 minutes of processing. The drop in voltage is due to a decrease in the air gap resistivity, whereas the current peak is produced by the capacitive discharging of the plasma [17]. Note that, in this mode the current peak value is slightly higher in the positive half-period ($\sim 10 \text{ mA}$) than in the negative half-period (7.5 mA). The parameters of all discharge modes, including mode 1, are summarized in Table 3.1.

Mode 2 discharge (Figure 3.2b) is generated using the same conditions as mode 1, but at a distance of 3 mm instead of 1 mm. At $t = 2.5 \text{ min}$, the observed I-V characteristics are very similar to those of mode 1. However, at $t = 30 \text{ min}$, when water is cathode, the voltage-drop (from ~ 2.5 to 1 kV) is more pronounced and the current peak ($\sim 25 \text{ mA}$) is higher than the

corresponding values recorded in mode 1. When water is anode, the voltage-drops of mode 1 and mode 2 are similar.

For **Mode 3**, the sinusoidal high voltage ($V_{\text{pk-pk}} = 10$ kV, frequency = 10 kHz) is applied across an air gap distance of 3.5 mm (Figure 3.2c). A comparison of modes 2 and 3 shows that a slight increase in d (from 3 mm to 3.5 mm) induces strong changes in the electrical characteristics of the discharge. In fact, the current peak appears only when water is anode, and at $t = 30$ min, the voltage drops from ~ -2.2 to -1.2 kV, and the current peak value is ~ 8 mA. It is worth noting that when water is cathode, the voltage peak undergoes a slight decrease, while the current slightly increases from 0 to 2 mA.

Mode 4 (Figure 3.2d) is achieved using the same conditions as mode 1, but at a frequency of 5 kHz instead of 10 kHz. This mode is used to highlight the influence of discharge number on the efficiency of water processing. The I-V characteristics, in terms of magnitude and time evolution, are very similar to those reported in mode 1.

Finally, **Mode 5** (Figure 3.2e) is accomplished with a negative pulse. The high-voltage amplitude and frequency are set at 5 kV and 10 kHz, respectively, and $d = 3.5$ mm. This mode is used to study the effects of coupling the two polarities (water as cathode and water as anode) and coupling the electric field with the discharge (water anode), by comparing them to those observed in modes 2 and 3, respectively.

Table 3.1. Summary of the discharge modes (1-5) and the related parameters.

| Discharge mode | air-gap distance, d | Electrical excitation waveform | Repetition rate | Time to observe voltage drop |
|----------------|-----------------------|---|-----------------|------------------------------|
| 1 | $d = 1$ mm | Sinusoidal ($V_{pk-pk} = 10$ kV): discharge occurs in the two half-periods | 10 kHz | 4 minutes |
| 2 | $d = 3$ mm | Sinusoidal ($V_{pk-pk} = 10$ kV): discharge occurs in the two half-periods | 10 kHz | 5 minutes |
| 3 | $d = 3.5$ mm | Sinusoidal ($V_{pk-pk} = 10$ kV): discharge occurs in the second half-period (<i>i.e.</i> , water anode) | 10 kHz | 3 minutes |
| 4 | $d = 1$ mm | Sinusoidal ($V_{pk-pk} = 10$ kV): discharge occurs in the two half-periods | 5 kHz | 3.5 minutes |
| 5 | $d = 3.5$ mm | Negative pulse ($V_{pk-pk} = 5$ kV): discharge occurs during the negative voltage pulse (<i>i.e.</i> , water anode) | 10 kHz | 4.5 minutes |

3.3 Result and discussion

In this section, the results are presented and discussed. The characteristics (namely, charge and energy) of electrical discharges in modes 1-3 and their influence on deionized water properties (namely, water acidity and conductivity) are discussed in Section 3.1. Meanwhile, Section 3.2 discussed the changes in discharge characteristics and water properties observed upon the addition of MB to deionized water. Finally, the effect of discharge mode on of MB degradation is presented in Section 3.3.

3.3.1 Characteristics of electrical discharges and their influence on water properties

The injected charge (Q_{inj}) and energy (E_{inj}) are calculated using relations (1) and (2) when water is cathode, and relations (1') and (2') when water is anode.

$$Q_{inj} = \int_0^{T/2} i(t)dt \quad (1)$$

$$E_{inj} = \int_0^{T/2} v(t)i(t)dt \quad (2)$$

$$Q_{inj} = \int_{T/2}^T i(t)dt \quad (1')$$

$$E_{inj} = \int_{T/2}^T v(t)i(t)dt \quad (2')$$

where $i(t)$ and $v(t)$ are the electrical current and voltage across the electrode, respectively, and T is the period.

The I-V characteristics of each discharge mode were monitored throughout the entire process. These properties are used to calculate Q_{inj} and E_{inj} values at different time intervals. Figure 3.3 presents the temporal evolution of Q_{inj} and E_{inj} for experiments where water was cathode (Figures 3.3a and 3.3b), as well as for those where water was anode (Figures 3.3c and 3d). For all investigated cases, two phases could be discerned: phase 1 from 0 to ~10 min, and phase 2 for $t > 10$ min. In phase 1, Q_{inj} increases linearly until it reaches a plateau in phase 2. Discharge modes 1 and 2 exhibit no significant difference in phase 1 when water is cathode. Nevertheless, in phase 2, Q_{inj} of mode 1 is approximately 10 nC higher than that of mode 2. Meanwhile, when water is anode, the rates of increase in Q_{inj} (phase 1) depends on the discharge mode, and the maximum attained values (phase 2) are ~95, 80, and 75 nC for modes 1, 2, and 3, respectively.

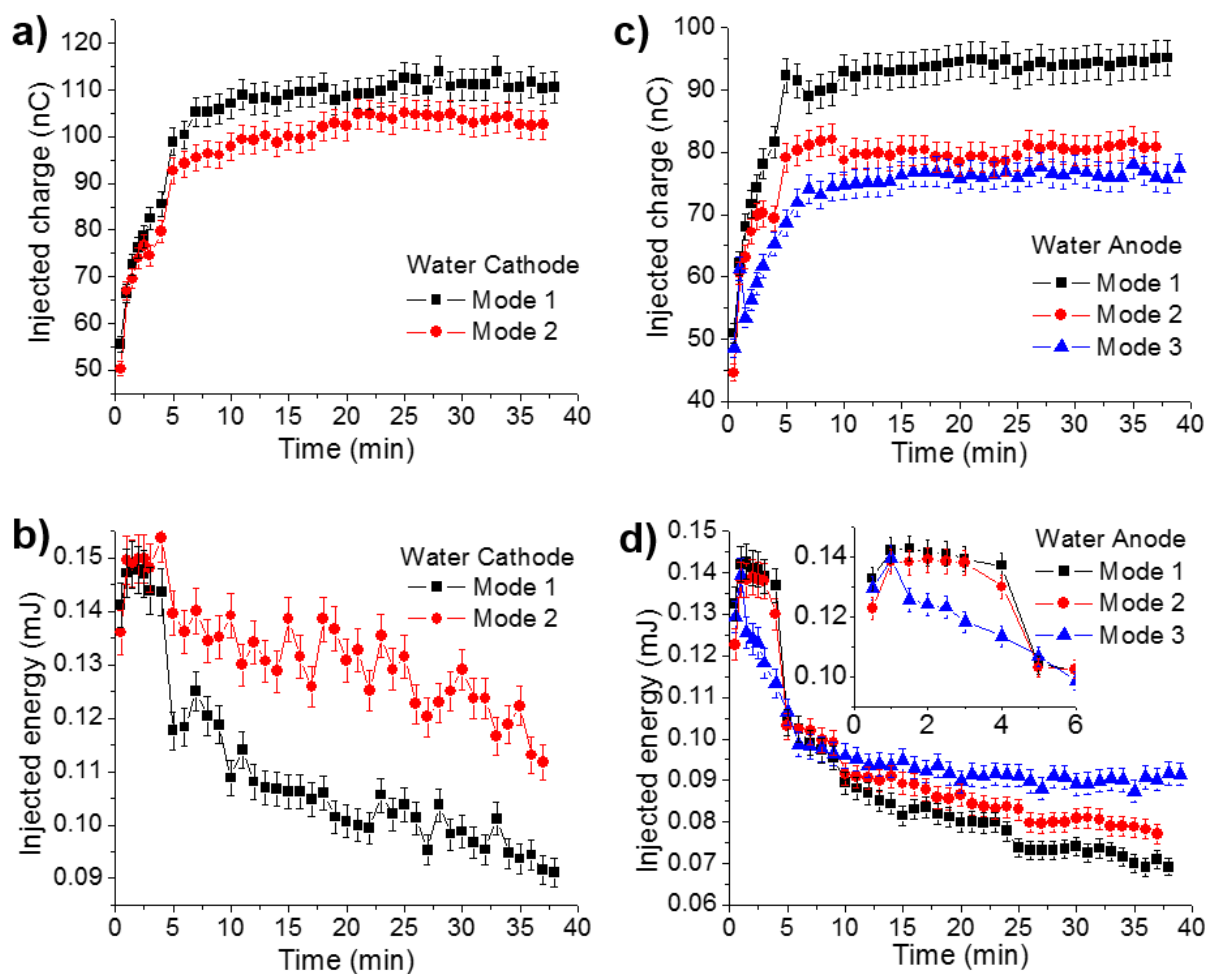


Figure 3.3. Temporal evolution of the injected charge (Q_{inj}) and energy (E_{inj}) observed in discharge modes 1, 2, and 3 when water is cathode (a and b), and when water is anode (c and d).

As for E_{inj} , its temporal evolution in phase 1 ($t < 10$ min) is not as straightforward as that of Q_{inj} . After a few minutes of processing, E_{inj} increases to peak values of ~ 0.15 or ~ 0.14 mJ when water is cathode or anode, respectively. Later, it rapidly decreases to values lower than the initial ones. The rate (*i.e.*, the slope) at which E_{inj} decreases is highly dependent on the discharge mode when water is anode, but not so when water is cathode. In phase 2, E_{inj} continues to decrease, despite the stability in discharge current (Q_{inj}). This behaviour is related to the voltage-drop observed in I-V characteristics. Overall, the results show that, when water is cathode, Q_{inj} and E_{inj} values are higher than those measured when water is anode. The trends in electrical characteristics observed herein are similar to those reported for other

configurations [20]–[23]; however, they are still not very well understood. The main difficulty originates from the rather complex plasma-water interactions, as well as the continuous change in water properties.

In this context, and to investigate the influence of discharge mode on water properties, we measured water acidity and conductivity during plasma processing. The results are presented in Figure 3.4 for modes 1, 2 and 3.

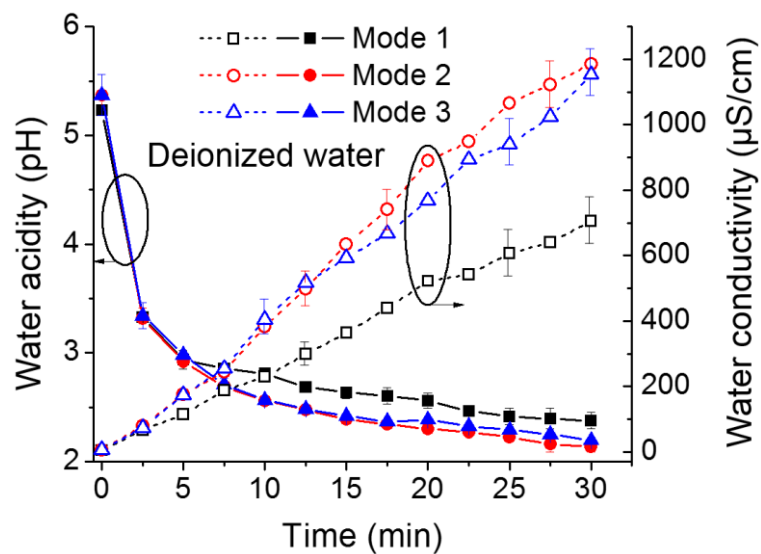


Figure 3.4. Temporal evolution of water acidity and conductivity during plasma processing in discharge modes 1, 2 and 3.

The plots of variation in water acidity as a function of time exhibit two phases (1 and 2), similar to the ones previously identified for Q_{inj} and E_{inj} . In phase 1, $t < 10$ min, water acidity rapidly decreases from ~ 5.4 to ~ 2.6 pH, regardless of the discharge mode. Meanwhile, in phase 2, $t > 10$ min, the decrease in water acidity becomes slow, with slight dependence on discharge mode. For example, after 30 minutes of processing, water acidity value is ~ 2.2 pH in modes 2 and 3, compared to ~ 2.4 pH in mode 1. The observed decline in water acidity indicates that the water becomes acidic upon plasma processing, probably due to the production of acid-like species such as nitric acid (HNO_3) and peroxyntrous acid (HNO_2) [12], [13], [24]. For the

conditions applied in this study, other species such as H^+ , OH^- , NO_2^- , and NO_3^- , could also be produced in water via the well-known kinetic scheme [12], [13].

On the other hand, water conductivity increases quasi-linearly as a function of time. After 30 minutes of processing, water conductivity increases from ~ 5 to ~ 1200 $\mu\text{S}/\text{cm}$ in modes 2 and 3, and to ~ 700 $\mu\text{S}/\text{cm}$ in mode 1. As the major difference between modes 1, 2, and 3 is the gap distance ($d = 3$ and 3.5 mm in modes 2 and 3, respectively, and $d = 1$ mm in mode 1), we believe that it is an important parameter influencing the concentration of ions and water conductivity. The observed increase in water conductivity indicates an enrichment of ions in water, mostly by H^+ and OH^- . In a previous study, it has been shown that NO_2^- and NO_3^- contribute little to water conductivity under plasma conditions similar to our own [25].

In general, the results show that changes in the electrical characteristics of the discharge significantly alter the properties of water. Interestingly, the profile of temporal evolution of water acidity is similar to that of Q_{inj} (both show two phases with similar time-scale). However, the relationship between the electrical characteristics of the discharge and water acidity or conductivity is not straightforward, especially considering the previously reported results showing that water acidity does not significantly influence the discharge [14], [22]. Many authors have characterized the liquid phase after plasma processing under various conditions. For example, Lu *et al.* [13], in a configuration very similar to ours, have measured the concentration of various species produced in water, namely H_2O_2 , NO_2^- , and NO_3^- . Moreover, they showed that the concentration of H_2O_2 and NO_3^- produced in spark discharge is higher than that produced in glow discharge. As for Porter *et al.* [25], they reported the concentration of various species, including H_2O_2 and NO_3^- , and they successfully correlated the concentration of various species to the measured water conductivity using a simplified model. In fact, the electrical characteristics of the discharge cannot be correlated to water conductivity or water

acidity, because the electrical characteristics of the discharge reflect phenomena occurring in the plasma and at the plasma-water interface rather than those occurring in the bulk volume of water. Furthermore, since the water is not agitated nor cooled (to avoid interference with species transport), the electrical characteristics of the discharge performed herein can only provide local information regarding the plasma and the plasma-water interface. However, water conductivity and acidity are global measurements that pertain to the entirety of the liquid volume.

3.3.2 Effect of MB on discharge characteristics and on water properties

To investigate the efficiency of the various discharge modes in removing organic pollutants from water, MB was added to deionized water at an initial concentration of 10 mg/L. Figure 3.5 shows the electrical characteristics of the discharge (mode 1) in deionized water with and without MB at $t = 2.5$ min (Figure 3.5a) and $t = 30$ min (Figure 3.5b).

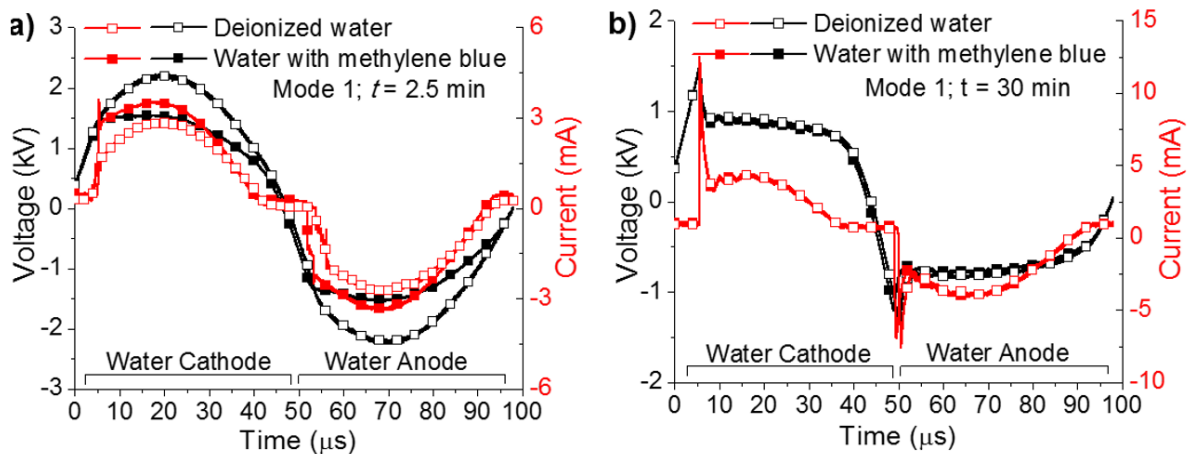


Figure 3.5. Current-voltage (I - V) characteristics in deionized water with and without MB at a) $t=2.5$ minutes and b) $t=30$ minutes.

As explained earlier, the electrical characteristics of the discharge conducted in this study are local and relate to the plasma-liquid interface. Therefore, changes in liquid composition will influence the discharge characteristics. This is clearly evident by comparing

the I-V waveforms obtained in water with MB to those without MB, at $t = 2.5$ min (Figure 3.5a). Indeed, when MB is added, a voltage-drop is observed, and the measured current is slightly higher than that of deionized water. Such modification may be related to the change in composition of water upon the addition of MB. As time goes on, I-V characteristics of the two solutions become indistinguishable (Figure 3.5b). Although the results are only shown for discharge in mode 1, sensitivity to the liquid composition is also observed for the other discharge modes (not shown here).

Besides I-V waveforms, Q_{inj} is also highly sensitive to liquid composition. Figure 3.6 presents the temporal variations in Q_{inj} for mode 1 and mode 2 discharges in deionized water with and without MB. The two phases observed previously are also distinguishable in the plots of Figure 3.6, for all investigated conditions. Phase 1 exhibits a linear increase in Q_{inj} and is more sensitive to water composition than phase 2, with greater rates of increase perceived for pure deionized water. The same trend is observed in phase 1 for discharge modes 1 and 2, however, Q_{inj} values measured in mode 2 are slightly lower than those measured in mode 1, with some difference observed in phase 2 as well.

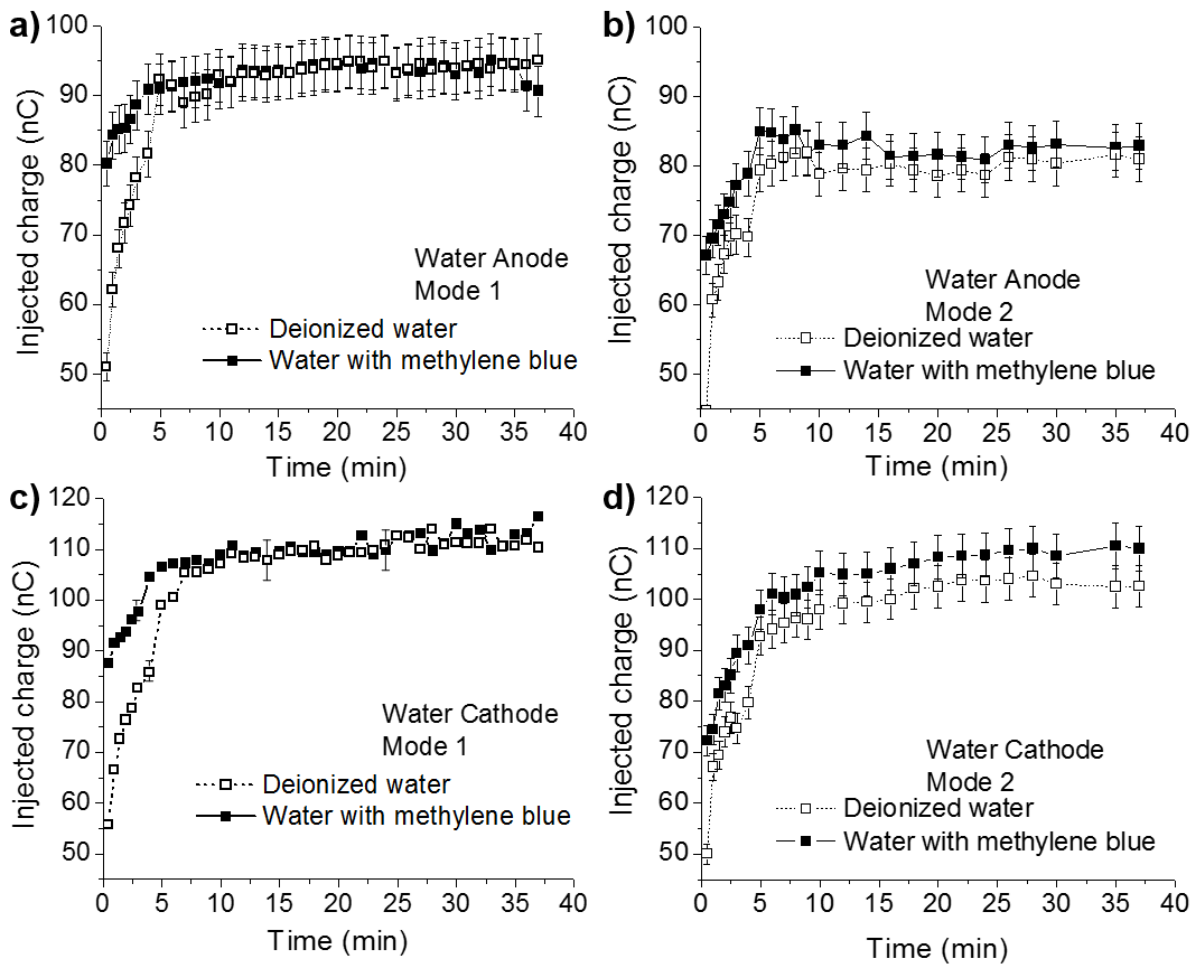


Figure 3.6. Temporal evolution of the injected charge (Q_{inj}) during discharges in modes 1 (a and c) and 2 (b and d) in deionized water with and without MB.

Figure 3.7 depicts the temporal evolution profiles of water acidity and conductivity, with and without MB, for discharge modes 1 and 2. The results show that the effect of MB on water conductivity is negligible for $t < 10$ min. However, for $t > 10$ min, the conductivity values of water + MB are relatively lower than those of water without MB. In fact, after 30 min of plasma processing, a conductivity difference as high as $\sim 150 \mu\text{S}/\text{cm}$ is discerned. It is worth noting that, in literature (*e.g.*, [27], [28]), an increase of water conductivity is often reported due to fragments originated from the degradation of MB. Our results show that the measured conductivity in water with MB is relatively smaller than that measured in water. Such variance in water conductivity may be explained by interactions between the various species in liquid; further characterization of the solution is needed to identify and quantify the various species in

solutions. On the other hand, the presence of MB in deionized water does not significantly affect the temporal evolution of water acidity within 30 min of plasma processing, regardless of discharge mode.

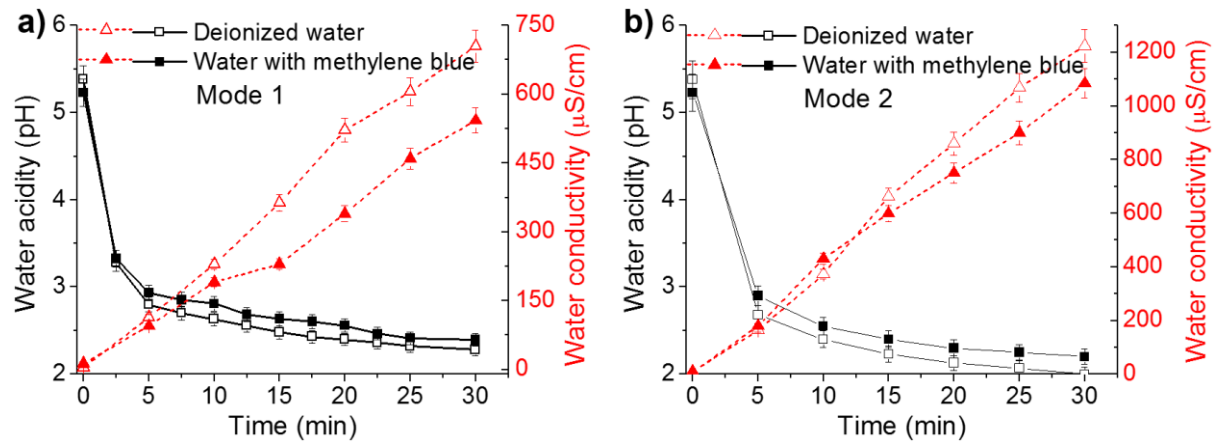


Figure 3.7. Temporal evolution of water acidity and conductivity, with and without MB, for discharge modes 1 (a) and 2 (b).

3.3.3 Degradation of MB by various discharge modes

The degradation of MB, a widely used standard pollutant, by various discharge modes was investigated by monitoring the absorption intensity at 663 nm, the wavelength that corresponds to ring-opening in MB structure [24]. The measured intensity is related to the concentration of MB, $C(t)$ (see Section 2.1), and the degradation percentage is given by the following equation:

$$Degradation (\%) = \left(1 - \frac{C(t)}{C(t=0)} \right) \times 100 \quad (3)$$

Degradation percentage were calculated at different plasma processing time intervals, and the curves obtained for modes 1, 2, and 3 are presented in Figure 3.8. Modes 1 and 2 show similar evolution, with the degradation percentage increasing linearly from 0 to ~80% during the first 15 minutes, and then it stabilizes at a maximum value of ~95%. As the major difference between mode 1 and mode 2 is the gap distance (1 mm vs. 3 mm, respectively), this parameter

seems to have no significant influence on the degradation percentage or mechanism. In contrast, the percentage measured for mode 3 are relatively low, and a plateau is not observed even after 40 min of plasma processing. Such difference in MB degradation percentages can be related to variations in the Q_{inj} and/or E_{inj} values of the corresponding discharge modes. Indeed, in phase 2, Q_{inj} and E_{inj} values are ~ 180 - 200 nC and ~ 0.18 - 0.21 mJ, respectively, for discharge modes 1 and 2, compared to ~ 75 nC and ~ 0.1 mJ, respectively, for discharge mode 3. At this stage, one concludes that the air-gap distance does not play a crucial role in water treatment, as long as the discharge occurs during both half-periods. In fact, as the air-gap distance is augmented, the plasma column increases, but the plasma water interface does not change significantly (also confirmed by imaging, not shown). Therefore, as a first approximation, the density of reactive species in the plasma column does not significantly influence the chemistry induced in water. This is confirmed by the water acidity and conductivity measurements discussed earlier. Meanwhile, the chemistry induced in the bulk volume of water is strongly influenced by the plasma-water interface.

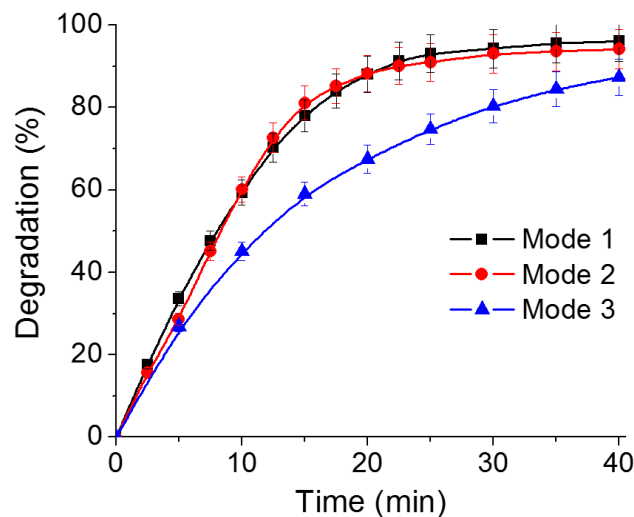


Figure 3.8. Temporal evolution of MB degradation percentage during plasma processing in discharge modes 1, 2, and 3.

Discharge in mode 3 occurs only when liquid polarity is anode, *i.e.*, for a given processing time, the number of discharges is reduced by 50% relative to modes 1 and 2. This explains why Q_{inj} and E_{inj} values of mode 3 discharge are about half those of modes 1 and 2. It is worth noting that, despite the absence of discharge in mode 3 when water is cathode, a high electric field is still applied across the gap.

To investigate the decrease in MB degradation percentages for mode 3, experiments were conducted in mode 1 at a repetition rate of 5 kHz, *i.e.*, mode 4. In parallel, the sensitivity of MB degradation to the electric field preceding discharges in mode 3 was assessed by experiments that use negative pulses only, *i.e.*, mode 5. Figure 3.9 shows the temporal evolution profiles of Q_{inj} , water acidity, and water conductivity for discharge modes 4 and 5, and compares them to those of modes 1 and 3.

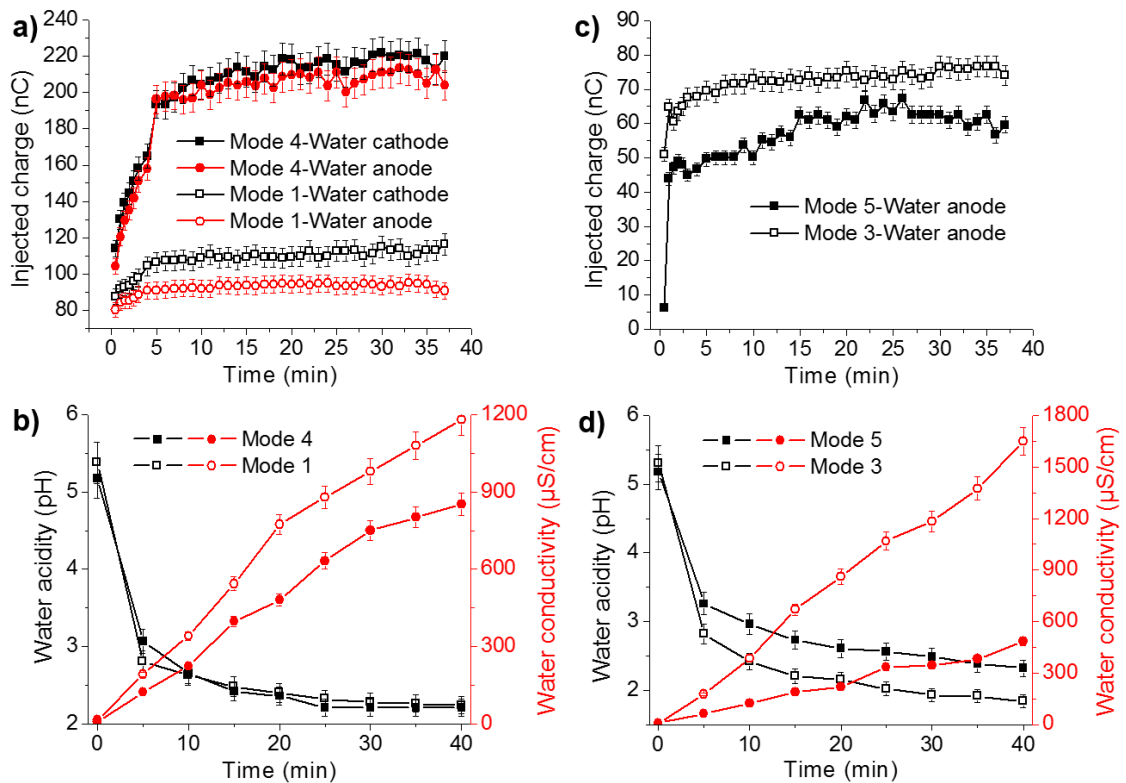


Figure 3.9. (a) and (b) Temporal evolution of profiles of the injected charge (Q_{inj}), water acidity, and water conductivity in modes 1 and 4. (c) and (d) Temporal evolution of the injected charge (Q_{inj}), water acidity, and water conductivity in modes 3 and 5.

Although the number of discharges in mode 4 is reduced by 50% relative to modes 1 and 3, Q_{inj} shows an increase by a factor of ~ 2 (Figure 3.9a). For instance, when water is cathode, the plateau is observed at ~ 110 nC in mode 1 and at ~ 220 nC in mode 4. Meanwhile, the magnitudes of the currents measured in modes 1 and 4 are very close, *i.e.*, ~ 10 mA and ~ 9 mA, respectively, when water polarity is cathode, and ~ 7 mA and ~ 6 mA, respectively, when water polarity is anode. However, as the repetition rate decreases from 10 to 5 kHz, the duration of the non-zero current interval significantly increases from ~ 40 μ s to ~ 80 μ s (see Figures 3.2a and 2d), which explains the observed variations in Q_{inj} . The water acidity profiles of modes 1 and 4 are very similar, however, water conductivity is substantially reduced upon lowering the discharge frequency from 10 kHz (*i.e.*, mode 1) to 5 kHz (*i.e.*, mode 4) (Figure 3.9b).

The effect of electric field preceding discharge in mode 3 is evaluated by comparing the corresponding discharge characteristics to those of mode 5 (negative pulses only), as shown in Figures 3.9c and 9d. Q_{inj} values exhibit difference of ~ 20 nC only between the two modes (Figure 3.9c). Similarly, water acidity is not strongly affected, with a variation of 0.5 only in pH values. However, the water conductivity is highly influenced by the electric field. For example, after 40 minutes of plasma processing, discharge in mode 3 leads to a water conductivity value that is three-time higher than the value induced by discharge in mode 5 (~ 1600 vs. ~ 550 μ S/cm). Since the I-V characteristics of discharges in modes 5 and 3 are similar when water is anode, the observed difference in water conductivity must be associated with the electric field present during the first half-period (*i.e.*, when water is cathode) in mode 3. In fact, this electric field could play a very important role in the transport of species from plasma phase to liquid phase. To better understand the influence of this parameter, further studies are required.

The effects of discharge number and electric field on MB degradation have also been studied, and the results are presented in Figure 3.10. For $t < 20$ min, a slight difference in MB degradation percentage can be noticed between modes 1 (10 kHz) and 4 (5 kHz), but for longer times, the difference is negligible. Both discharge modes lead to a maximum degradation of 95% after 25 min of processing. This means that neither the number of discharges nor the Q_{inj} have a significant influence on the efficiency of MB degradation.

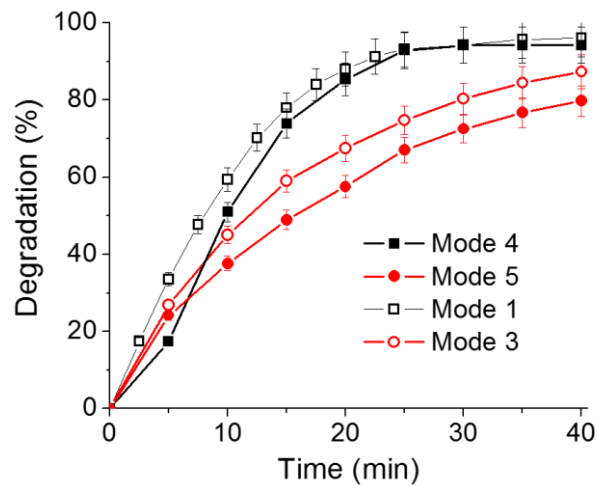


Figure 3.10. Temporal evolution of MB degradation percentage during plasma processing in modes 4 and 5. For the purpose of comparison, MB degradation rate profiles of modes 1 and 3 are added to the figure.

On the other hand, by comparing the MB degradation percentages of modes 3 and 5, a difference of ~10% is noticed. This may be explained by the enhanced transport of charged species towards water in mode 3, due to the electric field induced by positive voltage during half-period. Note that, positive pulsed discharges are highly unstable, and thus, their influence on MB degradation percentage is not investigated here. However, recently, it has been reported that the concentrations of reactive species, mainly H_2O_2 , NO_2 , and NO_3 , are highly dependent on water polarity [13].

To quantify the efficiency of MB degradation, the yield of 50% MB removal ($Y_{50\%}$) was calculated for each discharge mode using equation (4) [26].

$$Y_{50\%}(\text{g/kWh}) = \frac{V(L) \cdot [C(t = 0) - C_{50\%}(t)]}{\sum_i P_i(W)t_i(h)} \quad (4)$$

where V is the liquid volume (0.05 L), $C(t = 0)$ is the initial concentration (0.01 g/L), $C_{50\%}(t)$ is half of the initial concentration (0.005 g/L), and $\sum_i P_i t_i$ is the sum of energy needed to degrade 50% of MB (calculated from electrical measurements). The results are summarized in Table 3.2.

Table 3.2. $Y_{50\%}$ values for each discharge mode and other useful data.

| Discharge mode | Initial concentration | Time to remove 50% of MB | $\sum_i P_i t_i$ (10^{-4} kWh) | Yield, $Y_{50\%}$ (g/kWh) |
|----------------|-----------------------|--------------------------|-----------------------------------|---------------------------|
| 1 | 10 mg/L | 8.4 min | 2.43 | 0.93 |
| 2 | 10 mg/L | 8.4 min | 2.63 | 0.85 |
| 3 | 10 mg/L | 11.7 min | 2.79 | 0.81 |
| 4 | 10 mg/L | 10.1 min | 2.23 | 1.01 |
| 5 | 10 mg/L | 15.4 min | 2.85 | 0.79 |

The highest efficiency ($Y_{50\%} = 1.01$ g/kWh) was obtained for discharge in mode 4, followed by discharge in mode 1 (0.93 g/kWh) and mode 2 (0.85 g/kWh). The elevated MB degradation yield observed in mode 4, compared to mode 1, can be related to the relatively long plasma lifetime (~ 80 μs vs. 40 μs , see above). Indeed, once ignited, the plasma continuously (during the half-period) produces reactive species at the plasma-water interface, thereby enhancing MB degradation. The difference between discharge modes 1 and 2 lies in the relatively short distance of mode 1 ($d = 1$ mm for mode 1 and 3 mm for mode 2). This indicates that longer plasmas do not lead to greater degradation efficiencies. In fact, more energy is dissipated (lost) in the plasma column when the distance is longer. The $Y_{50\%}$ values

calculated for discharges in modes 3 and 5 are 0.81 and 0.79 g/kWh, respectively. Although these modes are less efficient in removing MB than modes 1, 2, and 4, the reported values indicate that the electric field of mode 3 enhances degradation. Compared with other plasma-based water treatment processes reported in the literature, the plasma configurations proposed herein exhibit, by far, a high MB degradation efficiency (Table 3.3).

Table 3.3. Energy yields needed to remove 50% of MB ($Y_{50\%}$) using various plasma reactors.

| MB concentration (mg/L) | Type of plasma reactor | $Y_{50\%}$ (g/kWh) | Ref. |
|------------------------------------|---|--|------------------|
| 10 | AC-driven air plasma in contact with water (mode 4) | 1.01 | This work |
| 50 | Microwave plasma jet in water | 0.3 | [27] |
| 50 | Microwave plasma jet in contact with water | 0.033 | [28] |
| 12 | Diaphragm discharges | 0.042 | [29] |
| 5 | Radio-frequency discharges | 0.037 | [30] |
| 10 | Microwave plasma in water with air bubbling | 0.155 | [11] |
| 13.25 | Pulsed corona discharges in water with O ₂ bubbling | 0.341 | [31] |
| 13 | Pulsed corona discharges in water | 0.064 | [31] |

3.4 Conclusion

This study presents the characteristics of five plasma discharge modes in contact with water, as well as their efficiencies in degrading methylene blue (MB), a representative water

pollutant. Modes 1, 2, and 3 were run at air-gap distances of 1, 3, and 3.5 mm, respectively, and at a repetition rate of 10 kHz (sinusoidal). Anode and cathode water polarities were evident for modes 1 and 2, whereas the polarity of water in mode 3 was only anode. Discharge mode 4 was effectuated at an air-gap distance of 1mm, similar to mode 1, and at a repetition frequency of 5 kHz. Finally, discharge in mode 5 was run under the same conditions as in mode 3, but without the preceding high voltage when water polarity is anode. The electrical characteristics of each discharge mode are presented in detail, and temporal variations in water properties, namely water acidity and conductivity, are discussed. For deionized water with and without MB, the electrical characteristics of the investigated discharges showed high sensitivity to water composition, but not to the water acidity or conductivity. This is due to the fact that the electrical characteristics of the discharge were determined locally at the plasma-water interface, whereas water acidity and conductivity are global values pertaining to the bulk of water volume.

Regarding MB degradation, modes 1 and 2 showed similar efficiencies, which indicates that the air-gap distance, and thus, the length of the plasma column, has no significant effect on degradation. Mode 4 also presented an efficiency similar to that of mode 1, implying insubstantial dependence on the number of discharges. The comparison between MB degradation efficiencies in modes 3 and 5 suggested that the electric field applied between two successive discharges (in mode 3) plays a very important role in the transport of charged species from plasma phase to liquid phase, thereby promoting the degradation of MB.

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Chapitre 4 – Conclusion

Dans ce mémoire, nous avons principalement intéressé à l'interaction d'un plasma d'air couplé directement avec de l'eau, en utilisant une décharge soutenue par une source de tension en courant alternatif (AC).

Les principales avancées scientifiques de ce mémoire sont :

- La description de l'évolution temporelle et en fonction de la distance inter électrode d'une décharge dans l'air en couplage direct avec l'eau. Cette étude a permis de mieux décrire la morphologie de la décharge dans l'espace inter électrodes et à la surface de l'eau. Suivant la valeur de l'espace inter électrode, il y a deux modes de décharges. En particulier, à long écart (> 5 mm) et lorsque la polarité de l'eau est anode, l'émission lumineuse à la surface de l'eau montre une structuration de l'émission à la surface de l'eau. L'évolution temporelle de cette structuration dans la demi-période montre un lien direct avec la puissance instantanée de la décharge.
- La description de l'évolution en fonction du temps d'opération d'un plasma d'air en contact avec l'eau alimenté par une source de tension AC. L'évolution des caractéristiques électriques et des propriétés de l'eau a été faite pour 5 modes d'opération en fonction du temps ont été rapportée. L'efficacité de dégradation du méthylène bleu en solution du dispositif plasma a été quantifiée pour chacun de ces modes. Les caractéristiques électriques de chacun des modes d'opération sont sensibles à la composition de l'eau, et non à la conductivité ou l'acidité de l'eau. La présence des deux polarités, positive et négative, de tension à la pointe à l'intérieur d'une période du signal d'excitation sont importantes pour assurer un traitement efficace du bleu de méthylène.

Ainsi, plusieurs perspectives s'ouvrent à la suite de ce mémoire, tant au niveau de la physique fondamentale de l'interaction des plasmas en contact avec les liquides que pour le développement de nouvelles applications utilisant les plasmas en contact avec les liquides. Au niveau fondamental,

la formation de motif autoorganisé reste encore incompris. Malgré les pistes suggérées par ce mémoire, il reste encore à caractériser les propriétés fondamentales tels que la source du motif, la charge des points plasmas à la surface et l'influence des propriétés du liquide sur la formation des motifs. Des travaux ont déjà commencé à répondre ces questions [1], mais davantage de travail reste à accomplir pour avoir une meilleure compréhension de ce genre de phénomènes. Au niveau du développement de nouvelles applications des plasmas en contact avec les liquides, la compréhension sur les différents paramètres qui influencent le traitement des eaux doit être améliorés. L'influence des paramètres, tels que la polarité de la tension appliquée, l'intensité de la tension appliquée et l'espace inter électrodes, doit être considéré lors de la conception d'un montage de ce genre [2]. Les propriétés de la molécule à traiter doivent aussi être prise en comptes lors de l'élaboration du montage [3]. Des travaux futurs s'efforceront à trouver d'autres applications à cette technologie qui utilise seulement l'électricité comme source d'énergie.

Enfin, ce mémoire aura servi à mettre en lumière ce défi qu'est de concevoir un montage utilisant la technologie plasma pour le traitement des eaux usées et d'en trouver les paramètres optimaux. De plus, il aura servi à améliorer la compréhension de l'interaction plasma en contact avec les liquides.

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Annexes