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Faculty of Physics

NON-THERMAL ATMOSPHERIC PRESSURE PLASMAS IN CONTACT WITH LIQUIDS FOR PRACTICAL APPLICATIONS

Ph.D. Thesis Summary

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1. INTRODUCTION

1.1. Motivation and objectives

Plasma represents a fascinating matter that holds very special properties. Not only it is aesthetically pleasant, but also its highly energetic components recommend it for numerous applications in varied research field. Plasma in contact with liquids represents a recent research direction that still holds mysteries in terms of both, fundamental processes and possible applications. Many species are generated at the plasma-liquid interface. Water, oxygen species and nitrogen species are able to react and form other active molecules which can further interact with substances they come in contact with or can diffuse in the treated liquids. Consequently, the properties of the liquids change and its potential for practical applications develops.

This thesis aims to enlarge the knowledge about the interaction of plasmas with water based liquids and more importantly to enhance the potential application area of plasmas in contact with liquids. Therefore, the main objectives of this work were:

- the identification of the main species forming in the liquid and gas phases during the plasma exposure of water.
- the characterization of the plasma activated water.
- the degradation of organic dye solutions by plasma treatment and by exposure to plasma activated water.
- the evaluation of the effect of plasma exposure and plasma activated water exposure of biological molecules.
- bacterial decontamination due to microorganism interaction with the plasma activated water.
- nanoparticle synthesis at plasma-liquid interaction.

1.2. Thesis structure

This thesis presents experimental results obtained as an outcome of the interaction of plasmas with liquids. Including this introductory section, the work is structured in six main chapters that describe the theoretical basis of the work, the experimental conditions and the obtained results. The first three chapters introduce theoretical aspects related to the chosen research field and details about the experiments, while the last chapters present the experimental results as well as corresponding discussions and conclusions.

Chapter 2 presents a short introduction of the plasma field including the main processes occurring in the plasma, a description of the non-thermal plasmas and a short characterization of the main cold plasma discharge approaches. In addition, this chapter presents the specific interactions occurring at plasma-liquid interface as well as the main approaches used for plasma in contact with liquid generation. Finally, the chapter presents an overview of the main plasma in contact with liquids applications including environmental, material based and biomedical applications.

Chapter 3 is dedicated to the experimental conditions. It describes the plasma sources used during the experiments, the investigation techniques applied for gas phase and liquid phase diagnostics as well as the used materials and working procedures.

Chapter 4 includes the diagnostics results of the gas phase and liquid phase at plasma-water interaction. The main species in the plasma gas phase are identified and the effects of the plasma treatment on distilled water are assessed.

Chapter 5 refers to the studied applications of plasmas in contact with liquids. Firstly, the effects of the direct discharge and of the plasma activated water on five different organic dyes are determined. Next, the influence of activated water and plasma exposure on two proteins is presented. Furthermore, the plasma activated water application for bacterial decontamination is described. Finally, results obtained as the discharge treatment was used for gold nanoparticles synthesis are portrayed.

Chapter 6 is reserved for the final conclusions corresponding to the experimental findings and describes the future perspectives for the work done in the thesis.

The last part corresponds to several Appendices including the list of abbreviations, the list of software resources, the list of figures, the list of tables and finally an overview of the academic results of the author.

Keywords: non-thermal plasma, reactive species, plasma activated water, colorant degradation, bacterial inhibition, nanoparticle synthesis.

2. THEORETICAL ASPECTS

2.1. Atmospheric pressure plasmas

2.1.1. Plasma fundamentals

Plasma is considered the fourth energetic state of the matter. Even if from macroscopically point of view it is neutral, plasmas contain electrons, ions, neutrals and photons. In addition, due to its charged species, plasmas are always characterized by the existence of electric and magnetic fields in their occupied space. The energy transferred to the discharge from the external source (electric field) is divided between the different processes occurring in the plasma. Therefore, parts of the energy are used for translations, excitations, ionizations and dissociation. It is known that temperature is a measure for energy. Considering the relations between the different temperatures, plasmas can be divided in three categories: complete thermodynamic equilibrium (CTE) plasmas, local thermodynamic equilibrium (LTE) plasmas and non-equilibrium plasmas.

2.1.2. Non-thermal plasmas

Non-equilibrium plasmas are also known as non-thermal plasmas or as cold plasmas. They are characterized by an inequality relation between the different temperatures of the system: $T_e >> T_i$ and T_n.

Discharge gas pressure represents an important parameter for plasma generation as it is directly connected to the breakdown voltage. At atmospheric pressure, the collision frequency between particles is higher than at low pressure. Therefore, a redistribution of the energy is favoured.

2.1.3. Non-thermal plasma setups

Multiple atmospheric pressure plasmas (APPs) have been developed during the years. However, from the plethora of configurations, only some setups are used for plasma in contact with liquids applications. A few of the most utilized setups are corona discharges, dielectric barrier discharges, atmospheric pressure plasma jets and micro-discharges.

2.2. Plasmas in contact with liquids

2.2.1. Plasma in contact with liquids setups

Many discharge setups were developed having different working parameters. However, all systems can be included in one of the following categories: (a) direct discharges in liquid, (b) discharges in the gas phase over a liquid and (c) discharges in multiphase environments. The discharge gases vary from air to noble gases and mixtures. Other parameters that change are plasma generation time, electron density, gas temperature, energy and power density. Another variation factor is represented by the electrode geometries. Figure 2.1 shows a representation of some of the discharges used for plasma liquid interaction. In terms of liquids, the most used is water, but also salt solutions, ethanol or body fluids are exposed to treatments.

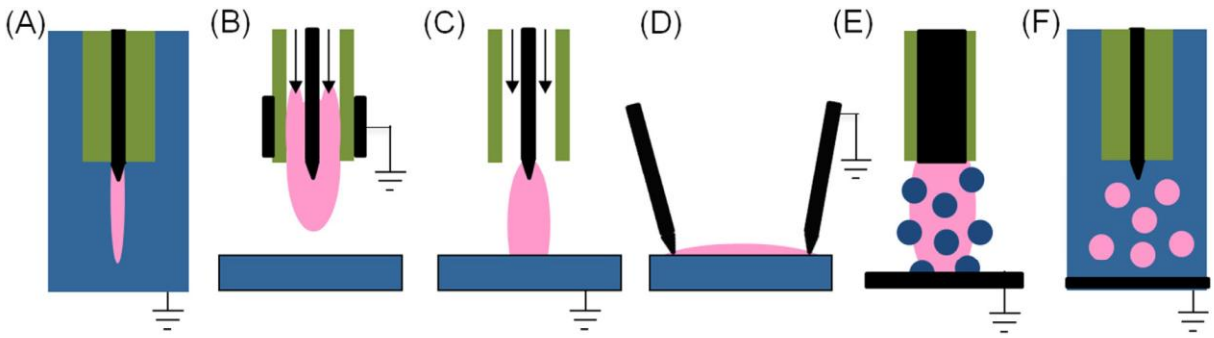

Figure 2.1. Schematic representations of some of the discharges used for plasma-liquid interaction - (A) direct discharge in liquid, (B)–(D) gas phase discharges and (E) and (F) multiphase discharges. In more detail: (B) plasma jet without direct contact with liquid, (C) gas phase plasma with liquid electrode, (D) surface discharge, (E) gas phase plasma with dispersed liquid phase (aerosols) and (F) discharges in bubbles. Blue = liquid, pink = plasma, green = dielectric, black = metal electrodes. [1].

2.2.2. *Elementary process at plasma-liquid interface*

The processes occurring when plasmas are in contact with liquids are very complex. One schematic representation is shown in Figure 2.2. When plasmas are in contact with liquids, multiple species are transferred from the liquid phase to the gas phase due to evaporation and sputtering and from the gas phase to the liquid phase due to diffusion.

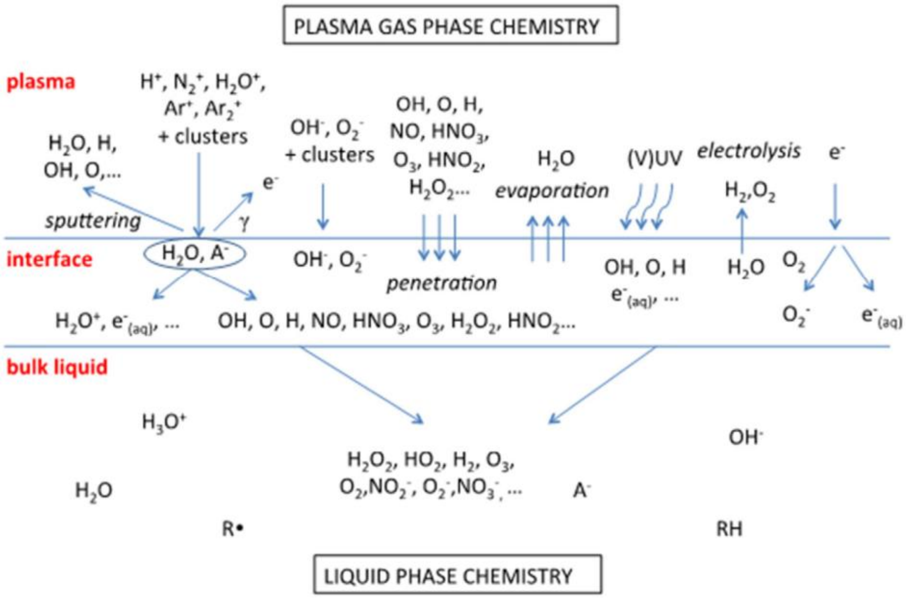

Figure 2.2. Schematic representation of the processes occurring at plasma-liquid interaction [1].

2.2.3. *Plasma activated water*

The liquids that suffer plasma treatment are referred to as plasma activated liquids. A particular case is the one in which the treated liquid is water. In this case the name of plasma activated water (PAW) is widely used. All PAW solutions exhibit physical and chemical properties that are very different from the ones before plasma exposure. Plasma activated water is considered to be a ‘cocktail’ or a ‘soup’ of active species. Many oxygen and nitrogen species were detected in PAW samples. Short lived species like superoxide radical, hydroxyl radical, nitrite, or peroxynitrite were evidenced to form in the PAW solutions. Other species are the ones with longer lifetimes as hydrogen ion, hydrogen peroxide and nitrate. The formation of all these species is very dependent on several parameters like discharge gas, plasma energy, electrode configuration, gas humidity, contact time between the discharge and the water.

2.3. Applications of plasmas in contact with liquids

A wide range of utilizations of plasmas in contact with liquids have emerged as during the last two decades, the focus was directed on a broad range of applications including environmental remediation [2], analytical chemistry [3], [4], disinfection [5], sterilization [6], medical treatment [7], nanomaterial synthesis [8], material processing [9], [10].

2.3.1. Environmental applications

The environmental applications of plasmas in contact with liquids involve the removal of different types of contaminants from plasma-exposed liquids, especially water.

2.3.2. Biomedical applications

Applications of plasmas in contact with liquids are blood coagulation, bacterial inactivation and mammalian cell treatment. Plasma treatments proved to have antimicrobial effects on a wide range of bacteria and more recently, the sole effect of PAW on bacterial cells was also investigated.

2.3.3. Material synthesis and engineering

The main application of plasmas in contact with liquids for material synthesis and engineering refers to nanomaterials from a liquid or a solid precursor.

3. EXPERIMENTAL DETAILS

3.1. Plasma generation systems

3.1.1. Noble gas μ-jet

The experimental setup used for He and Ar μ-jet generation is presented in Figure 3.1 and is based on a laboratory made free-running RF oscillator that is described in detail in [11].

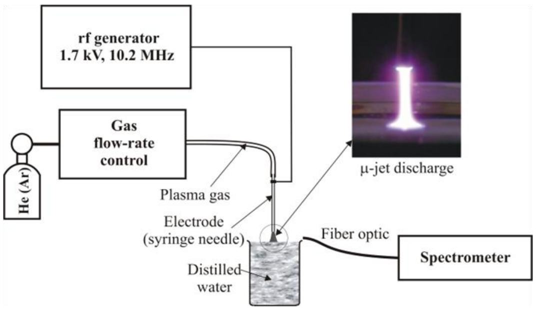

Figure 3.1. Schematic representation of the setup used for He and Ar μ-jets generation.

3.1.2. Air μ-arc

The setup used for the generation of the air μ-arc is very similar to the one used in the case of the μ-jets. The main difference is represented by the powered electrode of the discharge (Figure 3.2).

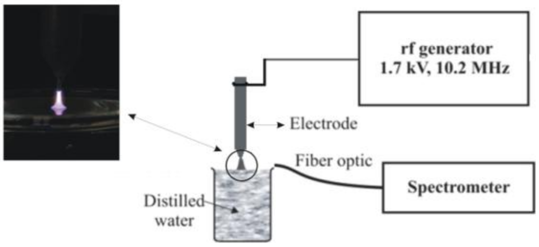

Figure 3.2. Schematic representation of the setup used for the generation of the air μ-arc.

3.1.3. Argon in liquid plasma

The in liquid plasma generator (Figure 3.3) is similar to the previous two setups in terms of applied electrical signal. However, the main differences consist in the main electrode and the generation of the plasma inside the treated liquid.

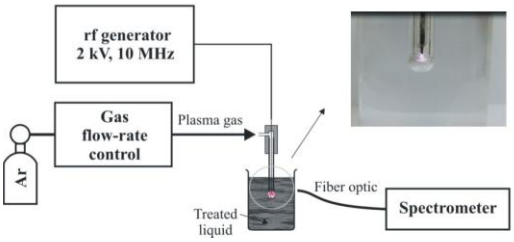

Figure 3.3. Schematic representation of the setup used for the generation of the in liquid discharge.

3.1.4. Direct current micro-jet

The direct current DC-SE PRO setup, with a schematic illustration shown in Figure 3.4 , was used for plasma treating aqueous precursor solutions for gold nanoparticle synthesis.

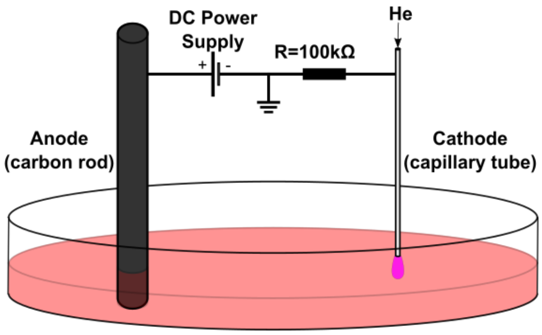

Figure 3.4. Schematic representation of the plasma DC-SE Pro setup.

3.2. Plasma characterization

The plasma discharges were characterized by means of optical emission spectroscopy diagnostics. Plasma optical emission was collected with fibre optic connected to two Ocean Optics High-Resolution Fiber Optic Spectrometers.

3.3. Material characterization tools

3.3.1. UV-vis spectroscopy

The absorbance measurements made in this work were performed using a Perkin Elmer, Lambda 650S and a Jasco V-630 UV-vis spectrophotometer

3.3.2. Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectra were performed in attenuated total reflectance (ATR) mode using a Jasco 4000 FTIR spectrometer equipped with one reflection ATR accessory with ZnSe crystal.

3.3.3. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed using a SPECS PHOIBOS 150 MCD system, equipped with a monochromatic Al K_α X-ray source (250 W, hν = 1486.6 eV).

3.3.4. Transmission electron microscopy

The TEM measurements were recorded using a JEOL JEM-2100F and a Tecnai F20 field emission, high resolution Transmission Electron Microscope

3.3.5. Determination of the physical and chemical properties of the liquid

The properties of the liquids were measured using specific tools.

3.4. Other analytical techniques

3.4.1. Hydrogen peroxide determination

The hydrogen peroxide concentration in the investigated liquids was estimated using the colorimetric method reported in [12]–[14].

3.4.2. Nitrate estimation

All solutions were investigated by UV-vis spectroscopy measurements using the specific absorption peak at 301 nm.

3.5. Materials

Several chemicals were used throughout the experiments. All of them were bought from recognized suppliers and were of analytical grades.

3.6. Experimental procedures

3.6.1. Water activation

Distilled water samples were activated via plasma exposure. The treated volumes had values between 10 ml and 35 ml and the treatment time varied from 2 to 30 minutes.

3.6.2. Colorant degradation

The colorant degradation experiments were performed using five different colorants: methylene blue, rose bengal, congo red, malachite green and crystal violet. Experiments in which the dyes are in contact with PAW and experiments in which they are in contact with the discharges were made.

3.6.3. Protein modification

The protein modification experiments were made using two different methods. The first one involves the direct plasma exposure of the two proteins. Solutions of Collagen (Col) and bovine serum albumin (BSA) underwent plasma exposure for time intervals up to 20 minutes or were exposed to PAW.

3.6.4. Bacterial decontamination

The inhibition effect of the PAW samples was investigated by using *Staphylococcus aureus (S.aureus)* bacteria as test microorganism.

3.6.5. Nanoparticle synthesis

For obtaining the naked gold nanoparticles and collagen coated gold nanoparticles, precursor solutions of gold (III) chloride trihydrate ($HAuCl_4$•$3H_2O$) underwent plasma treatment for time intervals of 10 minutes.

4. RESULTS AND DISCUSSION - PLASMAS IN CONTACT WITH WATER

4.1. Plasma diagnostics

4.1.1. Noble gas plasma μ-jet

Emissions lines and bands of nitrogen, hydrogen, oxygen, OH radical as well as helium and argon are visible.

4.1.2. Plasma μ-arc

The optical emission of the air μ-arc discharge is dominated by the nitrogen molecular bands which are very intense. Also a band corresponding to the ·OH radical is visible having a small intensity. Emission lines corresponding to hydrogen and oxygen are also present at 656 nm, respectively at 777 and 844 nm.

4.1.3. Plasma in liquid

The emission spectrum of the discharge generated in distilled water, contains emission lines corresponding to O, H, Ar atoms and molecular bands attributed to OH molecular species.

4.1.4. Discussions

The spectrum profile is considered to be the result of three main plasma processes: (a) the ionization and the excitation of the discharge gas, generating ions and free electrons; (b) the dissociation and ionization of the gas molecules that enter in the discharge from the environment (air) and (c) the dissociation, excitation and ionization of water molecules, and resulting products (OH, O, H). Therefore all spectra show the presence of nitrogen and hydroxyl radical bands as well as emission lines of oxygen and hydrogen together with the specific lines of the discharge gas. The existence of nitrogen-based species, oxygen, hydrogen and ·OH radical in the plasma-water interface region is very important for the modification of water characteristics.

4.1.5. Conclusions

The plasma micro-jets in He and Ar, the micro-arc in air and the in-liquid discharge were diagnosed by means of optical emission spectroscopy. Emission lines of O and H and emission bands of nitrogen and hydroxyl radical together with emission lines of He and Ar were all identified. While He and Ar are externally supplied in the discharge, the H and OH appear as a result of water dissociation and N_2 and O originate in the ambient air. Characteristic properties of the plasmas were also determined. The different temperatures in the discharges differ according to the non-thermal plasmas temperatures inequality rule. However, the electron density values are in the same order of magnitude. The properties of the plasmas depend on the configuration and discharge gas. While the Ar discharge promoted the strong emissions of ·OH, the helium and air discharges stimulated the emission of nitrogen. Whether the ROS or RNS are the main excited products, all plasmas generate active species in the gas phase proving that plasmas have a high potential to influence further any other material they encounter, liquid or solid.

4.2. Water activation

4.2.1. Treatment time dependence

Water evaporation

The long plasma exposure time results in big volumes of water being evaporated during the treatment. It can be seen that the longer the treatment time is, the higher is the value of the evaporated volume. Moreover, important differences in the evolution are highlighted for the three discharges as the helium discharge results in bigger evaporated volumes than the argon and air discharges.

Electrical conductivity and pH value

The conductivity dependence on the treatment time shows similar shape for all three discharges. However, the growth rate strongly differs, for a treatment time of 40 min the electrical conductivity of water treated with the air μ-arc is notably higher than in the case of the treatment with helium and argon discharges.

The pH measurements showed a remarkable drop in the pH of the treated solutions in the first minutes of treatment. From 5.9 pH units, it drops to values smaller than three. In the next minutes, the pH values continue to drop until reaching values smaller than two, but the ratio is not as prominent. Similar to the case of the conductivity measurements, the effect of the air discharge on pH is significantly more intense than the one of the helium or argon discharge.

RNS formation

The results recorded for nitrate show that the concentration grows rapidly with the treatment time, after 40 minutes of treatment exceeding the detection limit of 200 mg/l. Nevertheless, nitrite does not show a similar behaviour. Its presence was not evidenced for the 35 ml samples, even for the highest treatment times, regardless of the plasma gas. The effect of the air discharge is more pronounced than the one of the helium or argon.

H_2O_2 formation

Another very reactive species that is formed at the plasma-liquid interaction is hydrogen peroxide. It was observed that the increase of the treatment time produces an important growth of the H_2O_2 concentration. Moreover, in contrast with the other measured values where the air discharge produced the most remarkable effects, in this case, it is the argon discharge that produces the biggest concentration growth. After 40 min of treatment the hydrogen peroxide concentration obtained using the Ar discharge is 0.84 mM, using the He μ-jet it is 0.53 mM and in the case of the air μ-arc it is 0.33 mM.

4.2.2. Volume dependence

Water volumes between 15 and 35 ml of distilled water were treated for 20 minutes using the helium μ-jet. As expected, it can be seen that smaller volumes can be associated with higher electric conductivities and higher nitrate concentrations. These dependences suggest that the species responsible for the pH, nitrate and conductivity modifications are only formed at the plasma-liquid interface and then transferred to the liquid and that the generation rate of species does not depend on the treated volume, but more likely on other parameters (plasma gas, treatment time).

4.2.3. Time evolution

It was observed that all the measured characteristics tend to be stable for the time interval they were measured. Only very small variations are recorded in the first 2 days after the treatment. Moreover, the time stability is not affected by the plasma gas or the initial concentrations of active species that are formed in the PAW.

4.2.4. Water activation by in liquid plasma

Water samples underwent plasma exposure using the in liquid setup. The properties of the liquid changed with the treatment time. After 30 minutes of treatment, the electrical conductivity reaches values of 240 μS/cm, the pH values drops to 3.02, the hydrogen peroxide concentration is bigger than 100 mg/l which represents the detection limit of the test strips. The concentrations of nitrate and nitrite also grow during the treatment time

4.2.5. Discussions

The results obtained by applying the diagnostics methods on the two distinct phases (gas phase and liquid phase) complete each other and show a good agreement. The high spectral emission of the ·OH radical and low nitrogen emissions observable in the argon micro-jet discharge and in the in-liquid discharge is associated with a big H_2O_2 concentration formed in the liquid phase. Simultaneously, the intense emission of nitrogen and low emission of ·OH radical in the air plasma spectrum is related to high nitrate concentrations. In the case of helium as discharge gas, the emission spectrum shows balanced intensities of OH radical and nitrogen. This can be correlated to medium levels of hydrogen peroxide and HNO_3 as compared to the other two discharges. Therefore, it can be deduced that high levels of the OH radical in the gaseous plasma phase induce the formation of high concentrations of H_2O_2 in the liquid phase while high presence of nitrogen in the gaseous phase produces high nitrate concentrations in the liquid. The electrical conductivity and the pH value proved to be dependent mainly on the concentration of nitric acid, which shows strong acidic properties. At the pH values that characterize the PAW, the acid reaches equilibrium with its hydrolyzed species H^+ and NO_3^-.

4.2.6. Conclusions

PAW was generated using three micro-discharges in He, Ar and air and an in-liquid discharge in Ar. Emission spectroscopy measurements showed important differences between the discharges especially in terms of OH and nitrogen contributions. Furthermore, the high emission of the OH radical was associated with high concentrations of hydrogen peroxide in the PAW, while high nitrogen emission is associated to high NOS concentrations. Moreover the electrical conductivity and the pH value modifications proved to be caused especially by the nitrogen active species. The active species are formed at the plasma-liquid interface and do not depend on the treated volume. Finally the time evolution of the PAW was assessed, proving that new properties of the liquid are stable for more than 21 day, a time interval that is much longer than the similar literature work. This long stability suggests that by choosing wisely the treatment conditions, it is possible to obtain plasma activated liquids with a farther expiration date.

5. RESULTS AND DISCUSSION - APPLICATIONS OF PLASMAS IN CONTACT WITH LIQUIDS

5.1. Colorant degradation

Five different colorants were used in the tests: **methylene blue** (MB), **crystal violet** (CV), **malachite green** (MG), **rose bengal** (RB) and **congo red** (CR).

5.1.1. Degradation by plasma activated water

Solutions of PAW and colorants were formed and were investigated by absorption spectroscopy for several days. It was observed that the interaction with PAW starts to change the spectral characteristics of the colorants immediately after the solutions are formed. The spectra are further modified in the following days as the PAW degrades the colorants (Figure 5.1). Longer treatment times show more rapid discoloration effects.

Figure 5.1. Aspect of the control and the PAW-MB solution formed with PAW obtained after 50 minutes of treatment 2 days after preparation.

Figure 5.2 and Figure 5.3 show the discoloration curves for the dye - PAW solutions, respectively for the dye - nitric acid solutions. CR and RB are discoloured due to the low pH and in the case of MB, CV and MG, the low pH of the PAW solutions is not the sole degradation agent of the dyes.

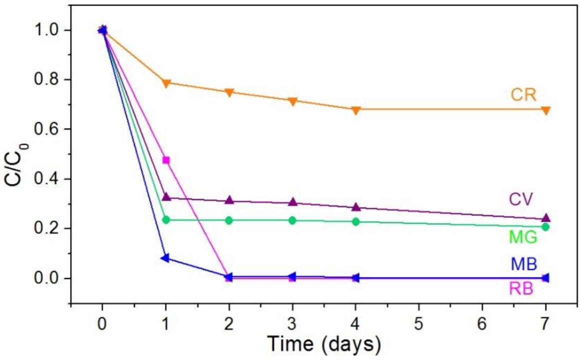

Figure 5.2. Colorant degradation by PAW treated for 50 minutes.

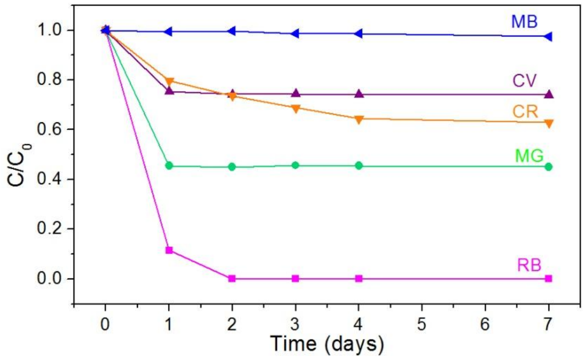

Figure 5.3. Colorant degradation by nitric acid solutions with a pH value of 1.79.

The storage potential of the PAW solutions was also investigated. The PAW was kept in dark closed containers for several days and then was mixed with the dyes. It was seen that for the first two days, the PAW shows identical discoloration properties.

5.1.2. Degradation by direct exposure to plasma

Solutions of the five colorants were exposed to direct plasma treatment for several minutes. The effect of the discharge was very rapid as all colorants were completely discoloured in under 30 minutes.

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5.1.3. Discussion

In the case when plasmas in contact with liquids are used for dye degradation, there are two types of active agents that need to be considered. The first type is represented by the long-lived species that are formed at the plasma liquid interaction and can further become part of the solution. Examples are the hydrogen ion, hydrogen peroxide, ozone and nitrate. The second category is formed by the short-lived species and includes O_2^-, OH^-, peroxynitrite and nitrite. As well as the energetic electrons which, given the energy of the plasma, can easily interact with the colorants. All these species can change the dye molecules by changing or breaking molecular bonds, or by changing the aqueous environment of the colorant.

Considering the interaction of PAW with the utilized dyes, it can be observed that some patterns emerge. Firstly, it can be seen that PAW affects all dyes. Furthermore, the longer the treatment time is, the more pronounced the discoloration is. In addition, during the first hours after the colorant is mixed with the PAW, the degradation is more pronounced than in the following days. It has to be considered that in this experiments, the only species that can affect the dyes are the long lived species, especially the H^+ in the low pH value solutions and the hydrogen peroxide. The tests have also shown that in the case of some of the colorants (CR and RB) the discoloration can be attributed directly to the low pH value of the PAW. In the case of the CV and MG, the degradation is only partially due to pH and in the case of MB the acidic character of the solution does not affect the discoloration.

Another aspect that needs to be considered is that the active species accumulated in the PAW are in a limited amount. The treatment time is very important as it dictates the final concentration of RONS in the PAW. The limited concentration of active species can only result in a limited amount of dye molecules that are discoloured. As the dye interacts with the active agent, it is consumed and fewer active molecules remain to interact with the dye. This represents a potential explanation for the trends shown when PAW treated for 10 minutes is mixed with the dye and only a partial discoloration of the dye occurs during the first days and then stops. It also explains why at the beginning, when the concentration is higher, the discoloration rate is intense and in time, as the concentration decreases and less acute discoloration rates are visible. The discoloration process could also be affected by the lifetime of the active agent. Therefore, if the agent has just a limited lifetime, the discoloration time interval is limited.

In the case of the direct treatment, all three categories of active agents can be involved in the discoloration process. The discharge represents an unlimited source of RONS, H^+ and even electrons that can interact continuously with the dye molecules. Using the direct plasma treatment, all colorants are completely degraded in a very short timeframe, in contrast with the PAW mediated degradation process where the degradation is slow and sometimes limited. This comparison highlights the importance of the short-lived active species that have a remarkable contribution on the discoloration process.

5.1.4. Conclusions

The effect of plasma treatment was evaluated on five different organic dyes. The colorants were both discoloured by exposure to plasma and to plasma activated water. The results show that the treatment time is a very important parameter for the discoloration process as it influences the amount of active species acting on the dye molecules. The long-lived species proved their degradation ability in the PAW experiments, while the short-lived species established their importance in the direct treatment experiments. Each discoloration approach has its own advantages and disadvantages. The direct plasma exposure is a very rapid one, as the colorants were completely degraded in less than 30 minutes, but the contact with the discharge is needed at all times. The PAW degradation is more time consuming and can show selective results, depending on the colorant. However, the PAW treatment can be applied without the necessity of a plasma generator and the PAW solutions proved to maintain their degradation ability for at least two days.

5.2. Protein modification

5.2.1. Collagen

The plasma treatment changes the properties of the water including its pH value, facilitating the dissolution of the protein. It can be deduced that the tertiary structure of the protein is affected. The amide bands are present in the FTIR spectra, but their peak positions are modified due to the interaction with plasma and PAW.

Collagen samples were also analyzed by means of XPS spectroscopy. The survey spectra showed that the elemental concentration changes with the plasma exposure. Table 5.1 shows the elemental ratios of the atomic contributions as calculated from the XPS survey spectra. It can be observed that both nitrogen and oxygen concentrations grow with respect to carbon. The formation of new C-O bonds was evidenced.

Table 5.1. Element ratios as obtained from XPS survey measurements.

Sample	C1s (%)	N1s (%)	O1s (%)	N1s/C1s	O1s/C1s	O1s/N1s
Collagen control	78.2	3.1	18.7	0.04	0.24	6.03
Col-PAW-20	75	3.5	21.5	0.05	0.29	6.14
Col-D-20	72.1	4.5	23.4	0.06	0.32	5.20

5.2.2. Albumin

The second protein that was studied is bovine serum albumin (BSA). The BSA is characterized by the presence of the Amide I band at 1652 cm^{-1}, the Amide II at 1542 cm^{-1} and Amide III at 1237 cm^{-1}. Other peaks are visible at 1396 cm^{-1}, 1454 cm^{-1}. The ν(C=O) peak at 1748 cm^{-1} and ν(C-H) bands at 2854 cm^{-1} and 2925 cm^{-1}are well represented. It was seen that both, PAW and direct plasma exposures generate modifications at spectral level. The amide bands are still present in the spectra, which means that the deep core of the protein is still present, but the peaks position change and the general aspect of the spectrum is altered.

Table 5.2. Element ratios as obtained from XPS measurements.

Sample	C1s (%)	N1s (%)	O1s (%)	S2p (%)	N1s/C1s	O1s/C1s	O1s/N1s	S2p/C1s
BSA control	67.9	14.5	16.9	0.7	0.214	0.25	1.17	0.010
BSA-PAW-20	63.8	13.9	21.6	0.7	0.218	0.34	1.55	0.011
BSA-D-20	60.8	13.5	24.8	0.9	0.222	0.41	1.84	0.015

XPS measurements on the control, the BSA-PAW treated for 20 minutes and BSA directly treated for 20 minutes samples show that the main elements that form the protein are carbon, oxygen, nitrogen and sulphur. The data obtained from the XPS survey spectra, shown in Table 5.2, point out the changes in elemental concentration. The most striking changes refer to the oxygen content. In the case f the PAW experiment, it can be seen that O grows in concentration. Therefore, it can be deduced that O groups are added to the molecule through the formation of new bonds.

5.2.3. Discussions

The two proteins used in the study are very different. Collagen is a very resistant molecule with a fibrillar shape and BSA is a globular protein that is very susceptible to its environment. These differences resulted in a different behaviour of the two molecules when exposed to PAW and direct plasma treatment.

In the case of the first series of experiments, when the proteins were introduced in PAW, collagen seems not to be affected as its FTIR spectrum shows only minor changes in terms of band positions. In contrast, the BSA appears to be more affected than collagen. Not only that the band maxima changed their positions, but also a new absorption band appears to be formed. The XPS measurements completed the data. They proved that in the case of both, collagen and BSA, the amount of C-O bonds is increased after exposure to PAW. The modification in the case of BSA is more striking.

The direct plasma treatment proved to be more aggressive than the PAW. Again, in the case of collagen, no important modifications appear to be produced. However, in the case of BSA, the spectrum shows a very intense and broad new band which can be attributed to newly formed molecular bonds. The XPS data confirmed the formation of new C-O and COOH functionalities and showed that the concentration of oxygen in the molecule is increased. The XPS data also highlighted some modifications in the collagen molecule and proved that new C-O bonds are formed even if this is not visible in the FTIR spectrum. All the modifications produced by the direct plasma exposure are more noteworthy than the ones generated by the PAW.

Proteins are intricate molecules that show complex interactions with other molecules. This is the reason why it is difficult to identify the exact mechanisms through which the two studied proteins change at the interaction with plasma and plasma activated water. However, two important plasma generated denaturation factors can be distinguished. The first one is the low pH value that is known to affect proteins like BSA [16]. The second factor is represented by the reactive oxygen species. The effect of the long-lived ROS is observable in the modifications that are generated by PAW, especially to BSA, when the probable source of new oxygen bonds is represented by H_2O_2. The effect of the short-lived ROS appears to be more pronounced, as the protein modifications generated by direct plasma exposure are more dramatic than the ones generated by PAW. In the plasma emission spectra, emission lines of O and the emission band of OH radical are visible. These two species are generated continuously during the plasma-liquid interaction. Consequently, even is their lifetime is short, during the direct treatment, they can still create new oxygen containing functionalities at the surface of the proteins.

5.2.4. Conclusions

Two proteins, collagen and bovine serum albumin were exposed to direct plasma treatment and to PAW solutions. The effects of the two treatments differ from protein to protein. In the case of collagen, the FTIR results show that no important changes occur in the secondary structure of the proteins, as the specific Amide bands are just lightly changed. However, the XPS measurements highlighted important differences between the control, PAW exposed and direct plasma exposed samples. The oxygen concentration at the surface of the protein increases due to plasma treatment as a result of newly formed C-O bonds. In the case of albumin, the plasma effects are more evident than in the case of the collagen. The FTIR measurements highlight important shifts of the Amide bands and more importantly, they evidence the formation of a new absorption band suggesting the formation of new chemical bonds. The XPS results enriched the knowledge revealing that new created bonds are C-O and COOH.

A common trend in the case of both proteins refers to the more intense effect of the direct plasma exposure of the proteins in comparison to the PAW exposure of the molecules. Important changes are induced on both, collagen and BSA, but their structure is not fundamentally affected. In the continuously growing field of biomedical applications of plasmas, the effect of the treatment on the core components of the human body needs to be fully investigated.

5.3. Bacterial decontamination

The current work investigates the potential of the PAW for *Staphylococcus aureus* inhibition.

5.3.1. Volume ratio dependence

It appears that the PAW can aid the development of the microorganisms if used in small quantities. In the case in which the inhibitory agent exceeds the nutrient broth in volume, the effect of the plasma treatment loses its relevance due to the fact that the bacteria are inhibited by the important changes of nutrient concentration and osmotic properties of the liquid [17]. The volume ratio in which the effect of the water activation process is evidenced the most is 1:1.

5.3.2. Treatment time dependence

The effect of the treatment time on the interaction between PAW and *S.aureus* was investigated. It was observed that for low treatment times, the PAW appears to be beneficial for the microorganisms and to stimulate their growth. By increasing the treatment time to 30 minutes, the PAW becomes harmful for the bacteria and a mild inhibition effect of the PAW is highlighted. A further increase of the treatment time results in a stronger inhibition degree of the bacteria.

5.3.3. *Discharge type influence*

Three types of discharges were used to activate the PAW for identical treatment time. The use of the different discharges offers different results for each discharge. It was seen that the air discharge offers the lowest inhibition rate while the Ar discharge shows the more intense effect.

5.3.4. *Storage potential*

The storage potential of the PAW was investigated. Before the addition to the bacteria, the PAW samples were stored under room temperature, dark conditions, in closed plastic containers. Figure 5.4, shows the results. It can be seen that even if the ratio slightly varies, the inhibition effect of the PAW is still considerable.

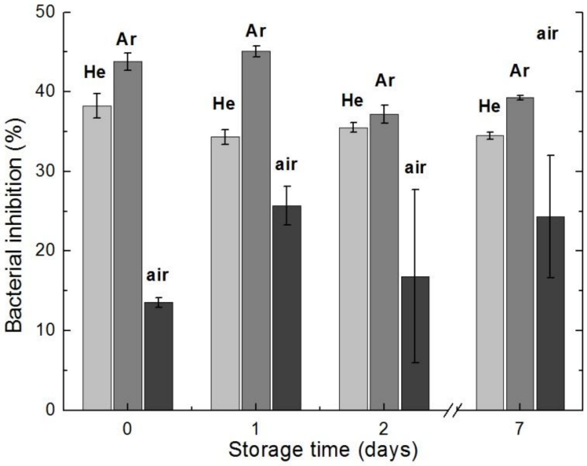

Figure 5.4. Bacterial inhibition effect of PAW - storage time dependence.

5.3.5. *Discussion*

The results show that a small quantity of PAW active species added to bacteria growth medium does not affect the evolution of the microorganisms or, contrary to the expectations, aid their growth process. This trend is evident both in the case of volume ratio and treatment time dependencies. However, a higher quantity of active species formed in the activated water results in a considerable inhibition effect of *S.aureus*. This is most evident when the treatment time is increased to 50 minutes and the discharge type is changed.

The hydrogen peroxide emerged as the main active species that is formed at the plasma-water interaction in terms of *S.aureus* inhibition. Comparing these results with the literature it can be seen that the opinions regarding the main factors of bacterial inhibition at plasma-water interaction are divided. Considering all the opinions, it could be supposed that there are several mechanisms that contribute to the inhibition process. The pH value, the reactive oxygen and the reactive nitrogen species can all be responsible for antibacterial effects. Depending on the species generated by the plasmas, the final concentrations of RONS in the PAW or the time the activated water is in contact with the microorganisms, one of the agents mentioned above could become dominant, similar to this work in which H_2O_2 proved to be the main agent.

The storage potential of the PAW proved to be in this case at least 7 days. This contrasts with the results presented in [18], where the lifetime of the water was considered 25 minutes. In [19], the authors showed that the inhibition effect of the PAW is reduced remarkably in the first 30 minutes after plasma exposure. Shen et al. [20] have investigated the antimicrobial effect of PAW stored at different temperatures and concluded that the PAW stored at room temperature loses its antimicrobial efficiency in a few days after the plasma exposure and that the storage under freezing conditions at -80 deg. C proved to increase the storage potential of the PAW. Traylor et al. [21] have shown that when a PAW sample interacts with a bacterial culture for short time intervals (15 min), the inhibition efficiency shortly drops with the increase of the storage time, but when the PAW interacts with the microorganisms for 3 hours, the storage potential of the activated water can reach up to 7 days. However, if the results concerning the over 21 days time stability of the PAW properties, previously published in [22], are considered and the main antimicrobial agent of the PAW is identified as the H_2O_2, also regarding the 24 hour PAW incubation time with the microorganisms, the long storage potential shown by the PAW samples can be explained.

5.3.6. Conclusions

The distilled water activated by exposure to non-thermal plasmas showed important inhibitory effect on *S. aureus*. The treatment time of the liquid samples, associated with different concentrations of active species that are formed in the water can also be associated with varied effects on the bacterial cultures. While a small treatment time corresponds to an almost inexistent effect on the microorganisms, 50 minutes of treatment result in considerable inhibition effects. The argon discharge proved to generate the most antimicrobial PAW, and the main inhibition agent was identified to be the hydrogen peroxide, while the low pH value did not substantially impact the process. The inhibition potential of the PAW samples proved to be very stable, for 7 days after plasma exposure the changes were minor, even if the water samples were stored at room temperature. The plasma activated liquids represent a very complex medium as it contains several chemically active agents. When it takes contact with bacterial cells, several antimicrobial mechanisms can be stimulated inhibiting the development of the microorganisms. The processes are not fully understood yet, but each work is a step forward for more clarity.

5.4. Gold nanoparticles synthesis

The chemical route of noble metal nanoparticle synthesis supposes the electron exchange between a metal salt and a reducing agent in the presence of a stabilizing agent. In the case of gold,

$HAuCl_4$ is transformed in $AuCl_4^-$ in water solution and then reduced to Au^0. The gold atoms nucleate and are stabilized under the presence of capping agents.

5.4.1. Naked nanoparticles

Electrostatically stabilized gold nanoparticles were first synthesised using a plasma assisted method by Patel et al. [23]. Gold was reduced and stabilized without the addition of any other chemicals at the interaction between a $HAuCl_4$ solution with plasma.

The dependence of pH value and precursor concentration were investigated. The LSPR peak maximum wavelength varies from 537 nm to 588 nm prove the formation of gold nanoparticles with a wide interval of sizes and shapes. TEM images were recorded for observing the shapes and sizes of the nanoparticles at extreme low, extreme high and not modified pH values. The properties of the nanoparticles are summarized in Table 5.3. Important differences in terms of shape and size are visible.

Table 5.3. Summary of the sizes and shapes of the nanoparticles obtained for different conditions of pH and precursor concentration. The symbols in the Shapes column refer to the bidimensional representation of the nanoparticles in the TEM images: Δ = triangle, ◊ = rhomb, ○ = circle, r = rod, 5 = pentagon, 6 = hexagon, i = irregular.

$HAuCl_4$ Concentration	pH value	Size range	Average Size	Shapes
mM		nm	nm	
0.0025	2	1.5-7.5	4	○
	N	1.2-19	9.7	Δ○
	12	1.1-10.8	3.3	○
0.05	2	1-29.8	4	○
	N	1.1-47.4	14.2	Δ◊○56ri
	12	1-12.8	4.9	○
0.1	2	1.6-57.3	14.7	○Δ
	N	2.6-268	42	Δ◊○56ri
	12	1.1-7.5	2.8	○
1	2	1.1-8.9	3.7	○
	N	1.6-300	73.4	◊○Δ65
	12	1-16.7	6.3	○

5.4.2. Collagen coated nanoparticles

Collagen coated gold nanoparticles were synthesised by precursor exposure to the in liquid plasma. The start precursor is composed of $HAuCl_4$ salt, collagen and NaOH which controls the pH value of the solution to be 10. This proved to be the best option in terms of solution stability. In just ten minutes of treatment, the solution changes its colour to red indicating the formation of the NPs. The colloids show a LSPR peak with a maximum at 532 nm after just 5 minutes of treatment. The position of the absorption maximum shifts with treatment time.

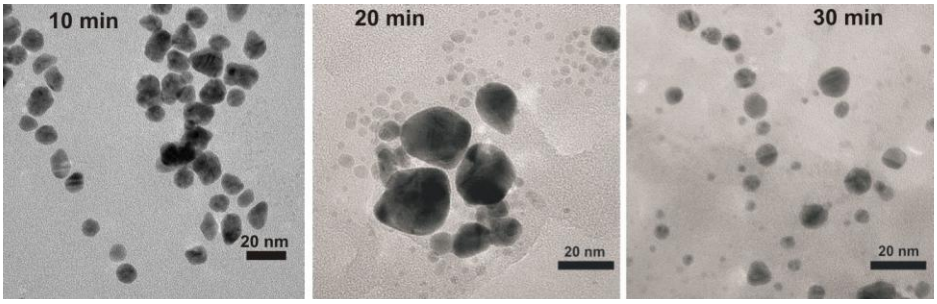

Figure 5.5. TEM images of the collagen coated gold nanoparticles obtained for different treatment time intervals.

Figure 5.5 displays TEM images of the gold nanoparticles obtained for 10, 20 and 30 minutes of plasma exposure. Longer treatment time intervals seem to result in the formation of smaller nanoparticles with more rounded shapes. Purified nanoparticles underwent XPS and FTIR measurements proving that the nanoparticles are indeed covered with the protein. Moreover, it was observed that the colloids synthesized using plasma treatments of 10, 20 and 30 minutes exhibit high stability.

5.4.3. Discussions

Gold nanoparticles can easily be generated at plasma-liquid precursor interaction. Both, naked nanoparticles or protein stabilized nanoparticles were obtained in only 10 minutes of plasma exposure. A broad distribution of particles was obtained. Nanoparticles can have sizes starting with 1 nm and reaching several hundreds of nm. The shapes of the particles can also be varied as the two dimensional TEM projections of the NPs are circular, triangular, pentagonal or hexagonal. Rod like nanoparticles were also formed in the stabilizer free method.

The pH value of the solution proved to be a very important factor for the qualities of the colloidal nanoparticles. Firstly, it influences the degree of gold reduction, apparently impeding the process at very low pH values. It also influences the size and shape of the nanoparticles as the extreme conditions contribute to the formation of nanoparticles with limited dimensions and rounded shapes. The stability of the colloidal solutions is also affected by the initial characteristics of the precursor. Too big concentrations of $HAuCl_4$ can result in the agglomeration of the nanoparticles rapidly after preparation. The same result is shown when low pH values are used. In contrast, the use of optimal synthesis parameters facilitates the formation of colloidal solutions that are stable for several days.

5.4.4. Conclusions

Two types of gold nanoparticles were synthesised from liquid salt precursor using plasma treatments. Plasma proved to be an efficient gold reducing agent in both AC and DC configurations. The plasma synthesis is a one step, rapid method that involves a minimum number of chemicals. In both cases, for the generation of collagen coated and naked nanoparticles just 10 minutes of plasma exposure were needed to obtain stable colloidal solutions. The properties of the nanoparticles can be modified as they depend on parameters like precursor concentration, solution pH value and treatment time. The pH value of the precursor solution and the H_2O_2 concentration in the treated solutions are interconnected and can strongly influence the final properties of the NPs. Varied shapes, including spheres, polygons and rods can all be obtained. Also, the sizes of the NPs can vary from a few nm to more than 100 nm.

The plasma treatment for the generation of nanoparticles is a very promising synthesis method. The developing of fully controlled naked nanoparticles would allow the use of the NPs in a very wide area of applications. Furthermore, the synthesis of collagen coated nanoparticles represents the first step towards the obtaining procedure of fully customized coated nanoparticles for specific purposes.

6. FINAL CONCLUSIONS AND FUTURE PERSPECTIVES

Atmospheric pressure non-thermal plasmas in contact with liquids proved to be a versatile tool for multiple practical applications as they were used for water activation, colorant degradation, protein modification, bacterial inhibition and nanomaterial synthesis.

The gas phase of the plasmas in contact with liquids is characterized by the presence of multiple reactive oxygen and nitrogen species depending on the discharge parameters. These species interact with themselves or with other molecules and further diffuse in the treated liquids changing their properties and their reactivity. Plasma activated water is characterized by acidic pH values, high electrical conductivities and by big concentrations of hydrogen peroxide, nitrites and nitrates which are formed at the plasma-liquid interface. A very important feature of the new water properties is that they are constant for long time intervals even at room temperature.

The reactivity of the plasma activated water recommend it for organic dye discoloration applications. Five different colorants were degraded by direct plasma exposure, but also at the interaction with PAW. The effect of the water is not as rapid as the effect of the direct treatment, but the PAW has the advantage that it does not require the colorant direct interaction with the discharge and that it holds its degradation properties a few days after its activation.

The plasma treatment also proved to affect the biological material it comes in contact with. BSA and collagen were both affected by the interaction with the discharge and with the PAW. Even if the fundamental protein structure was not affected, important changes of the proteins were recorded as new C-O and COOH bonds were created at the protein’s surface.

The PAW also proved to be very effective for bacterial decontamination. *Staphylococcus aureus* was remarkably inhibited by the presence of big volumes of PAW, while small volumes of activated water appear to aid the bacteria in their development. The PAW inhibition properties proved to be considerable for at least 7 days after activation. Moreover, the most important PAW species in terms of antimicrobial properties was revealed to be the hydrogen peroxide.

The active species generated by the plasma also proved important for nanoparticles synthesis. Naked NPs and collagen coated NPs were obtained at plasma-liquid interaction. The final properties of the particles depend on the precursor and plasma exposure conditions. Varied shapes and sizes characterize the NPs, but by controlling the treatment time, the pH value and the H_2O_2 concentration, the dispersion degree can be narrowed. Moreover, the so synthesised nanoparticles have shown a remarkable time stability as the naked nanoparticles can resist several days and the collagen coated nanoparticles can resist several months without aggregating.

The properties of the plasmas in contact with liquids recommend them for numerous applications. However, some of the action mechanisms still need further investigations. It is a research field that is found at the dawn of its existence, which means that the future perspectives are unlimited. In terms of environmental applications, the plasma treatment could find its use in waste water treatment. However, attention needs to be paid to the secondary products resulting due to pollutant degradation. Investigations of their structure, toxicity and effects need to be made. In terms of biological applications, PAW applications for sterilization of a broader range of microorganisms could be investigated. Also, treatments on biofilms and solid substrates need to be considered because the organization of the microorganisms is known to change their behaviour. The biomedical applications of plasmas also need further work. The basic mechanisms of interaction between plasma and biomolecules need to be evaluated in close to body conditions, given that until now only the effect on a limited number of molecules is known. Moreover, the effect of plasma needs to be differentiated between healthy and distressed tissues, so that the beneficial and harmful effects could be identified. Finally, the material synthesis and engineering field can be enhanced by developing new materials and by taking to a new level the current ones. Gold nanoparticles could be better tuned in terms of shapes and sizes, but could also use a widening of the capping agent spectrum.

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APPENDIX 5 - SCIENTIFIC ACHIEVEMENTS

Thesis related articles

- **Iulia-Elena Vlad**, Sorin Dan Anghel, *Time stability of water activated by different on-liquid atmospheric pressure plasmas*, Journal of Electrostatics 87, 284-292 (2017).
- S.D. Anghel, D. Zaharie Butucel, **I.E. Vlad**, *Single electrode Ar bubbled plasma source for methylene blue degradation and concurrent synthesis of carbon based nanoparticles*, Journal of Electrostatics, 75, 63-71 (2015).
- **I E. Vlad**, O T. Marisca, A Vulpoi, S Simon, N Leopold and S D. Anghel, *Simple approach for gold nanoparticle synthesis using an Ar bubbled plasma setup*, Journal of Nanoparticle Research, 16:2633, (2014).
- **I.E. Vlad**, C. Martin, A.R. Toth, J. Papp, S.D. Anghel, *Staphylococcus aureus interaction with plasma activated water*, 2017, Journal of Electrostatics, submitted.

Other ISI articles

- S.D. Anghel, **I.E. Vlad**, *Characterization of a Dielectric Barrier Discharge Generated in Open Space with Flowing Working Gas*, Romanian Journal of Physics, Vol. 61, Nos. 5–6, P. 999–1008 (2016).
- **E. Vlad**, C. D Tudoran and S. D. Anghel, *Adhesivity improving of pet by treatment in low pressure plasmas generated at 40 KHz and 1 MHz. Comparative study*, Romanian Reports in Physics, Vol. 68, No. 1, P. 305–315 (2016).

Thesis related conference contributions

- **Iulia-Elena Vlad**, *Non-thermal plasmas in contact with liquids – aplications of plasma activated water (plasma nontermică în contact cu medii lichide – aplicații ale apei activate cu plasmă)*, The 2nd edition of the Interdisciplinary Conference of the Babeș-Bolyai University Doctoral Students (Conferința Interdisciplinară a Doctoranzilor Universității Babeș-Bolyai, ediția II), June 23-25 2017, Baru, Romania. [Oral Talk]
- **I.E. Vlad,** S.D. Anghel, *Plasma Activated Water – Degradation Agent for Organic Colorants*, COST TD1208 International Conference on Electrical Discharges with Liquids, 14-17 March 2016, Kocaeli, Turkey. [Oral Talk]
- **Iulia-Elena Vlad**, *Water activation by non-thermal plasma treatment* (*Activarea apei prin tratament cu plasmă non-termică)*, Quality and Excellence in Doctoral Research, 16-20 December 2015, Băile Felix, Romania. [Oral Talk]
- **I.E.Vlad**, C. Martin, A.R. Toth, J. Papp, S.D.Anghel, Plasma activated water – stability and antimicrobial effect, XXXIII International Conference on Phenomena in Ionized Gases (ICPIG), July 9-14, 2017, Estoril/Lisbon, Portugal.
- C. Martin, I.E. Vlad, A.R. Toth, J. Papp, S.D. Anghel, Biomedical application of non-thermal plasma in contact with liquids, Young Researchers in Sciences International Conference, August 14-19 2017, Cluj-Napoca, Romania.
- E. Muntean, I.E. Vlad, S.D. Anghel, *The degradation effect of a plasma micro-jet discharge at the interaction with organic dyes*, 2nd Autumn School on on Physics of Advanced Materials (PAMS-2), September 8-14, 2016, Cluj-Napoca, Romania.
- **I.E.Vlad**, V.A. Olariu, S.D. Anghel, *Protein Modification at Plasma – Liquid Interaction,* 6th International Conference on Plasma Medicine (ICPM-6), September 4-9, 2016, Bratislava, Slovakia.
- **I.E. Vlad**, E. Muntean, S.D. Anghel, *Interaction of an atmospheric pressure plasma micro jet with water based liquids*, XXXII International Conference on Phenomena in Ionized Gases, Iași, România, 26-31 July 2015.
- **E. Vlad,** O. T. Marisca, A. Vulpoi, S. Simon, N. Leopold, S. D. Anghel, *In-liquid plasma application for gold nanoparticle synthesis,* Advanced Spectroscopies on Biomedical and Nanostructured Systems, Cluj-Napoca, Romania, 7-10 September 2014.
- S. D. Anghel, I. E. Vlad and D. Zaharie-Butucel, *Atmospheric pressure plasma in contact with liquids for nanoparticle synthesis*, Advanced Spectroscopies on Biomedical and Nanostructured Systems, Cluj-Napoca, Romania, 7-10 September 2014.

Iulia-Elena Vlad, Oana Teodora Marișca, Nicolae Leopold, Sorin Dan Anghel, *Collagen Coated Gold Nanoparticle Synthesis Using an Innovative Plasma Assisted Approach,* Young Researchers in BioSciences International Symposium, Cluj-Napoca, Romania, July 2014.