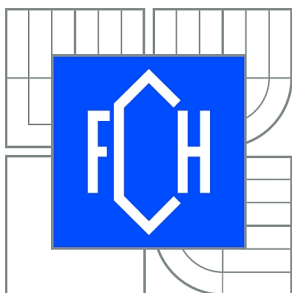




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BRNO UNIVERSITY OF TECHNOLOGY



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STUDY OF PLASMA - LIQUID INTERACTIONS

INTERAKCE PLAZMATU S KAPALNOU FÁZÍ

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2. Hydrogen peroxide production in audio frequency discharge in water solutions.
3. Discharge in gaseous bubbles in liquids - hydrogen peroxide production and application for dyes decomposition.
4. High frequency discharge in water solutions and in water solutions with organics.
5. Interaction of atmospheric pressure plasma jet with solutions.

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ABSTRACT

The presented Ph.D. thesis is a detailed investigation into the properties of electric discharges generated in liquids. These type of discharges have become a popular topic during the last decade, mainly due to many practical applications which are utilised at the present time in everyday life. The discharges in liquids can provide a wide range of unique chemical reactions that are not possible under thermodynamic equilibrium. Due to this fact, underwater electric discharges have been found to be very useful in many industrial areas such as biomedicine, waste water treatment, ecology and nanoengineering. The thesis investigates diaphragm electric discharge, underwater discharge, underwater bubbles discharge and discharge generated microplasma in contact with liquids.

A variety of chemical particles are produced by electric discharge in water such as hydroxyl radicals, hydrogen radicals, peroxoradicals and atomic oxygen or ozone. This work is focused mainly on the hydrogen peroxide generation, which is one of the most important stable reactive components generated in the system. It is a strong oxidizing agent, due to its versatile and environmentally friendly properties which are widely used by industry. One such application is the so called Advanced Oxidation Process, which is a modern method, attracting attention as an emerging clean and efficient technology for waste water treatment. The advantage of this technology is that it can completely or partially destroy organics at ambient temperature by converting them into various harmless intermediates and end products, such as carboxylic acids, carbon dioxide and halide ions.

A special batch chamber, constructed at the Brno University of Technology, Faculty of Chemistry, Czech Republic, was used for the first stages of the experiments. This discharge chamber is separated by a diaphragm membrane with a pin hole at its center. A single high voltage electrode is placed in each part of the chamber, which is filled by water solution. High frequency voltage (1 and 2 kHz) was used as a power source, to treat an NaCl solution (1.5 l) with different initial conductivity (100 – 800 mS/cm⁻¹). An interesting and important result occurred. DC voltage caused a problematic issue of overheating the solution, reducing the effective experiment time, using the high frequency voltage did not produce this unwanted effect. The electric discharge occurred throughout the operation and the hydrogen peroxide was generated without any influence to the electrolysis. This kind of system has been practically shown to be more energy efficient.

The second part of the experiment investigated the discharge generated by gas bubbles in liquids. This experimental set up was created at the Ghent University, Department of Applied Physics, Belgium. This chamber consisted of a small thin capillary, which allowed a gas (He, Ar, N₂ or Air) to flow directly in the liquid medium. This innovation allowed a bubble system to be created on the surface of the capillary, which supported plasma generation while the DC power supply was connected to the system. In this department, two type of studies were undertaken. The hydrogen peroxide generation and organic dye destruction dependence on the applied current were studied. NaH₂PO₄ · 2H₂O solution (5 μS.cm⁻¹, V= 750 ml) was used to hydrogen peroxide production, similarly Direct Red 79 (20 mg.l⁻¹) and Direct Blue 106 (20 mg.l⁻¹, V= 750 ml) solutions were chosen for the organic dyes destruction study. It was observed that strong oscillations of hydrogen peroxide production occurred during the

discharge operation at the low current of 10 mA. Probably, the supplied energy has not provided a stable discharge operation, so only low concentrations of hydrogen peroxide (about 0.35 mmol/l) were found. The maximal hydrogen peroxide concentration (about 1 mmol/l) was measured when the applied current had reached its maximal value of 30 mA. All these facts lead to the conclusion that the hydrogen peroxide concentration increases with an increasing applied current. The organic dyes decomposition was also dependent on the applied energy. The higher the current applied, the better the dye destruction obtained. The maximal destruction was noticed in the Direct Blue 106 solution when 30 mA current was applied. All these facts together showed that this experimental technique is suitable for an industrial application, especially when its configuration allows a versatile practice use.

The third part of this thesis took place at the Queen's University of Belfast, Centrum for Plasma Physics, UK. Here a special commercial medical device, Arthrocare, was utilized to implement some experiments. In this part of study, four different types of solutions were treated by a high frequency plasma scalpel and the changes of these liquids evaluated. It was found that the hydrogen peroxide concentration has reached the maximal value in solutions with a small addition of an alcohol (0.25 %). Four different treated liquid 0.15 M water solutions of BaCl₂, Na₂CO₃, KCl and NaCl (V= 20 ml) were used. The initial conductivity of the samples was around 13 mS.cm⁻¹. The pH values were found to have decreased after the plasma operation and the biggest difference between the initial and final value were noticed in solutions with ethanol added. The temperature of the solution quickly increased up to 70 °C after only three minutes of plasma treatment, while the conductivity was changed slightly during that time. Some of the active particles presented in the solution were detected by spectra, mainly OH radicals which are understood as precursors to hydrogen peroxide. Knowledge gained during this investigation provided a complete characteristic about the influence of additional of organic compound on the plasma process. It was obtained that plasma still can be generated in such solution kind which can be considered as the first step to plasma created in the pure organic liquid medium.

The last part of this work looked at atmospheric pressure microplasma jet interaction with the liquid phase. This experimental technique was constructed at the Nanotechnology & Integrated Bio-Engineering Centre (NIBEC), University of Ulster, UK. A gold (III) chloride trihydrate (HAuCl₄.3H₂O) aqueous solution (2.5 μM, 0.05, 0.1, 0.2, 0.6 and 1 mM) with only distilled water added, were used as the treated medium. The discharge was initiated by a high DC voltage (2 kV) were the processing current reached 0.05 – 5 mA. There was a 0.03 mmol/l hydrogen peroxide concentration in the distilled water after 10 minutes operation, and a 0.51 mmol/l hydrogen peroxide concentration in the salt solution over the same time period. As expected, the hydrogen peroxide concentration increased proportionally to the increased discharge current. Interestingly, even a very low current (0.05 and 0.2 mA) generates stable plasma and produces hydrogen peroxide which can be understood as a very good result. Here, H₂O₂ behaviour as an oxidizing agent which converts a gold precursors into gold nanoparticles.

ABSTRAKT

Tato práce se zabývá detailním studiem vlastností elektrických výbojů generovaných ve vodných roztocích. Tyto elektrické výboje se staly v posledním desetiletí velmi populárním tématem, a to zejména díky mnoha praktickým aplikacím, které jsou v současnosti využívány v každodenním životě. Výboje v kapalinách mohou poskytnout široké spektrum unikátních chemických reakcí, které není možné provést za podmínek termodynamické rovnováhy. Proto jsou podvodní elektrické výboje velice užitečnými v mnoha průmyslových oblastech, jako je biomedicina, čištění odpadních vod, ekologie a nanoinženýrství. Práce zkoumá tzv. diafragmový elektrický výboj, podvodní výboje a výboj generující mikroplasma, které je v přímém kontaktu s vodní hladinou.

Elektrickými výboji ve vodě je produkováno velké množství různorodých částic, jako například hydroxylové radikály, vodíkové radikály, peroxoradikály nebo atomární kyslík a ozón. Práce je zaměřena především na generaci peroxidu vodíku jakožto jednu z nejvýznamnějších stabilních složek generujících se v systému. Peroxid vodíku je zároveň velmi reaktivní, z chemického hlediska se jedná o silný oxidant, který díky své universálnosti a ekologicky šetrnému charakteru je velmi hojně využíván v mnoha oblastech průmyslu. Jednou z těchto aplikací jsou tzv. Pokročilé Oxidační Procesy patřící mezi velmi moderní metody, které budí pozornost zejména v oblasti čištění odpadních vod. Velkou výhodou této technologie je úplné, nebo alespoň částečné rozložení struktury organických sloučenin za teploty okolního prostředí. Tyto látky se tak stávají neškodnými meziprodukty či produkty, jako například karboxylové kyseliny, oxid uhličitý nebo halogenidy.

Pro první část této práce byla využita speciální výbojová komora skonstruovaná na Fakultě chemické Vysokého Učení Technického v Brně. Tato komora byla rozdělena tenkou diafragmovou přepážkou na dvě poloviny, přičemž uvnitř přepážky se nacházela malá dírka. V každé části komory se nacházela jedna elektroda, a obě dvě části komory byly vyplněny kapalinou. V průběhu experimentu bylo ze zdroje do kapaliny aplikováno vysokofrekvenční napětí (1 and 2 kHz), které tak vlastně upravovalo roztok chloridu sodného (1.5 l), který se vždy lišil svou počáteční vodivostí ($100 - 800 \text{ mS/cm}^{-1}$). Během tohoto studia byl zpozorován velmi důležitý výsledek. Tento druh napětí, v porovnání s DC, nezpůsobuje nežádoucí přehřívání roztoku během jeho úpravy. Elektrický výboj hoří po celou dobu plazmové operace a peroxid vodíku je generován bez jakéhokoliv vlivu na elektrolýzu. Prakticky se tak potvrdilo, že tento druh systému je energeticky výhodnější.

Druhá část práce se zabývala zkoumáním elektrického podvodního výboje v prostředí bublin vybraných plynů. Experimentální aparatura pro tento účel byla sestavena na Gentské Univerzitě v Belgii, konkrétně na oddělení aplikované fyziky. Tentokrát výbojová komora obsahovala malou tenkou kapiláru, která umožňovala průchod plynu (He, Ar, N₂ a vzduchu) do prostředí zkoumaného roztoku. Tato inovace zajišťovala tvoření bublin přímo na povrchu kapiláry, což podporovalo generaci plazmatu. Jako zdroj energie bylo použito DC napětí. Ve spolupráci s tímto oddělením se provedly dva typy měření. Jednalo se o generaci peroxidu vodíku a odbourávání organických barviv přítomných ve zkoumaném roztoku. Ke generaci peroxidu vodíku byl použit roztok NaH₂PO₄ · 2H₂O ($5 \mu\text{S}\cdot\text{cm}^{-1}$, V= 750 ml) a podobně, ke zkoumání rozkladu barviv byly použity roztoky barviv Direct Red 79 ($20 \text{ mg}\cdot\text{l}^{-1}$) a Direct

Blue 106 (20 mg.l^{-1} , $V= 750 \text{ ml}$). Během úpravy roztoku $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, při které bylo použito napětí 10 mA , byly zpozorovány silné oscilace v produkci peroxidu vodíku. Pravděpodobně v tomto případě dodávaná energie nestačila k zajištění tvorby stabilního elektrického výboje, a proto byly naměřeny pouze velmi nízké koncentrace peroxidu vodíku (asi 0.35 mmol/l). Maximální koncentrace peroxidu vodíku (asi 1 mmol/l) byla zaznamenána při aplikaci proudu 30 mA . Všechna tato fakta vedou k závěru, že koncentrace peroxidu vodku narůstá se zvyšující se dodávanou energií. Rozklad organických barviv byl také závislý na dodávané energii. Čím vyšší byla dodávaná energie, tím více barviva se odbouralo. Maximální úbytek byl zaznamenán u roztoku barviva Direct Blue 106, kdy byl aplikován proud 30 mA . Všechna tato fakta společně ukazují, že experimentální zařízení je vhodné pro průmyslovou aplikaci, a to zejména díky speciální konfiguraci, která umožňuje mnohostranné praktické využití.

Třetí část práce probíhala ve spolupráci s Queen's University of Belfast, Centrum for Plasma Physics, UK. K realizaci experimentů bylo využito speciálního medicínského přístroje tzv. Arthrocaru. V této části studia byly upravovány různé roztoky, a to pomocí HF plazmového skalpelu. Bylo zjištěno, že hodnota koncentrace peroxidu vodíku dosahovala maxima v roztocích s nepatrným přídatkem alkoholu (0.25%). Celkem byly studovány čtyři 0.15 M roztoky BaCl_2 , Na_2CO_3 , KCl a NaCl ($V= 20 \text{ ml}$), jejichž počáteční vodivost se pohybovala kolem 13 mS.cm^{-1} . Z výsledků bylo patrné, že hodnoty pH klesají během plazmového opracování, přičemž největší rozdíl byl zaznamenán v případě, že roztok obsahoval malý přídatek ethanolu. Zahříváním roztoku se velmi rychle měnila teplota, která vždy stoupla až na hodnotu $70 \text{ }^\circ\text{C}$, a to po pouhých třech minutách měření. Počáteční vodivost během experimentu vzrůstala pouze nepatrně. V optických emisních spektrech byly identifikovány především radikály OH, které jsou chápány jako prekurzory peroxidu vodíku. Znalosti získané během tohoto studia poskytují komplexní obraz o vlivu přídatku organické sloučeniny na generaci plazmatu. Bylo zjištěno, že plazma v takovémto roztoku lze úspěšně generovat, což může být považováno za první krok ke generaci plazmatu v samotných organických kapalinách.

Poslední část práce byla zaměřena na tzv. mikroplazmatický jet v přímém kontaktu s kapalnou fází. Tato experimentální práce byla realizována na pracovišti Nanotechnology & Integrated Bio-Engineering Centre (NIBEC), University of Ulster, UK. Jako vodivé médium byl použit roztok trihydrátu kyseliny chlorozlatité s různou počáteční vodivostí ($2.5 \text{ } \mu\text{M}$, 0.05 , 0.1 , 0.2 , 0.6 and 1 mM) nebo pouze destilovaná voda. Vznik výboje byl iniciován vysokým stejnosměrným napětím (2 kV), kde proud dosahoval hodnot $0.05 - 5 \text{ mA}$. Po 10 minutách experimentu bylo v destilované vodě naměřeno pouze 0.03 mmol/l peroxidu vodíku, zatímco ve zbylých roztocích byla zjištěna koncentrace peroxidu vodíku 0.51 mmol/l . Podle očekávání rostla koncentrace peroxidu vodíku opět v závislosti na aplikovaném napětí. Zajímavým zjištěním je fakt, že při tomto druhu měření bylo generováno stabilní plazma i při velmi malém výbojovém proudu (0.05 and 0.2 mA), a tedy i peroxid vodíku vznikal při velmi malé vstupní energii, což může být považováno za velmi dobrý výsledek. Peroxid vodíku zde totiž vystupuje jako redukční činidlo, které převádí zlatité ionty (chápané jako prekurzory zlatých nanočástic) na Au^0 atomy.

KLÍČOVÁ SLOVA

elektrický výboj v kapalinách, diafragmový výboj, bublinový výboj, organická barviva, plasma skalpel, peroxid vodíku, pH, vodivost

KEY WORDS:

electric discharge in liquids, diaphragm discharge, bubble discharge, organic dyes, plasma scalpel, hydrogen peroxide, pH, conductivity

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1 INTRODUCTION

1.1 Plasma as the fourth state of matter

Despite the general belief, we live in a world of three states of matter, in fact, there is one more state which is commonly used in our daily lives and which creates approximately 99% of the observable universe [1]. This state is called plasma and requires a special introduction.

Plasma in the physical or chemical sense is in principle an ionized gas. Ionized means that at least one electron is not bounded to an atom or molecule, converting the atoms or molecules positively charged ions. Plus, a condition of so called Debye's sphere has to be accomplished which determines a state of quasi-neutrality. The free electric charges – electrons and ions – make plasma electrically conductive (sometimes even more than gold or copper), internally interactive and strongly responsive to electromagnetic fields. Due to this fact, plasma becomes a very interesting topic from the chemical or physical point of view. In the figure 1 a graphical representation of the states of matter, including the plasma state, is shown with their known transitions. As temperature increases, molecules start to be more energetic which leads to the matter transformation. The interactions between plasma and solid (liquid) phase are explained later.

Any ionized gas can not be called plasma (there is always some small degree of ionization in any gas). Ionized gas is usually called plasma when it is electrically neutral in large volume (the electron density is balanced by positive charges) and contains a significant number of the electrically charged particles, sufficient to affect its electrical properties and collective behaviour. How it has been already said, plasma consists of atoms which have lost electrons.

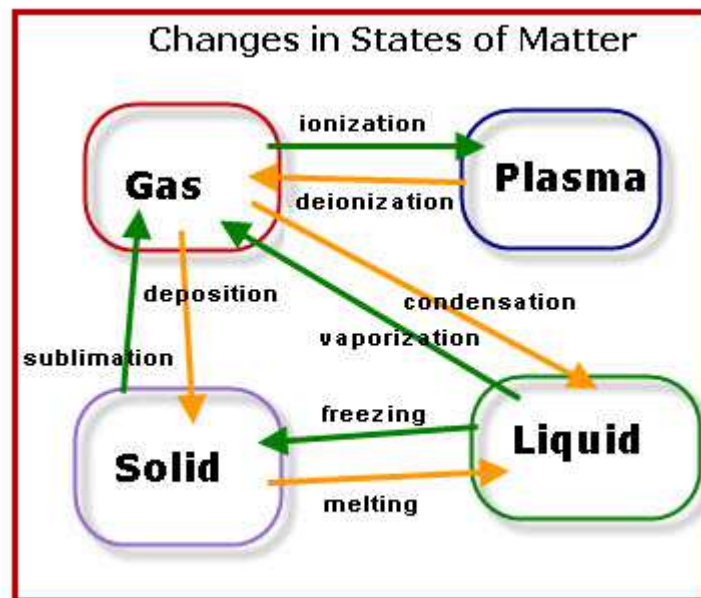


Figure 1 States of matter and their transitions with increasing internal system energy [2].

An energy is needed to strip electrons from atoms to make plasma. This energy can be of various origins such as thermal, electrical or light (ultraviolet light, intense visible light from laser or nuclear fission). Plasma can be accelerated and steered by electric and magnetic fields

which allow it to be controlled and applied. With insufficient sustaining power, plasma recombine into a neutral gas [1-3].

1.2 Plasma and its history

The term plasma was the first used by the American chemist Irving Langmuir (the owner of Nobel Prize) in 1927. He was reminded of the way blood plasma carries red and white corpuscles by the way ions and electrons are carried in gases with high applied voltages. He was investigating with his colleague Lewi Tongs the physics and chemistry of tungsten – filament – light bulbs too finding the way to greatly extend the lifetime of the filament (a goal which he later on achieved). In the process, he developed the plasma sheaths theory – the boundary layer which is formed between plasma and solid surfaces [4].

1.3 Natural plasma

How it has been already ment, plasma creates comprise the majority of the observable universe. There are many phenomena that have got a plasma character such as solar corona, solar wind, Earth's ionosphere, stars or Sun. Practically, Sun is the biggest source of the thermal plasma occurred in the nearby nature. Its plasma surface where there is temperature between 5600 and 5700 K is shown by figure 2. In the Earth's atmosphere, plasma can be very often observed as a lightning strokes. Air is normally non-conducting which means a large potential differences between clouds and Earth can be generated during a storm. Another common natural plasma observed on Earth is called Aurora Borealis. While normal lighting occurs at relatively high pressures (low altitudes, typically up to 15 km), the Aurora Borealis is generated at low pressures at high altitudes, typically between 70 and 100 km.

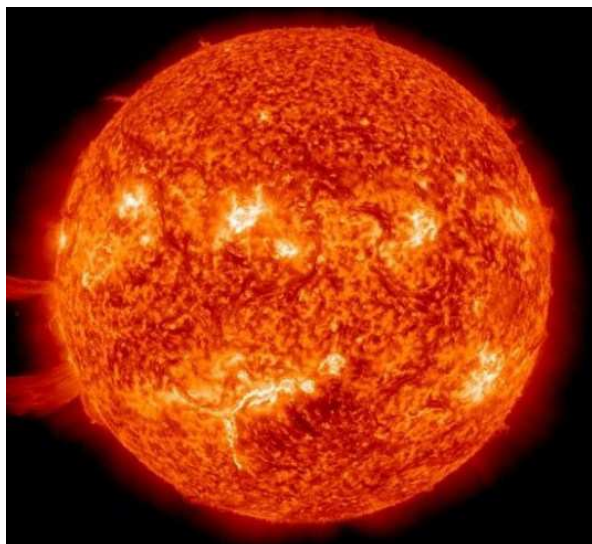


Figure 2 The plasma surface of the Sun [5].

1.4 Technological plasmas

Plasma can be also effectively made in laboratories. These technological plasmas are basically generated by passing an electric current through a gas and they are practically

divided into two main groups: thermal and non-thermal plasma. As in gas, the temperature of the plasma is defined by the average kinetic energy of the particle, molecule, atom, neutral or charge. It mainly depends on the individual particles that are included in its. Thus plasma, as multicomponent system, is able to appear multiple temperature. In electric discharges that are used to plasma generation in the laboratories, energy from the electric field is first accumulated by electrons between collisions. Then the energy is transferred, by other collisions, from the electrons on the heavy particles which causes a loss of a part of their energy. Due to the fact that electrons are much lighter than the heavy particles, they lose only small part of their energy (Joule heating). That is the reason why electron temperature in plasma is initially higher than heavy particles temperature.

1.4.1 Thermal plasma

In thermal plasma, all its components (electrons, ions and neutral particles) have similar temperature that reaches between 10^3 and 10^4 K. Ionization and chemical processes in such plasma are determined by temperature (and only indirectly by electric fields through Joule heating). The gas pressure is usually closed to atmospheric. The significant fraction of the gas particles are ionised. Plasma processing using atmospheric plasma has been useful in variety of applications so far, mainly to increase or active surface reactions and it is utilized for metal recovery, welding or waste treatment. Thermal plasma in nature is for example solar plasma.

The main source of thermal plasma made in laboratory is an arc discharge. It is generated at high pressure while external circuit resistance is low. This is called a thermal arc discharge and it is placed between two electrodes. Thermal arcs normally show high currents and the voltages of the order of tens of volts. They produce large amounts of thermal energy at very high temperatures (10 000 K). Arcs are also used together with gas – flow to generate high – temperature plasma jets.

1.4.2 Non – thermal plasma

A variety of plasmas exist with different conditions. It means, they are characterized by multiple different temperatures related to different plasma particles and different degree of freedom. It is the electron temperature which exceeds that of heavy particles. The electron temperature is much higher than heavy particles temperature. It has range from 10^4 to 10^5 K, while ions and neutral constituents, and processed materials are at about a few hundred Kelvins. Ionization and chemical processes in such kind of plasma are determined by electron temperature and, also, they are not sensitive to temperature of gas. These kinds of plasmas are normally generated in a wide range of pressures that start at very low value of Pascal and reach the order of ten Atmospheres. The pressure needed to discharge operation depends on the electrode configuration and power supply. Such weakly ionized plasma can be produced by different kinds of pulsed discharge systems [6-8].

One of the most important part, which are chemists interested in, is a plasma chemistry because it allows even chemically non-equilibrium processes realised. The experimental techniques for plasma generation in laboratories are basically two electrodes inserted into a system and connected to a power supply. The tube can be evacuated or filled with a gas. As the voltage is applied, the current increases too and it causes an electron avalanche. If the

pressure is low and external circuit has a large resistance, discharge develops. This is called low-current, high-voltage discharge which is widely used to generate non-thermal plasma. A generation of electric discharges in liquid medium, between two electrodes, is described in detail in chapter two (2).

Corona discharge

Another source leading to non-thermal plasma generation is called corona discharge. It occurs at high voltages and atmospheric pressure. The electric field is sharply non-uniform. The field near one or both electrodes has to be much stronger than in the rest of gas. This occurs near sharp points, edges or small diameter wires that become to be a low power plasma sources. Electron temperature in corona is normally around 1 eV and the gas is close to room temperature. This kind of devices is mainly used in the treatment of polymer materials, for example some companies apply the corona discharge on the clothing to provide sufficient adhesion. The corona discharge is considered as a representative of the atmospheric pressure non-thermal plasma source. The following figure 3 represents a multichannel corona discharge.

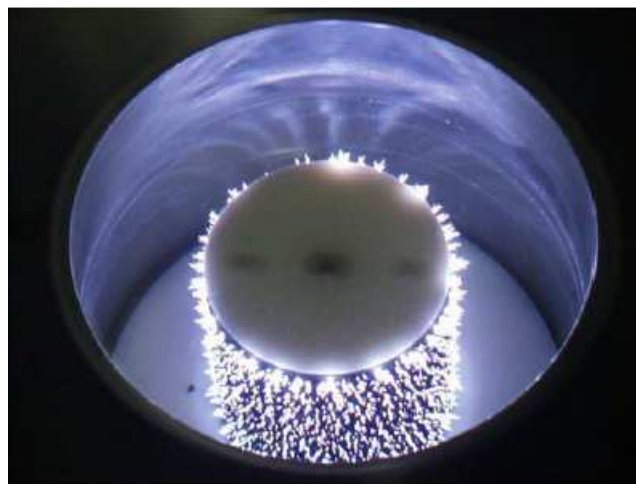


Figure 3 The multichannel corona discharge [8].

The polarity of an electrode where the high electric field is located indicates two types of corona: positive corona (the high electric field zone is located around the anode) and negative corona (the high electric field is concentrated around the cathode). The ionization in the negative corona is caused by multiple avalanches which does not happen in case of positive corona because the electric field at the cathode is basically too low. It means here are ionization processes connected to formation of so-called positive streamers.

Naturally, the electric field is not sufficiently high in whole corona chamber and so the effective charged particle generation occurs only in the certain area. This zone is located around an electrode where the electric field is high enough. This is the most important part of corona system and is called an active corona volume. All of chemical processes and reactions take place here.

Pulsed corona discharges

Because the application of the continuously operating coronas are limited due to low power and current, their practical use for materials treatment is also in a low rate. To increase the corona current and corona power, the voltage and electric field should be increased. An attractive solution for this problem is a non-thermal discharge generated at atmospheric pressure by the pulsed corona discharge. The principle of this type of discharge is a pulse power supply which generates very short high voltage pulses with a steep front and short rise time that results in a higher corona ignition voltage and higher power. The ideal distance between two electrodes is 1 – 3 cm, because than the total time to streamer propagation between tow electrodes is about 100 – 300 ns. This very short period manages to keep streamers during the operation and also it guarantees power transfer into non-thermal plasma. Thus the streamers are not inadvertently transform to sparks. This high-voltage rise pulses are very beneficial for some of the plasma processes because they guarantee higher electron energies which are in these reactions required to decrease the fraction of the discharge power going to vibrational excitation of molecules which causes ionization or dissiciation of the molecules. It means that the corona becomes due to these properties very powerful. A device generating the pulsed corona discharge in the liquid phase is shown in the following figure 4.

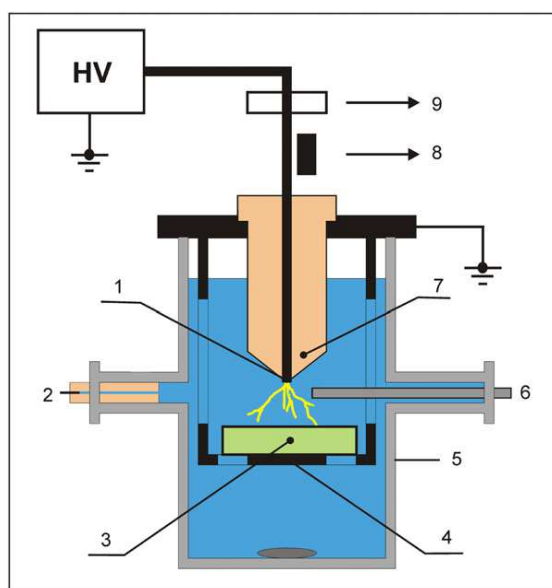


Figure 4 The schematic diagram of the technique for generating the pulsed corona discharge in the liquid phase with the needle-plate electrode geometry. 1-needle discharge electrode, 2-sampling port, 3-cylindrical spectrometric cell, 4-ground stainless steel electrode, 5-cylindrical glass vessel reactor, 6-quartz fiber for optical measurements, 7-teflon insulator, 8-voltage and current measurements ports (HV) pulse power supply [9].

This apparatus is used at Institute of Plasma Physics, Department of Pulse Plasma Systems, Academy of Sciences of the Czech Republic, Czech Republic where the UV radiation from the pulsed corona discharge in water has been studied. The study made by this department (2008) has concluded that the UV light intensity increases with the increasing applied voltage and also, it has positively affected the hydrogen peroxide generation [6-8].

Dielectric barrier discharge

One of the most practical plasma source which produces the non-thermal plasma at high voltage and atmospheric pressure is called dielectric barrier discharge and it produces technologically the oldest type of plasma which has been started to use to ozone generation in 1857 by Siemens. The first technique has consisted of two coaxial glass tubes and two external coaxial electrodes. The electric field has been applied by alternating voltage of sufficiently high amplitude which use to cause electrical breakdown in the following gas. Since the electric current is forced to pass through the glass walls that act as dielectric barriers the discharge has been named as dielectric barrier discharge.

An excellent property, which makes dielectric barrier discharge very attractive for industrial applications, is a fact that human body can be used as a second electrode without destroying the living tissue and so this kind of discharge has brought a huge progress mainly in biomedicine. The detailed description of plasma utilized in the biomedicine is given by next chapter (1.6.1). Also, this type of discharge allows to generate non-equilibrium plasma conditions at about atmospheric pressure. The typical dielectric barrier discharge is shown in the figure 5. As there is seen, the arrangements can be different for this type of setup. The electrodes can exhibit a horizontal direction to each other or they can be get into a round shape. In both cases, at least one dielectric layer is placed between these two electrodes where there are microdischarge filaments created. The materials which are widely used to make the device are namely glass, ceramics, quartz or some kinds of polymers [10].

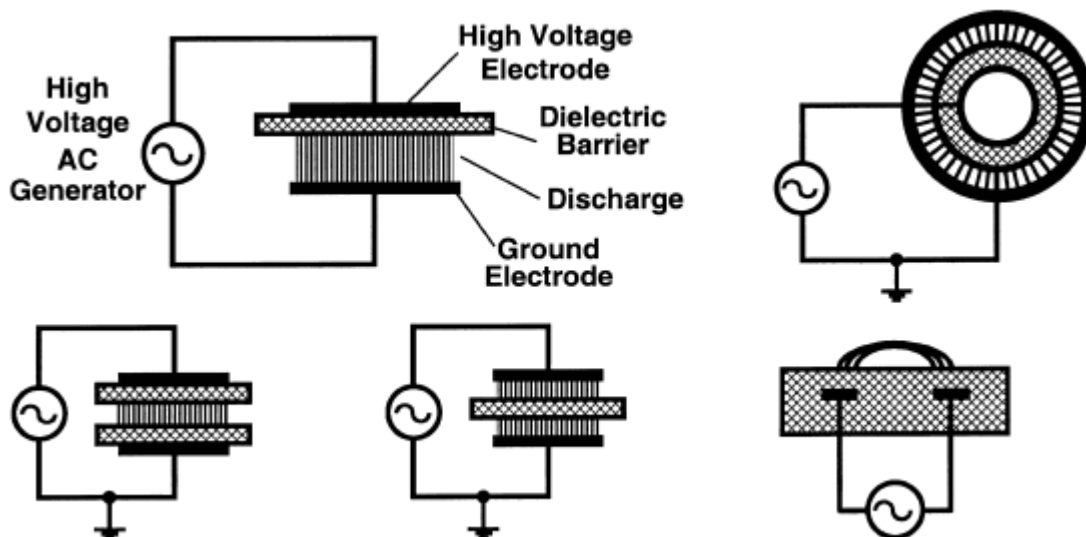


Figure 5 The typical planar and cylindrical dielectric-barrier discharge configuration [10].

Due to the specific dielectric barrier discharge configuration there is a large number of independent current filaments of nanosecond duration generated at about atmospheric pressure. These filaments are understood as little microdischarges which can be predicted by calculations. Also, there is a very helpful possibility to influence them by external conditions. One of these advantages of this microdischarges is, that a large fraction of the electron energy can be beutilize to excite atoms or molecules even in the background gas which causes

chemical reactions and it can also initiate emission of radiation. A frequency of the applied voltage can be different. It can range from low frequency to several hundred kHz. All of these excellent properties guarantee a variety of practical applications of dielectric barrier discharge in many industry fields which are shown in the following figure 6. As there is seen the dielectric barrier discharge has a variety of practical use mainly in the consumer industry. Based on optimized discharge conditions and modern power electronics a considerable progress has been made especially in the area of plasma displays and ozone generation that is described in detailed in the chapter (2.2) [10].

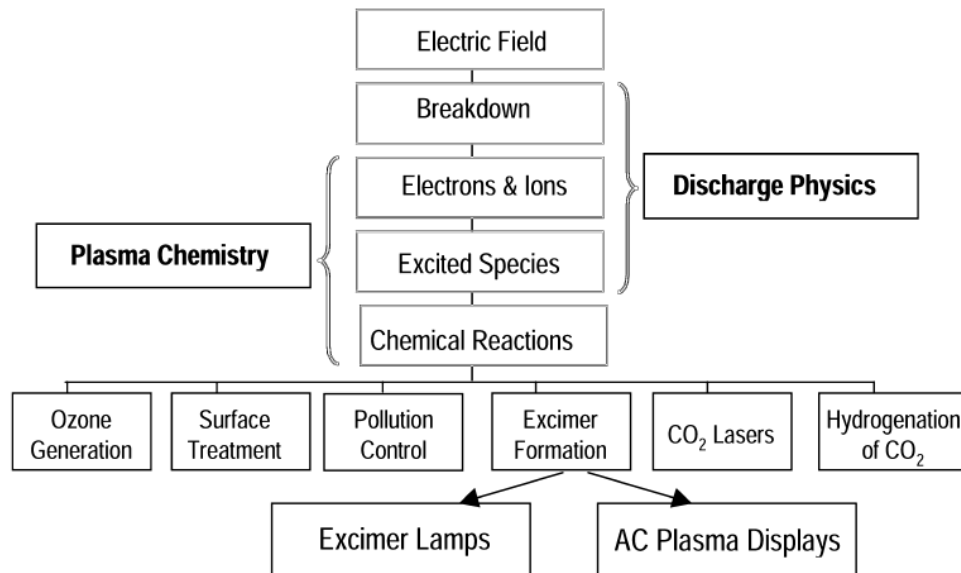


Figure 6 Schematic diagram summarizing the general principle of dielectric barrier discharge and its major applications [10].

1.5 Processes occurred under plasma conditions

Ionization is a key process in the plasma. Due to this fact plasma is an ionized medium. It practically means that there neutral atoms or molecules are converted into electrons and positive ions. These two groups (electrons and positive ions) are at the same time the most important charged particles in plasma. These particles are generated during so called ionizations processes which are responsible for all plasma generation/formation new electrons and positive ions.

Normally, the electron density and positive ions density are equal or really close each other. Than there is spoken about a quasineutral plasma formed. But there is also possibility of negative ions formation in the electronegative gases like O_2 , Cl_2 , $TiCl_4$ etc. These negative ions become the third main group of charged particles in the plasma.

There is also possibility of quite large complex ions generation in plasma. This normally happens in high pressure and low temperature plasma when positive and negative ions attach to neutral atoms or molecule, for example $N_2^+ - N_2 (N_4^+)$, $O^- - CO_2 (CO_3^-)$ or $H^+ - H_2O (H_3O^+)$. These complex ions have very specific properties, however they are basically not important for plasma catalysis or plasma surface treatment [1, 3, 7].

1.5.1 Electrons

Electrons are elementary, negatively charged particles with less mass than the mass of ions or neutral particles and, just because of their low mass and high mobility, they receive an energy from electric field much easier than ions. After that, they transfer their energy during collisions to all other plasma components and so they provide energy for other processes as ionization, excitation, dissociation and other plasma chemical processes. All operations are depended on number of electrons which have enough energy to start these reactions. For this reason, electrons are very important for plasma physics and plasma chemistry.

1.5.2 Positive ions

Atoms and molecules lose their electrons in the ionization process and so they practically form positive ions. Because ions are heavy particles, they take only a relatively small energy directly applied from electric field. The energy which is necessary to form a positive ion is called ionization energy and it is strongly dependent on the molecule. It is also considered as one of the most important parameters of plasma generation. Some examples of ionization energies are shown by following table 1.

Table 1 Ionization energies for different atoms and molecules.

Compound	Ionization energy [eV]
H ₂	15.4
He	24.6
Ar	15.8
OH	13.2
O	13.6
N ₂	15.6
N	14.5
H ₂ O	12.6

1.5.3 Negative ions

Negative ions are easily generated by electron attachment an electron to another atom or molecule. They are also heavy particles so they gain their energy mainly during the collisional processes. Energy that is needed to release this process is called electron affinity. Sometimes, electron affinity is defined as the bond energy between the attaching electron and atom (molecule). Its value is usually very low (much lower than ionization energy). Due to this fact a destruction of negative ions is sometimes cause even by thermal collisions with other heavy particles. The highest value of electron affinity have halogens and obviously their compounds, oxygen or ozone. The specific values are presented in the table bellow [7].

Table 2 Electron affinity for different atoms and molecules.

Compound	Electron affinity [eV]
H ⁻	0.75
O ⁻	1.5
Cl ⁻	3.6
OH ⁻	1.8
O ₂ ⁻	0.44
O ₃ ⁻	2.0

1.5.4 Elementary processes of charged particles

Generally, there are several ways how the particles in the plasma can react. The first, they can influence each other by their fields and the second, they can react together to cause either elastic or inelastic collisions. Elastic collisions do not cause any change in the chemical structure of the reacting molecules who they react with, which practically means that there is no exchange of energy and there is also no excitation observed. Thus they do not have any influence on chemical processes happening in the plasma. On the other hand these elastic collisions are responsible for a kinetic energy which leads to the conclusion that they have a direct influence on the conductivity, diffusion, and absorption of an electromagnetic radiation. During inelastic collisions the kinetic energy of the colliding partners is transferred into the thermal energy. The examples of these inelastic collisions can be excitation, dissociation or ionization. In some special cases, the internal energy of the excited molecules or atoms can be retransferred back into the kinetic energy [1, 3, 7]. Such kind of phenomenon is called as super elastic collision.

1.5.5 Ionization processes

As it has been already mentioned the key process in plasma is ionization. It is responsible for the creation of new electrons and positive ions thus for the plasma generation. There are four groups of the ionization mechanisms distinguished.

The first group is a direct ionization by electron impact, includes the ionization of neutrals. A non-excited atoms, radicals or molecules are attacked by an electron (whose energy is sufficient to provide the ionization) which results in the collision. These processes occur in the cold or nonthermal plasmas where the electron energy is quite high. But the number of excitation of neutral species is average.

The second group is a stepwise ionization by electron impact which includes the ionization of preliminary excited neutral species. These processes are common in the thermal plasmas. The degree of ionization such as amount of highly excited neutral species are quite high.

The third group is the ionization by collisions with heavy particles. These processes can happen during ion-molecule or ion-atomic collisions or in collisions of electronically or

vibrationally excited species. This happens whenever the total energy of the collisions partners is higher than ionization potential.

The fourth group is represented of the photoionization processes. Such situation occurs whenever the neutral collisions with photons lead to the electron-ion pair formation. This type of processes is namely important in the thermal plasma and also in some propagation mechanisms whenever nonthermal discharge is propagated [1, 3, 7].

1.6 Plasma applications related to this work

The general principle of plasma processing technologies is that the energetic electrons break up unreactive feedstock gases, creating a unique environment for non-equilibrium chemistry. The chemical species diffuse to the material surface to be deposited as thin films or to react with the surface to produce a new surface material, or, alternatively to make weaker the surface bounds and so enhance removal rates of atoms as plasma ions strike the surface. In addition, the chemistry may take place in the bulk of the plasma either creating new compounds or destroying compounds to produce a more acceptable substance.

Chemically reactive plasmas are widely used to modify the surface properties of materials. Plasma processing technologies are vitally important to several of the largest manufacturing industries in the world. Surface processes based on plasma are indispensable for many manufacturing such as automotive (plasma jets for pretreatment car interior parts), transportation (plasma pretreatment for aircraft construction or shipbuilding), electronics (plasma screens, plasma treatment for sensitive electronics), plastic packaging (plasma pretreatment advanced composite materials), textiles (material activation and functionalization with plasma treatment), new energies (plasma treatment to high material quality achieved – weather resistant, longterm stability) or furniture (plasma pretreatment to increase material quality). Apart from many other areas, two became the hottest topics during the last few years – plasma medicine (1.6.1) and plasma waste water treatment (1.6.2) [11]. Some of the practical illustrations are shown by figure 7 and figure 8.

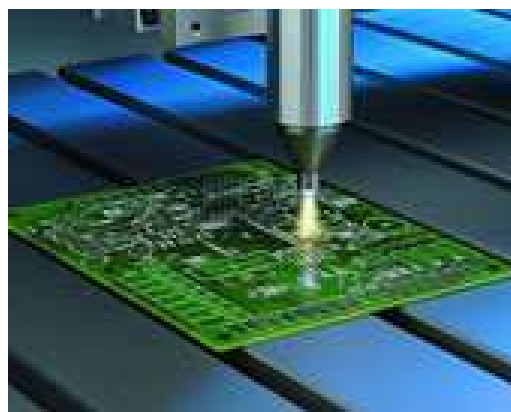


Figure 7 Plasma surface treatment using the plasma jet for sensitive electronics [11].



Figure 8 Plasma treatment of hydrophilises fabrics and technical nonwovens by jet technology [11].

1.6.1 Plasma surface modification in biomedicine

The application of various plasma sources and procedures in biomedicine has become a really hot topic of the contemporary research. It has been found a variety of applications, mainly plasma surface modification and plasma surgery. At the present time The European Cooperation in Science and Technology (COST) has granted a wide financial support to this subject. The goal of this project – Biomedical Applications of Atmospheric Pressure Plasma Technology – is an investigation in many medical fields such as surface treatment of biomedical devices, sterilization, therapeutics techniques or cancer treatments. All details are given at the appropriate link (www.cost.eu/domains_actions/mpns/Actions/MP1101).

Although many synthetic biomaterials have physical properties that reach and even exceed those of natural body tissue, they can often cause adverse physiological reactions such as infection, inflammation and thrombosis formation. Through the surface modification, biocompatibility as well as biofunctionality can be achieved without changing the bulk properties of the material. There are many ways by which to alter the interaction of biomaterials with their physiological environments. The plasma surface modification provides device manufacturers with a flexible, safe and environmentally friendly process that is extremely effective [12].

Electrosurgical devices were the first invented over 100 years ago. Recent historical accounts summarize the development of the technology up to about 1999. Over the last decade, there has been an increasing interest in and use of plasma forming electrosurgical techniques to enable more controlled surgical procedures, for example in otolaryngology, arthroscopy, dental treatment, surgery or blood medicine [13].

Due to the fact that living organisms are tied to water, the subject of many investigations during the last ten years has especially become plasma in contact with liquid. Plasma in conductive saline solutions is a viable candidate for tissue processing inside the body. This kind of plasma has been previously examined for many practical applications namely in electrosurgical and coblation technology [14,15].

A remarkable results has reached plasma generated in the liquid due to the fact that most biological fluids are conducting ionic solutions. These ionic solutions can be in touch with some saline solutions where there is the plasma generated and so the plasma can be in direct

contact with a human tissue. An interesting research has been implemented by K. R. Stalder and J. Woloszko when they have been interested in microplasma produced by electrical discharges in saline environments [16]. They have found that the microplasma that is generated in saline solutions is leading to improved surgical procedures and outcomes. These devices enable volumetric ablation of soft tissues with excellent control and minimal thermal damage of untargeted tissue. The fundamental physics and chemistry of water, both in the liquid and gas phase, play an important role in the microplasma formation and kinetics [17].

In otolaryngology a radiofrequency energy is used to excite the electrolytes in a conductive medium, such as saline solutions. The plasma has enough energy to break the molecular bonds within tissue causing the tissue to dissolve at relatively low temperatures, approximately 45 °C to 85 °C (significantly lower than traditional radio-frequency techniques) which causes volumetric removal of the target tissue with minimum damage of its surrounding. The lower temperatures are achieved as the radiofrequency current does not pass directly through tissue during this so called coblation process which means tissue heating is minimal. Most of the applied energy is consumed in the plasma layer, or in other words, by the ionization process. These ions then bombard tissue in their path, causing molecular bonds to simply break apart and tissue to dissolve. Coblation has been used for otolaryngological applications such as turbinate reduction, palate reduction, base of tongue reduction and various head and neck cancer procedures. The figure 9 shows a neck treatment by plasma scalpel used in otolaryngology [18-19].



Figure 9 The neck treatment by plasma scalpel used in otolaryngology [19].

The decreased thermal effect of coblation has made lots of changes including, less pain and faster recovery for cases where tissue is dissected. In cases where coblation is applied submucosally to reduce tissue volume (inferior turbinate, soft palate), the sudden reduction in volume may lead to immediate clinical benefits for the patient. Coblation is currently being examined and developed in various clinical studies to document the advantages it can make in otolaryngological applications.

There has been lots of investigation and research on the development and improvement of tissue-saving methods in dentistry. Although cleaning and sterilization of an infected tissue in

a dental cavity or a root channel can be achieved using mechanical techniques or laser therapy, during the treatments overheating and destruction of the living tissue can occur which may bring more complications and health hazards. Due to this there was a lot of research to develop non-thermal atmospheric plasma or in other words “plasma needle” in which the interactions of this type of plasma with living tissues related to dentistry and its ability of bacterial inactivation is examined. Plasma needle can be described as an efficient source of different radicals, which have the ability to remove bacterial contaminants from the living tissues. This technique operates at room temperature and therefore, also does not cause high destruction of the living tissue. Plasma treatment is potentially a novel tissue-saving technique, allowing irregular structures and narrow channels within the infected tooth to be disinfected and sterilized. Figure 10 shows one of the advanced dental equipment which is used in the dentistry [20]. The detail of plasma needle is shown by figure 11.



Figure 10 Advanced plasma equipment used in the dentistry: non-thermal argon plasma [20].

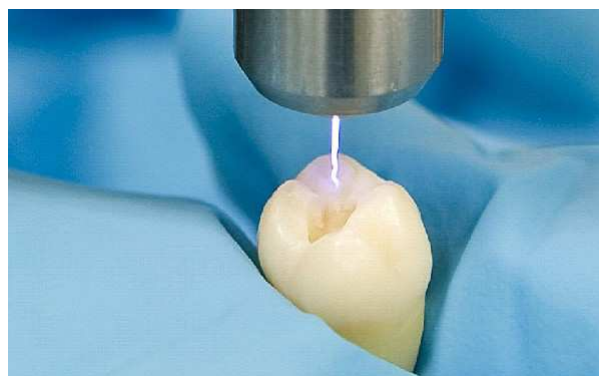


Figure 11 The detail of plasma needle [21].

Plasma surgery is an advanced technology for precise surgical dissection and coagulation, which has recently developed. This technology can help surgeons to achieve more, with less damage to the tissue, ultra-fine control, and accuracy. Recently a new device has been

developed called the “plasma jet“. This device uses a fine, electrically-neutral stream of pure plasma to cut and coagulate tissue. In the Plasma jet system, a low flow of argon gas is concentrated into a small space within the handpiece and excited by a low DC voltage applied between internal, bipolar electrodes.

Argon is the most abundant and widely accessible of the inert gases. It is heavier than air and therefore it can sit on the surface of tissue and displace the air. Argon can be also ionized easily and its chemical properties make it ideal for delivering monopolar current in a controlled fashion. Argon beam coagulators deliver a stream of ionized argon from their tip, creating a homogeneous current bridge to the target tissue. Voltage ionizes the argon, allowing a smooth conduction of current without electrode contact. Being heavier than air, the ionized gas settles uniformly on the tissue, creating a consistent and malleable eschar. As an additional benefit, the stream of gas also disperses blood and oxygen, increasing visibility of the treated tissue and decreasing smoke production [22].

The argon plasma, which is produced, is a mixture of high-energy argon atoms, ions and electrons that emerge from the tip of the handpiece in a precise jet stream. An important property of the plasma stream is that since it contains an equal number of positively charged ions and electrons, therefore, resulting plasma jet is electrically neutral. This means the Plasma jet differs markedly from all electrosurgical techniques, as in plasma surgery there is no external electrical current flow to the tissue. Using Plasma jet, surgeons are able to precisely cut and coagulate tissue while reducing the risk of surrounding thermal damage and burns that can occur with traditional electro-surgery which then may cause in more complications.

1.6.2 Advanced oxidation processes

At the present time, a waste water and its cleaning is becoming bigger and bigger problem. The waste water contains a lot of pollutants and it is very difficult to remove or at least eliminate them. Some of them have got a complex chemical structure, mainly the double bonds, and it is not possible to destruct them by normal biological or chemical ways. Advanced oxidation methods have gained growing attention as an emerging clean and efficient technology to solve this problem. The major advantage of this technology is that it can completely or partially destroy organics at ambient temperature by converting them into various harmless intermediates and end products, such as carboxylic acids, carbon dioxide and halide ions [23]. That is the reason why these methods are becoming more and more popular. Unfortunately, a big group of the problematic pollutants are presented in the water environment, which brings a question how to permanently remove them. Electric discharges in the liquid systems seem to be a promising way how to sort this problem out.

Of course, in the last few years an interest in gase-phase pollution has increased as well. The non-thermal plasma is used to generate highly reactive species which are able to decompose entrained pollutants even in atmospheric pressure gas streams [24]. However, thanks to the focus of this thesis, Advanced oxidation processes in the liquid systems are further discussed.

The principle of Advanced oxidation processes is an application of high electric energy in the liquid system. It causes a generation of very reactive particles which are used to destroy

organic contaminants as water flows into a treatment tank [25-26]. The most important oxidation reagents which are produced by Advanced oxidation processes are hydrogen peroxide H_2O_2 , hydroxyl radicals $\cdot OH$, oxygen radicals $\cdot O$ and ozone O_3 . The general scheme of Advanced oxidation system is shown by figure 12.

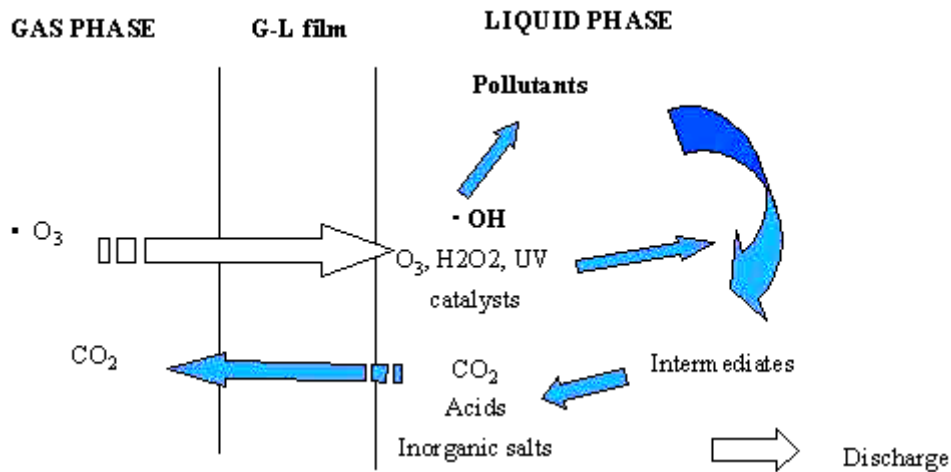


Figure 12 The scheme of Advanced oxidation system in water environment [26].

A general feature of these technologies is a significant consumption of the energy that is released for radicals production. New technologies are developed to provide sufficient quantity of energy that is necessary to the radicals production. There are several types of plasmas in interaction with liquid phase. Here, the non-thermal plasmas are generated in the examined techniques and applied into the liquid system. These methods belong to the group of so called electric underwater discharges and their properties have been studied in this work. Besides these systems, there are also other types of electric discharges which can be included in this group, for example DBD which has been detail described before.

1.6.3 Nanoparticles synthesis

An idea to produce nanoparticles by electric discharge has noticed a very interesting topic in the recent years. Especially a gold nanoparticles synthesis has become a very desirable field due to so called gold nanoparticles in colloids which have found an excellent applications in optical diagnostics and detection of cancer [27], therapeutic techniques [28], drug or gene delivery applications [29]. Naturally, there is a variety of methods how to produce gold nanoparticles, but unfortunately all of these chemical synthesis require an additional treatment by reducing or capping agents to stabilize the generated product [30]. It obviously brings a secondary problem with an elimination of these unwanted reagent from the surface of nanoparticles. Due to this fact, the possibility of creating nanoparticles in aqueous colloids with no additional of chemical agents is highly wanted to simplify subsequent functionalization steps.

Electric discharges seem to be a promising way how to create gold nanoparticles according these requirements. One of the possibilities is an atmospheric pressure microplasma jet which is in direct contact with the liquid where there are nanoparticles synthesized with no need

of reducing or capping agents. Generally, non-equilibrium low-temperature plasma processing at atmospheric pressure is gaining a vital importance in plasma science and technology mainly due to many practical applications in the such as biomedicine, surface modification of polymers, automotive, microelectronics or nanomaterials synthesis [31-33]. Especially, stable generation of plasmas at atmospheric pressure extends a new range of applications for plasma utilized in science and technology. The another remarkable advantage is an interfacing such kind of plasma with a wide range of the liquid solutions. Unfortunately, plasmas generated at high pressures cause instabilities and gas temperature is basically too high which is an unwanted effect for materials processing [34].

Recently, a new type of plasma in microscale has started to be investigated. It is called microplasma and it has opened a new possibility for the nanoparticles synthesis. At atmospheric pressure, the microplasma exhibits some very useful properties which differ from plasma generated at low pressure regimes. These excellent features of microplasmas has caused their wide range of material applications. Main advantages of using atmospheric pressure microplasmas for nanoparticles creation is continuous flow, microreactor volume operation which allows to control the particles growth and residence time leading to the precise formation of nanometer-sized particles, even less than 10 nm. For example, for biological synthesis colloidal nanoparticles are the most required and they can be generated just by microplasma [35-36].

Another advantage of this microplasma is the fact that it brings a new functionalization approaches that are totally different from both standard liquid electrochemistry as well as from gas-phase plasma synthesis. These new approaches based on plasma-induced non-equilibrium liquid chemistry have a great potential of combining some of the best advantages of plasma processing (non-equilibrium kinetics) and wet chemistry (solution processing). Obviously, there are other wet chemical methods to synthesize nanoparticles, but compare to microplasma operation they are slow and also require reducing or capping reagents.

Many of microplasma techniques have already been reported such as plasma generated by electrodes immersed in the liquids [37], gas-liquid interfacial low-pressure plasmas [38] or atmospheric plasma pressure plasma interfacing with liquid [39]. Generally, these investigations have concluded the possibility of controlling morphology and size and they have brought a detailed description of the studied properties, however the mechanisms is still not fully understood.

2 ELECTRIC DISCHARGES IN LIQUIDS

Electric discharges generated in the contact with liquids have been studied mainly during the last decade due to their wide potential practical applications. Many papers have been published and underliquid discharges have been proposed for the applications in biology [40], chemistry [41], electrochemistry [42] ecology, nanoengineering [43-46] and even in medicine [47]. The research in this hot topic is now supported also by the new COST Action *Electrical Discharges with Liquids for Future Applications* about that the details can be found at its web site http://www.cost.eu/domains_actions/cmst/Actions/TD1208.

A general properties of electric underwater discharges consist of five phenomena which occur at the moment of ignition. It is a strong electric field, shock mechanical wave, free radicals production, strong UV radiation and ozone production in case when oxygen or air bubbles are presented in the system.

2.1 The principle of electric discharge generation in the liquid phase

The principle of electric discharge that is generated directly in a liquid phase (the most often in the water solution) is an application of high energy into to the water medium which subsequently leads to its accumulation and discharge ignition. The energy, which is given into the solution from the source of high voltage, is transformed by plasma channel. The plasma channels are created by discharge between two electrodes that are immersed in the water phase. There are three different types of electrode system suitable to such discharge generation. The first construction consists only from two plane electrodes (13a). Due to a very high electric field intensity needed for the breakdown in the liquid ($1 \text{ MV} \cdot \text{cm}^{-1}$) this configuration requires an application of too high voltage or a too short distance between electrodes. Thus it is not used in practice. Next two configurations are suitable mainly for experimental utilize. The first is so called point to plane system (in the figure 13b) and the second one is system where there are these two electrodes separated by dielectric barrier with a small hole (in the figure 13c). In these cases the local electric field intensity increases on the point (tip or hole).

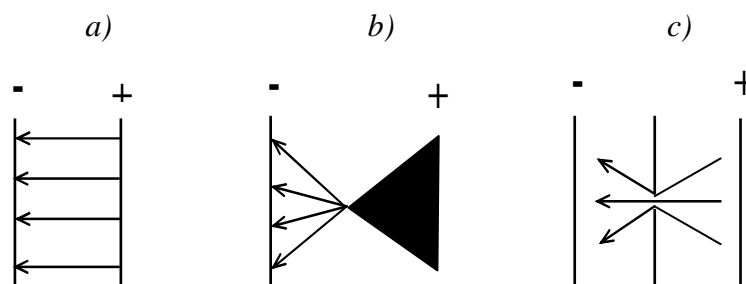


Figure 13 Three different electrode configurations: a) two plane electrodes, b) point to plane, c) pin-hole.

Generally, two different theories describing electric discharge creation in the liquids have been suggested: an electron and a thermal (bubbles) theory [48]. The electron theory says that due to high electric field free electrons in the discharge area are accelerated. The electric field can be applied on the point (point to plane system). Free electrons can subsequently colliding

with other molecules and make them ionized. It is the way how other free electrons are produced and electron avalanche (plasma or „streamer” channel) is formed. The electron avalanche leads to the water breakdown. A DC pulsed voltage is usually applied. In this case electrons are attracted to the electrode with high positive voltage. A free electrons flow causes a positive charge on the top of streamer. This positive charge increases an influence of the applied voltage and attracts other electrons of the secondary avalanche. In case electrons from the secondary avalanche mix with the ions from primary avalanche there is a positive space charge formed on the top of streamer and the intensity of electric field is increased again at the end of streamer. This propagation allows a new avalanches development because positive charges attract electrons from other secondary avalanches. This is the way how the streamer propagate in the space. It is the similar principle as atmospheric lightning generation. This theory practically means that whenever a positive polarity is used, the really long streamer channels can be formed. In case the polarity is opposite (the point becomes a cathode), the electron avalanche starts to propagate from the point (a strong electric field area). The positive space charge of the primary avalanche decreases the intensity of electric field at the end of streamer which is not satisfied for another avalanche development. In this case the streamer channels are shorter than by positive polarity.

There is an assumption in the thermal theory that the high current density in the high electric field area causes warming up and evaporation of the liquid, bubbles are formed and the streamer can spread in the water due to them. Thus the discharge is ignited in the gas phase.

Besides these two general theories the other mechanisms can be taken into account at the under liquid discharge generation and/or propagation. There is also another model which says that electric field is supported by water dissociation, respectively by ions H^+ and OH^- . These ions causes high conductive area from which the streamer spread as ionization wave. Another theory, which describes a streamer propagation, is based on a water evaporation on the top of streamer. A streamer resistance has been measured too much lower than by water. This, and the fact that the a speed of streamer in the deionized and drinking water are the same, proves the main influence of the ionized liquid on the current in the pre-discharge period. A protons mobility in the vapor phase (but not in the liquid phase) is satisfied for streamer spread [49].

The latest experimental results showed that electron theory of the discharge ignition is valid in the case when very short high voltage pulses are applied (nanosecond discharges). On the other hand, the discharge ignited in bubbles can propagate into the liquid by streamers, even if relatively low voltage is applied [50-51].

2.2 The main active particles produced by electric discharges in water and their properties

The strong electric field which is applied into the water medium causes physical and chemical changes in the solution. How is has been mentioned above the most important phenomenon is a reactive particles generation, mainly radicals as $\cdot H$, $\cdot O$ or $\cdot OH$, and stable compounds as hydrogen peroxide and ozone. The other processes such as UV radiation or shock waves generation depends on a conductivity of the liquid, electrode configuration and applied voltage (amplitude, waveform).

There is a lot of particles generated by electric discharge in the treated solution. Their general feature is high reactivity and an ability to oxidize harmful organic compounds which are dissolved in the water. Compare to common chemical methods, electric discharges can break even benzene structures to produce secondary products which can be easily decomposed by the classical chemical/biological methods.

2.2.1 Hydroxyl radical

This kind of radicals appear high reactivity with many organic compounds and it also has a very high oxidative-reduction potential (2.80 V). This potential guarantees also nonselectivity in the oxidation reactions which hydroxyl radicals participate in. They can react with every organic compounds, that is presented in the solution, and oxidize it. They belong to the group of the most important particles produced by electric discharge in water solution because very quickly react with the most of organic compounds and also with a large number of inorganic compounds. Their reactions can be separated into three main groups according a mechanism of the reaction:

- A cut of hydrogen atom:



- An electrophilic addition on the double (triple) bond:



- An induced charger transfer:



OH is too reactive and thus its lifetime is very short. If OH radicals concentration is high enough, they can effectively dimerize. This leads to hydrogen peroxide generation in the solution. A significance of hydrogen peroxide in the liquids system will be described in the following section [52].

2.2.2 Hydrogen peroxide

Hydrogen peroxide (H₂O₂) is a clear, colorless, inorganic liquid with a weak acidic pH. It has a slightly pungent odor. It is a versatile and environmentally friendly chemical with a wide variety of applications. It is commercially available as aqueous solution in various concentrations and grades. Because of the complete solubility of hydrogen peroxide in water, solutions of a wide range of concentrations can be normally made. Under normal conditions, hydrogen peroxide is extremely stable with demonstrated losses of less than 1% per year under ambient conditions. Heat and oxygen are generated during peroxide decomposition and even abnormal decomposition is easily handled by properly designed storage and handling systems. However, if severe contamination occurs or the solution is heated to higher temperatures, relieving devices may not be able to dissipate the volume of gas generated and the system may be overpressured.

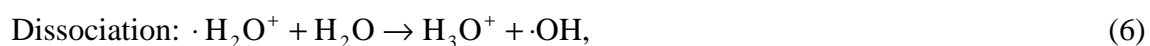
Hydrogen peroxide is not considered explosive, but explosive vapors can be formed when peroxide is mixed with certain organic materials. In addition, hydrogen peroxide is not flammable, but does generate large amounts of oxygen during decomposition that supports combustion [53-54].

Such as hydroxyl radicals, also hydrogen peroxide plays really important role in the plasma processes in water solutions. The first reason is that it is considered as a useful, but not perfect, indicator species for hydroxyl radicals in some plasma systems. The second reason is its generation in the water solutions, mainly for commercial applications in environmental and disinfection processes [55-58]. In the reaction, hydrogen peroxide basically behaves as oxidizing agent and reduces itself to the water. In case it shows reducing character, it oxidizes itself to the oxygen [59]. Basically, the hydrogen peroxide behaves as strong chemical oxidant with a standard chemical potential of 1.776 V. An overall reduction potentials view of the main chemical reactants are shown by table 3. The main oxidants, which this work have been focused on, are red.

Table 3 The overall reduction potentials of the main chemical reactants.

Oxidant	Reduction potential [V]
Fluor	3.053
Hydroxyl radical	2.7-2.02
Atomic oxygen	2.42
Ozone	2.076
Hydrogen peroxide	1.776
Potassium Permanganate	1.51
Chlorine Dioxide	1.5
Chlorine	1.356
Oxygen	1.229
Bromine	1.087
Iodine	0.536

It has been found that hydrogen peroxide is formed in the discharges in liquids due to hydroxyl radicals recombination. The mechanism of the $\cdot\text{H}$ and $\cdot\text{OH}$ radicals is as follows:



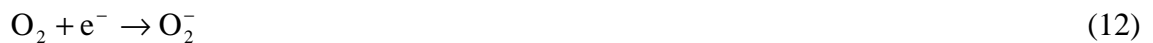
where e^{-*} means an electron with high kinetic energy. The radicals can either react with themselves and so form resulting H_2 and H_2O_2 molecules or they can make a water molecules again or diffuse from each and be disposable for some consequent reactions with solution. Which kind of reaction preferentially happens depends on electron energy distribution on the top of streamer. The schemes of such reactions are shown here:



All the system can be actually considered as a sequence of two reactions (reaction 10 and 11), which are separated, but which running at the same time. In the liquid solution, there is enough of water and a negligible part of other species and for this reason these two reaction can be considered as the reactions of the zeroth order [60]:



It has been mentioned above, the main way to hydrogen peroxide production is hydroxyl radicals recombination. However, sometimes the hydrogen peroxide concentration can be supported by other reactions. There are several other different ways how the peroxid can be formed in the liquid. The liquid phase chemistry in natural water involves the formation of a superoxide anion O_2^- . This anion is basicly formed by oxygen reaction with hydrated electrons generated by light interacting with compounds in the water:



Water electrolysis in acidic solutions with the introduction of oxygen bubbles leads to the formation of hydrogen peroxide starting with the electrode reaction:



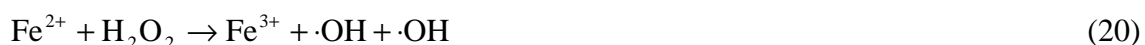
and followed by other three reactions:



It has been proven for this electrolysis pathway that all oxygen in the hydrogen peroxide comes from the gaseous oxygen and not from the water. Due to the nature of the low energy electrons in such classical electrochemical processes there are significant differences with the relatively high energy electrons generated in plasma – chemical processes in gases and some liquids [61].

Fenton's reaction

Hydrogen peroxide can be very easily decomposed by an iron (II), in case if it is presented in the water (see reaction 20). This reaction produces very reactive hydroxyl radicals and this is one of the most effective methods of the organic pollutants oxidation. The efficiency on Fenton's oxidation depends on H_2O_2 and Fe^{2+} concentrations, time and pH of reaction. The pH value should be in the range of 2.5 – 5 [62].



2.2.3 Atomic oxygen

The main reactions of atomic oxygen have been examined mainly by Andresen and Luntz [63]. It has been specially saturated hydrocarbon reactions and phenol oxidation. In addition, the atomic oxygen reacts with a water molecule and hydrogen peroxide to form hydroxyl radicals.



The hydroxyl radicals, which are produced by this way, can also oxidize some of harmful organic compounds which are presented in the solutions or waste water [63].

2.2.4 Ozone

Ozone is known as a strong oxidizing agent and potential disinfecting agent. It has been utilized in the European Union for a long time. For example, UV radiation at 188 nm and corona discharge methods can be also used to produce ozone. The bactericidal effect of ozone have been documented on a wide variety of organisms, including Gram positive and Gram negative bacteria as well as fungal spores and vegetative cells. There is wide range of applications of ozone present in industry, including food surface hygiene, sanitation of food

plant equipment, reuse of waste water, treatment and lowering biological oxygen demand and chemical oxygen demand of food plant waste. Also, treating fruits and vegetables with ozone has been found to increase shelf life of the products once recent researches prove that addition of ozone to food can help to degrade the food easily and no residues will remain [64].

Industrial ozone generation

Ozone can be generated from oxygen, air or from some mixtures where there are nitrogen or oxygen presented. The first step is naturally a dissociation of O_2 molecules by electron impact and by reactions with N atoms or excited N_2 molecules, if nitrogen is presented. After that, that this oxygen react in three-body system to form the ozone. Unfortunately, an undesired reaction still occurs during this process. In case of abundance of oxygen, the recombination of these oxygen atoms becomes a main reaction and there are O_2 molecules formed. Also, if the temperature of the system is too high, the ozone molecules are basically decomposed. Due to this reason a discharge modeling has been found as a very helpful method to identify optimum discharge conditions to a successful ozone generation. One of the devices which is used in the industry to waste water treatment by ozone is shown in the figure 14 [65-66].



Figure 14 Ozone generators for water treatment [10].

2.2.5 Chlorine

Chlorine is a member of the halogen family in the periodic table which is the most highly reactive group of elements. It actually means that chlorine react very easily with nearly all other elements. For example, with a metal it forms salts called chlorides. Due to its too high reactivity it is not possible to find a chlorine alone in the nature. It can be easily prepared commercially by electrolysis of the sodium chloride. In direct contact with water, it readily dissolves to form a hydrochloric acid (HCl) and hypochlorous acid (HOCl) plus unreacted Cl_2 . This solution is called chlorine water and it is very strong oxidizing agent that is used mainly to kill germs which is mainly utilized in the waste water cleaning processes.

Chlorine atoms are very useful mainly in organic chemistry due to their ability to replace a hydrogen atom in the structure of a molecule which makes this molecule more reactive with other compounds to form desired products. These products are subsequently utilized in many practical applications such as medicine (antiseptics) or industry (paper, metal, plastics, solvents, bleach, etc.).

The most acceptable way, how to create chlorine in the industry, is a membrane technology. It has been developed from the 70's of the last century. At the present time there are two manufacturers in the world which product a membrane intended for electrolysis – DuPont (USA) and Asahi Kasei Chemicals (Japan). This technology has offered a lot of advantages, the most important are generally lower energy costs. The schema of this membrane process is shown in the following figure 15. The principle of this technology is a separation of the anode and cathode space by ionexchange membrane. Only sodium and some water molecules of water can pass through this membrane and also there is one of the electrodes presented in each part. The brine is under pressure infused into the anode area where it is decomposed and chlorine is generated. Also, this proces produces a small amount of oxygen which is taken away. The diluted brine is collected in the bottom of the anode space and after this it is cleaned, it is supplemented by another salt and recycled for the next electrolysis. The water with sodium cations passes through membrane and reaches a cathode desk where there is hydrogen released due to water reduction. Subsequently, a sodium hydroxide is generated that circulates up to the desired concentration and after that it is brought into vaporizer to get thick. Some steam is utilized to this thickening. The lifetime of such membrane is up to four years with a proper treatment [67].

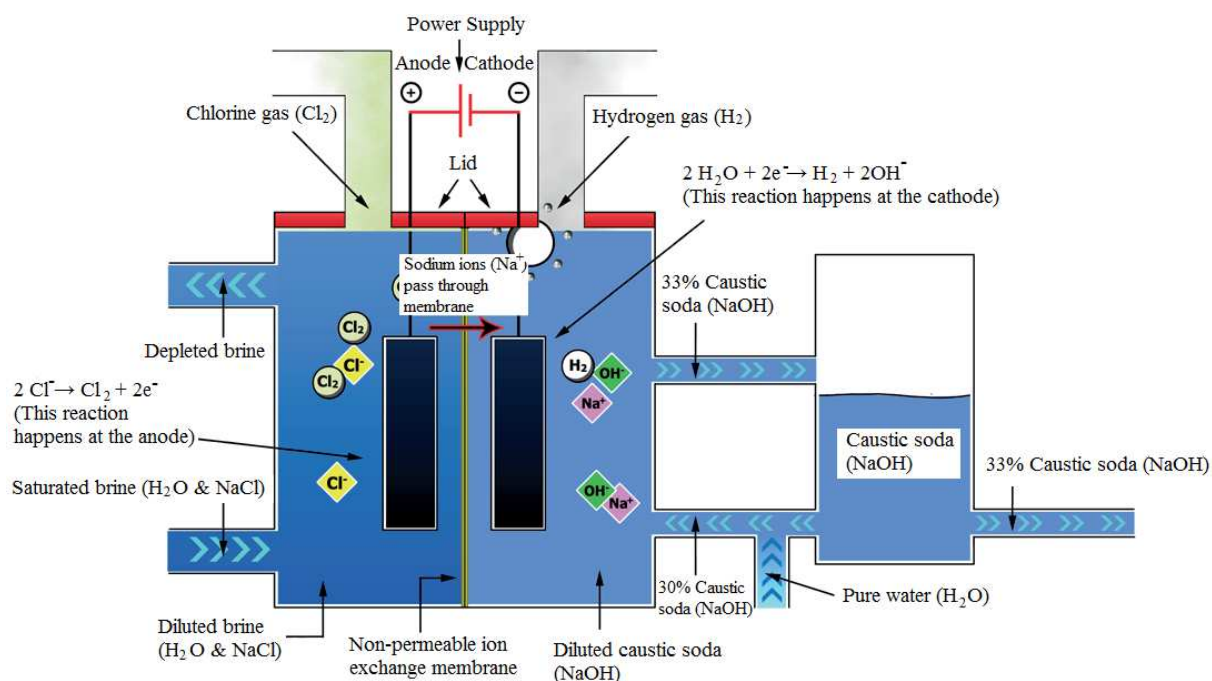


Figure 15 The schema of the membrane process of the chlorine production [67].

2.3 Conditions for the generation of electric discharges in liquids

There are several ways how to underwater electric discharges generate. A many designs of reactors can be used. These reactors differ in electrode configuration and character of the applied voltage. The most studied configuration is point to plane configuration where there is the pulsed DC high voltage very often utilized. According the type of electric discharge, a sparking, bunchy (streamer) and combined discharge character are distinguished. An AC voltage (at any frequency up to microwaves) can be also applied to discharge generation.

There are many types of electrode configurations which plasma in liquid can be generated in. But only one of them allow to plasma generation without direct contact plasma and electrodes. This is a pin-hole configuration which includes two main discharges (divided on l/d , where l is the pin-hole length and d is its diameter) – a diaphragm and a capillary discharges [68].

2.3.1 Diaphragm and capillary discharge

The principle of diaphragm (figure 16) and capillary discharge (figure 17) is a generation of plasma in one or more small holes which are located in an isolating dielectric barrier. It separates grounded electrode and electrode with high voltage. A shape of these electrodes is mostly planar. The discharge occurs after generation of gas bubbles which are created due to high thermal electric field. The discharge looks like a channel and it appears due to concentration of high electric field on the hole. Ionized channels start to propagate in the space from this hole. They grow in the direction between cathode and anode and they form positive and negative „streamers”. There are negative streamers on the anode side generated which create a dense net of thin channels that fill the hemispherical space. A velocity of these „streamers” is $10^3 \text{ m}\cdot\text{s}^{-1}$. On the cathode side, there are positive „streamers” formed which are consisted from one or several branched channels. Their velocity is higher than by negative „streamers” and reaches $10^4 \text{ m}\cdot\text{s}^{-1}$ [50].

Both of these discharges can be generated by pulse or nonpulse (constant) high voltage. In case if high DC high voltage is continuously applied into the system, only lower value is necessary to (ranks kV units) ignite discharge. The intensity of high electric field is concentrated on the hole of dielectric diaphragm membrane (or capillary). This leads to intensive overheating and boiling of the electrolytical medium in this area. There is a bubble formed from the evaporating water which a gradient intensity is created in. Consequently discharge is ignited inside this bubble. After electrical breakdown, the bubble expands till it reaches the size in which there is no possibility to keep discharge. The discharge switches off, bubble cavitates (sometimes with shock wave generation) and it is formed again in another growing bubble. In case of use DC or AC nonpulsed voltage ignition follows the principle of thermal (bubbles) theory [68-69].

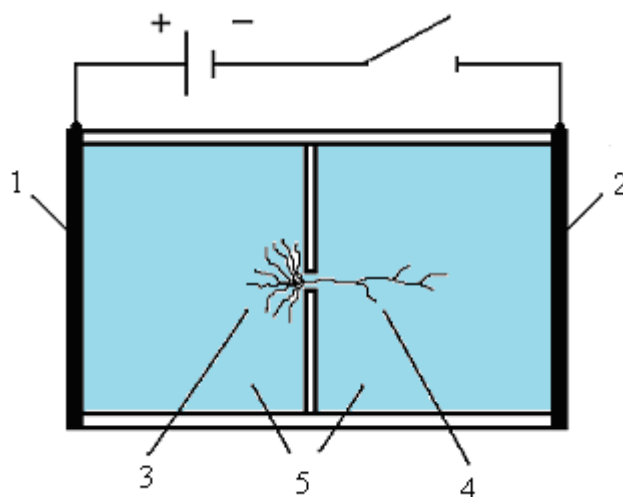


Figure 16 A simplified scheme of diaphragm discharge: 1-anode, 2-cathode, 3-negative plasma channels (discharge), 4-positive plasma channels (discharge), 5-conductive liquid medium [69].

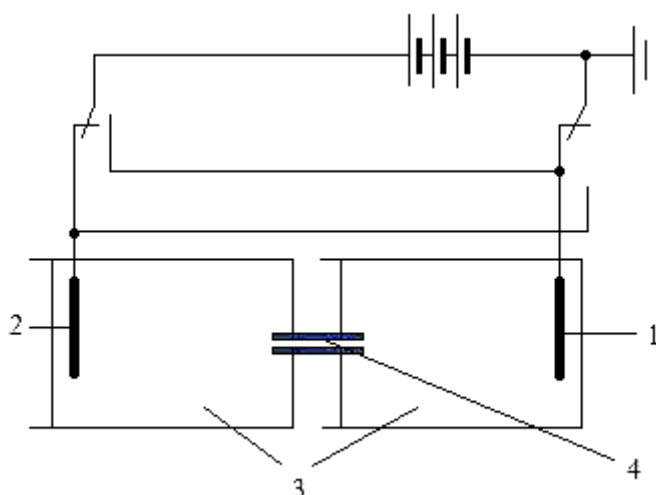


Figure 17 A simplified scheme of underwater capillary discharge: 1,2-electrodes, 3-conductive liquid medium, 4- narrow capillary where there is a discharge generated.

In case of diaphragm discharge configuration, a volume of the solution is separated into two parts by thin barrier with relatively large orifice (l/d is around 1). After electric pulse application, the intensity of forming electric field concentrates near to the small hole where there are plasma channels generated. These plasma channels have different properties in both parts of the reactor. While in the cathode part there is so-called a positive discharge generated, in the anode part there is negative discharge [70].

In case of the capillary configuration, the discharge is generated in the small hole which is placed in relatively massive material. The principle of discharge ignition is practically similar as in case of diaphragm discharge but spreading into space is limited by capillary and its shape. The first papers about capillary discharges were published in 2004 [71]. After that more workplaces started to be interested in this topic [72-73]. Except for the phenomenon and applications which have been already described, the capillary discharge allows quite new

appliance (in case the reactor chamber is separated into two parts as in case of diaphragm configuration). Because the capillary manages the discharge spreading into the space, a pumping effect from one part to the second part has been observed. For the first time, this phenomenon was observed when AC voltage was used and there was an asymmetric capillary placed in the experimental technique. It was proved subsequently that this happens in case of using DC voltage as well, in case of an asymmetric and even symmetric capillary configuration. This leads to the unpublished conclusion that the pumping effect coheres with the shape of bubble [74-75]. An illustration of plasma channels by underwater an electric discharge is shown by following figure 18.

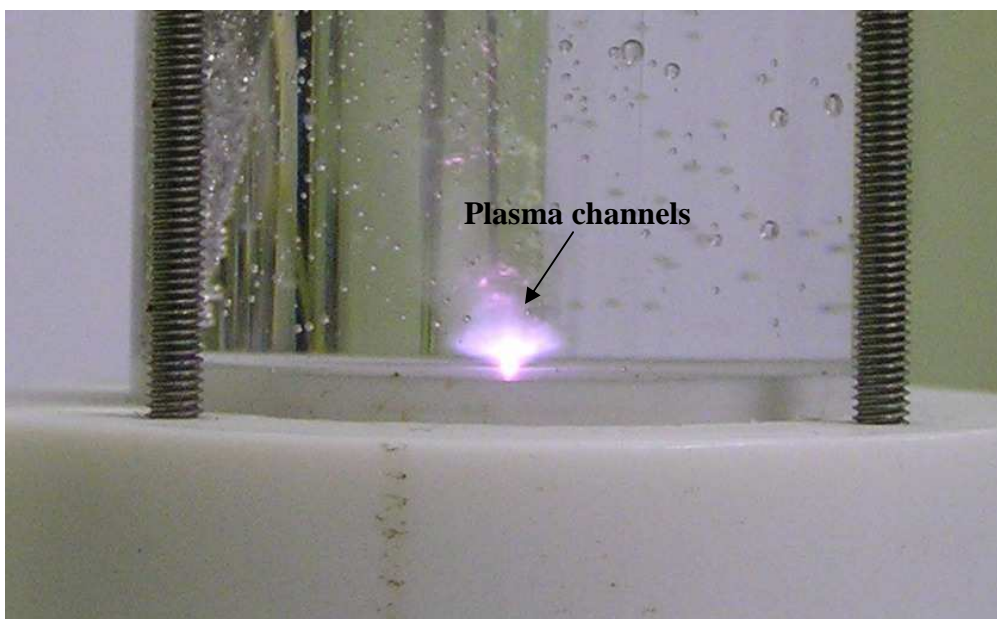


Figure 18 An illustration of plasma channels by an underwater electric discharge (He, 30 mA, 200 sccm, flow).

3 PLASMA DIAGNOSTICS

3.1 Spectra analysis

Spectrum is a very important part of the complex characteristic of the studied system. It can namely provide large information about examined solution which leads to a detailed knowledge about plasma. It generally shows which kind of elements or particles are presented in the solution and due to following spectrum interpretation some of the physical or chemical properties can be determined. Unfortunately, sometimes this interpretation can be complicated in case of the molecules with a chemical complex structure. Therefore it is appropriate to combine this spectrum interpretation with another identification method as for example mass spectroscopy or high-performance liquid chromatography.

3.1.1 Determination of the rotational temperature

This kind of temperature is very important because it can be considered as the temperature of neutral particles presented in the plasma. The basis for the rotational temperature determination is so called Boltzman's law. Its logarithmic adaptation a new formula is gained (see equation 24) which the rotational temperature can be counted from. Here, $I_{n',v',J'}$ represents an intensity of the rotational link, $J'+1$ is a value of singlet transition without change of orbital moment of the electron, B is the rotational constant for the molecule, k_B is Boltzman's constant and T_{rot} is the rotational temperature [76].

$$\ln \frac{I_{n',v',J'}}{J'+1} = -\frac{BJ'(J'+1)}{k_B T_{rot}} + konst. \quad (24)$$

When the left part of the equation is plotted depending on $J'(J'+1)$, so called pyrometric line is gained. From its slope K , it is possible to determine the rotational temperature according to the equation 25.

$$T_{rot} = -\frac{hcB}{Kk_B} \quad (25)$$

3.1.2 Determination of the vibrational temperature

The determination of this temperature is based again on the Boltzman's energy distribution law. Similarly, like in case of the rotational temperature, this law can be logarithmic adapted which leads to a new formula acquisition seen in the equation 26.

$$\ln \frac{I_{v',v''}}{v^4 \cdot A(v',v'')} = -\frac{E_{v'}}{k_B T_{vib}} \quad (26)$$

Here, v', v'' represents the band intensity, E_v is a vibrational energy of the level v , v' is the vibrational quantum number of the higher level, v'' is the vibrational quantum number of lower level, ν is a wavenumber of vibrational transition and $A(v', v'')$ represents probability of this transition. When the left part of the equation is plotted depending on the $E_{v'}$ the pyrometric curve is gained and from its slope K the vibrational temperature can be determined.

3.1.3 Determination of the electron temperature

The kinetic energy of free electrons can be obtained from the electronic transitions emission spectra if we suppose that electronic states are created directly by electron impact. We can again suppose Boltzman distribution of electronically excited states. Electron temperature reflects average electron energy, so it is one of the most important plasma characteristics. Moreover, based on the knowledge of the electron temperature it is possible to calculate by another way electron concentration. The electron concentration also says an information about positive ions, because according the law of quasi-neutrality, their concentration reaches approximately the same value. Again, due to the adaptation of the Boltzman's law, there is the simple formula gained shown in the equation 27.

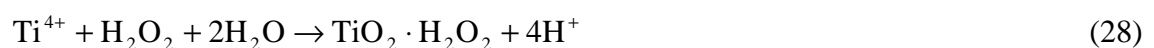
$$\ln \frac{I_{nm}}{A_{nm} \nu_{nm} g_n} = - \frac{E_n}{k_B T_{el}} \quad (27)$$

Here, A_{nm} represents the Einstein's coefficient of the probability of spontaneous emission, ν_{nm} is the transition frequency, g_n is the degree of degeneration, E_n represents the energy of the upper level and T_{el} is the temperature of the electrons. Similarly, when the left part is plotted depending on E_n it is possible to gain the line with slope K [76].

3.2 Hydrogen peroxide determination

Two different methods for the hydrogen peroxide determination have been utilized. These methods are based on a measurement of the intensity of hydrogen peroxide solution mixed with a reagent forming with hydrogen peroxide a colorful complex.

The first, a titanium sulfate [77] as the reagent has been used. This compound reacts together with H_2O_2 to form a yellow pertitanic complex according following equation 28. To gain this yellow complex it is necessary to retain a right ratio between titanium sulfate reagent and the studied solution which is 1:2. An evaluated advantage of this titanium complex is its stability (about 6 hours) which allows a later analysis. The equation of the calibration curve is $y = 0.4596 x$, where y represents the absorbance by the certain wavelength and x the concentration of H_2O_2 in the studied sample ($mmol.l^{-1}$). The absorption maximum of this yellow complex is at 407 nm and its intensity is directly proportional to H_2O_2 concentration in the complex [78].



An ammonium metavanadate has been used as the other reagent. The method is used on the reaction of H₂O₂ with the ammonium metavanadate in acid medium which results in the formation of red-orange color peroxovanadium cation. Again, the right ratio reagent and hydrogen peroxide (1:2) has to be kept. The product of this reaction has an absorption maximum at 450 nm and it has been found as very stable at room temperatures, under some conditions even up to 180 hours. This method has shown no interference with other components as for example Cl⁻ or Fe³⁺ [79].



3.3 Organic dyes

3.3.1 Characterization of the organic dyes

Colorants are characterized by their ability to absorb or emit light in the visible range (400-700 nm). In terms of chemical structure, colorants may either be inorganic or organic compounds. Both groups can be further sub-divided into natural and synthetic representatives. This second differentiation however may not be too meaningful, since, today as many natural colorants are produced synthetically. Colorants are either dyes or pigment.

Pigments are sometimes considered as a group of dyes. Pigments though consist of small particles, but are practically insoluble in those media in which they are applied. By the other words pigments have to be attached to a substrate by means of additional compounds for example polymers, paints, plastics or melts.

Dyes on the other hand are applied to various substrates (textiles, leather, paper, hair, etc.) from a liquid in which they are completely, or partially soluble. In contrast to pigments, dyes must possess a specific affinity to a given substrate. Unlike the most organic compounds, dyes possess colour because they absorb light in the visible spectrum (400–700 nm), have at least one chromophore (colour-bearing group), have a conjugated system, i.e. a structure with alternating double and single bonds, and exhibit resonance of electrons, which is a stabilizing force in organic compounds. In addition to chromophores, most dyes also contain groups known as *auxochromes* (colour helpers), examples of which is carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colourant and they are most often used to influence dye solubility [80].

The color of the dyes are altered by the Modifiers. The Color modifiers of methyl or ethyl groups are responsible for any alteration in the dyes; they alter the energy in the delocalised electrons. There is a progressive alteration of color by adding a particular modifier, for example Methyl Violet Series [80].

Dyes may be classified in several ways. According to a system of chemical classification (azo dyes, arylmethane dyes, cyanine dyes, thiazole dyes etc.), according to the nuclear structure (anionic and cationic dyes) or according to industrial utilize (for example acid, basic, direct, disperse or solvent dyes).

3.3.2 Application of the dyes

It is important to optimize the application of a dye for a given substrate to obtain the highest-possible fastness properties. The development of new structures usually gives rise to problems, which in turn, stimulates the search for even more powerful dyes and dyeing methods and, thus, influences dyeing technology in a fundamental manner. In contrast to dyeing by means of pigment application, which is based on mechanical anchoring of pigment particles on or in the substrate, colouration of dyes relies on physio-chemical equilibrium processes, namely diffusion and sorption of dye molecules or ions. These processes may be followed by the chemical reactions in the substrate, e.g., in the application of vat, reactive, azoic, and chrome dyes, self aggregation of dye molecules and ions in solution can influence the dyeing process. Similarly to painting with pigments, the art of dyeing textiles has a history several thousand years old. Today, the toxicity of some dyes is likely to be the most important problems to be solved in the near future. For this reason, two direct organic dyes have been subjected to investigation at this work. Direct Red 79 and Direct Blue 106. The detailed description of their structures and the results of their decomposition in the liquid system by plasma treatment and is given in part Results [81].

3.3.3 Direct dyes

Direct dyes are molecules that adhere to the fabric molecules without help from other chemicals. Direct dyes are defined as anionic dyes with substantivity for cellulosic fibres, normally applied from an aqueous dyebath containing an electrolyte, either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). Their principal use is the dyeing of cotton and regenerated cellulose, paper, leather and, to a lesser extent, nylon. Most of the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines, and oxazines. After treatment to improve washfastness properties, include chelation with salts of metals (usually copper or chromium), and treatment with formaldehyde or a cationic dye-complexing resin [82].

3.3.4 Determination of the organic dyes destruction

The decomposition of organic dyes has been determined also by spectroscopic method. It has been utilized an absorption maximum again of the dyes solutions – 640 nm for Direct Blue 106 and 430 nm for Direct Red 79.

3.4 Nanoparticles determination

The absorption measurement has been used to gold nanoparticles determination. Ultraviolet and visible (UV-Vis) absorption spectroscopy could be utilized to verify the presence of gold nanoparticles after processing. The absorption measurements have exhibited a peak at 544 nm which is due to typical plasmon resonance effects of gold nanoparticles formed. This absorption peak has shown a visible purple color.

4 AUDIO FREQUENCY DIAPHRAGM ELECTRIC DISCHARGE

4.1 Discharge chamber

The diaphragm discharge experimental set up has been constructed at the Brno University of Technology, Faculty of Chemistry. This device has been consisted from one big discharge chamber made form polycarbonate. There has been a wall, made of the same material, that has devided this chamber into two parts. Inside this wall, a thin diaphragm membrane (thickness 0.25 mm) with a small hole (diameter 0.25 mm) has been mounted. PET (polyethylene terephthalate) has been used as an acceptable material to membrane creation based on the previoused experiments [83]. It has fully complied the conditions that have been generated during the discharge operation. Due to this configuration, it has been possible to create a negative such as a positive discharge at the same time and compare their properties depending on treatment process. The different voltage (DC as well as high frequency AC) could be applied in the system easily on two stainless steel electrodes that have been placed in both parts of the big chamber (one electrode in each part). Also, there has been used a cover with safety switch placed on the top of discharge chamber to prevent a possible injury by high voltage. Only in case that the lid has been put on the chamber, the applied current could start to flow through the system. The complete photo of this experimental setup is shown in the figure 19.

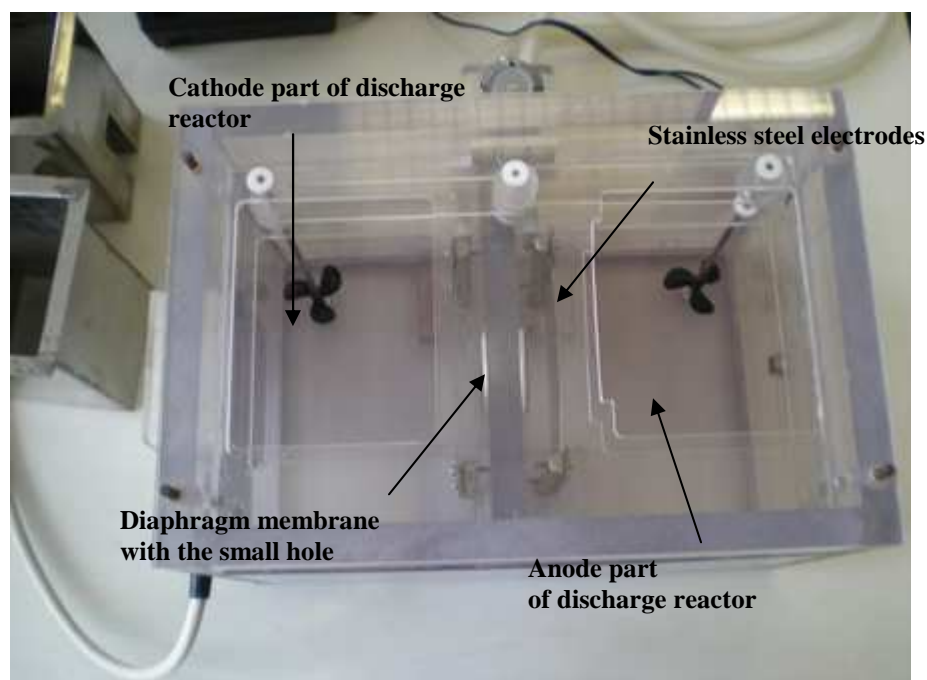


Figure 19 The photo of diaphragm discharge chamber.

4.2 High-voltage sources

Generally, there is a variety of voltage sources which can be used to the electric discharge generation in liquids. In some previous studies (as well as in this study for comparison) a DC voltage has been used to create the electric discharge in this chamber to study for example an

influence of the type of electrolyte on the stability and efficiency on the diaphragm discharge [84]. The value of the applied current was varied between 62 and 110 mA and the value of the applied voltage has reached approximately 1.5 kV nearly independently on current. The maximum value of the power has achieved 140 W. The specially designed HV audiofrequency power supply was used as the second power supply and it was also constructed at the Brno University of Technology, Faculty of Chemistry. The voltage and current have been applied directly into the diaphragm chamber to create an electric underwater discharge. The HF voltage of 15 kV amplitude and the frequency of 1 and 2 kHz have been utilized during the operation. An influence of HF voltage on the discharge properties have been examined. The initial idea for these experiments was to verify applicability of HF high voltage for the under liquid discharge generation because negligible effect of electrolysis and joule heating was supposed.

4.3 Examined water solutions

A water solution has been poured directly into the diaphragm chamber. It has been easily prepared by mixing of distilled water and sodium chloride. NaCl has been utilized as an inorganic salt which could be readily dissolved in the water without secondary undesirable effects. However, the main reason, why the salt has had to be added in the liquid, has been a setting of an initial conductivity of the studied solution. The value of initial conductivity is namely a key factor to underwater discharges generation [85]. Therefore several NaCl solutions with a different initial conductivity in the interval from 100 μS to 800 μS have been prepared. This range of initial conductivities has been chosen on propose because previous measurements have shown that these range is ideal for the mentioned discharge ignition using DC power supply [8]. A several factors have been studied. The first, a hydrogen peroxide production dependence on the applied voltage has been examined. Hydrogen peroxide is the main stable product generated by underwater discharge and reflects production of OH radicals that are the main active particles as it was pointed in the theoretical part of this work. Moreover, hydrogen peroxide generation reflects the stability and efficiency of the electric discharge and therefore its concentrations in the solutions have been investigated. Such as hydrogen peroxide, the pH and solution temperature and their dependences upon the initial conductivity of the solution and power supply kind and energy were observed.

A method based on the reaction with titanium reagent (see section 3.2) has been used to hydrogen peroxide determination. The absorbance of nascent yellow complex has been determined by a spectrophotometer Helios alpha. This device generally offers free wavelength selection and allows measurements at a fixed wavelength, which guarantees the desired accuracy of the results. The picture of this spectrometer is shown by the figure 20. The conductivity of the studied solution has been measured by GRYF 107 device and a multifunctional meter Inolab pH720 with an automatic temperature compensation has been used to pH and temperature determination.



Figure 20 Spectrophotometer Helios alpha.

4.4 Results

As it has been already investigated and published in many papers, an application of pulsed DC voltage requires relatively complicated energy supply. Generally, the application of high energetic pulses causes fast sputtering of electrodes and thus it significantly decreases electrode lifetime [86]. Here DC voltage applied on the electrodes in the diaphragm configuration is much regardful to the electrodes because the discharge itself is created in the diaphragm small hole and plasma streamers do not reach the electrodes. Thus the flux of ions accelerated by strong electric field does not bombard the electrode surface and the lifetime of the electrodes is prolonged. However, the previous measurements have shown that constant DC voltage induces a remarkable heating of the water solution [8]. The initial temperature of water solutions was about 23 °C and it has reached sometimes nearly 40 °C after only 20 minutes of the discharge operation. Moreover, in such DC system the electrochemical processes are not negligible. This remarkable temperature change of the examined solution basically has said that not all the applied energy has been utilized to the discharge creation and soem part was used other additional processes generation. By other words, the great part of energy is consumed by heating and not by chemical active species production, so the efficiency of iduced chemistry is significantly lower. This fact has become a big problem because the solution has been overheated in very short time and it has caused a hydrogen peroxide decomposition. An alternative solution for this problem has become mostly a cooling system that could extend a treatment time of the solution. But even by using this system the studied solution used to warm up quite rapidly.

The problem of overheating should be prevented by the application of high frequency voltage. In this case, the diaphragm discharge was generated using HV of 1 kHz and 2 kHz frequencies. As it is demonstrated in bellow (see figure 21), the liquid heating after one hour discharge operation is very low. The temporal evolution of hydrogen peroxide generation on the initial conductivity of the water solution is shown in the figure 22. How it can be seen, the hydrogen peroxide generation has reached a maximum at 500 and 800 $\mu\text{S}\cdot\text{cm}^{-1}$ by applying 1 kHz and 600 $\mu\text{S}\cdot\text{cm}^{-1}$ by applying 2 kHz. In the area of low initial conductivities, such as 300 or 400 $\mu\text{S}\cdot\text{cm}^{-1}$, the density of charge carriers is not sufficient and the discharge is non-stable; consequently it can not easily penetrate into the examined liquid.

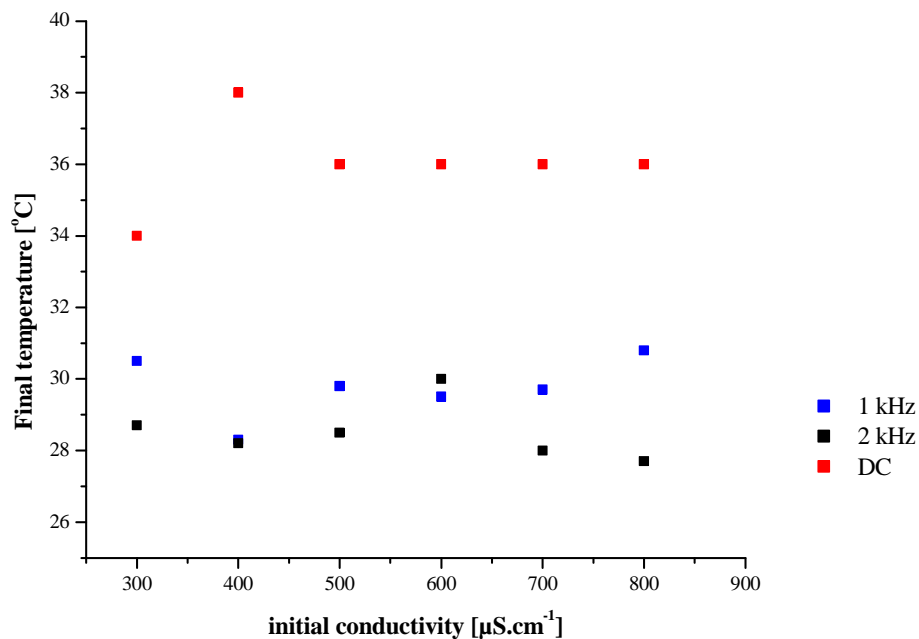


Figure 21 Dependence of temperature change on the initial conductivity of the studied solution after 20 minutes of plasma operation.

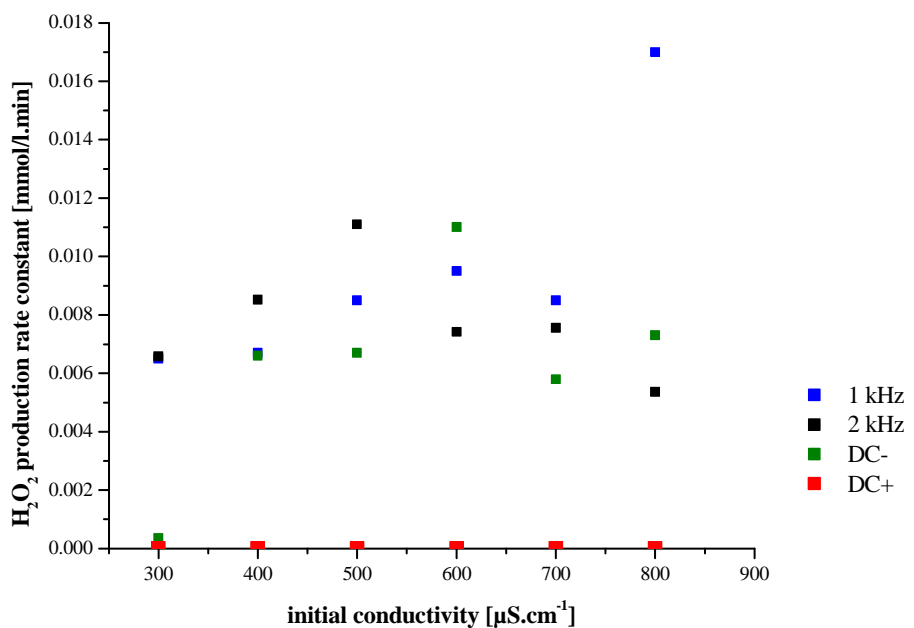


Figure 22 The dependence of hydrogen peroxide generation rate on the initial conductivity of the water solution.

In the area of too high initial conductivities, more than $900 \mu\text{S}\cdot\text{cm}^{-1}$, there are too much charge carriers, the liquid is not overheated in the pin hole region and the results is unfortunately the same. The discharge burns not in the stable regime and thus it can not

penetrate into the treated solution and hydrogen peroxide is not formed again. It practically means that stable discharge operation occurs only in relatively narrow conductivity interval of $500 - 800 \mu\text{S}\cdot\text{cm}^{-1}$ with our power supply. Outside this region, electric discharge burns irregularly.

The initial conductivities of the examined solutions are normally changed after plasma treatment [87]. Basically, they increase during plasma operation and reach higher values due to active particles generation as well as by electrodes erosion. Here, a different trend has been observed. The time evaluation of the liquid conductivity is shown below in the figure 23. It is possible to see that the conductivity values are nearly constant in HF diaphragm discharge. The same behavior has been observed at both our used frequencies (1 and 2 kHz). Based on this result, it can be supposed that conductivity change in DC systems is caused dominantly by electrodes erosion, the generated active particles (mainly hydrogen peroxide) have only very small contribution to the solution conductivity enhancement.

Besides the conductivity, the pH values of treated solution change during the plasma operation, too. Figure 24 shows the final pH values in different solutions after one hour of discharge operation. The initial pH has been in all solutions before treatment around 6.5. It can be seen, that all examined liquids have become just slightly acidic which is also different with respect to results obtained by DC voltage where pH values decrease quite easily down to 4 or 3. The reason why pH goes down is probably a hydrochloric acid formation during the process. In the DC- part, which means anode part of the system, has been an basic environment formed due to sodium hydrogen generated from sodium kations and OH groups.

Due to these results, which have been obtained during the plasma generation in this type of discharge reactor, it can be concluded that the utilize of HF voltage leads to the reactive particles production without undesirable overheating of the solution.

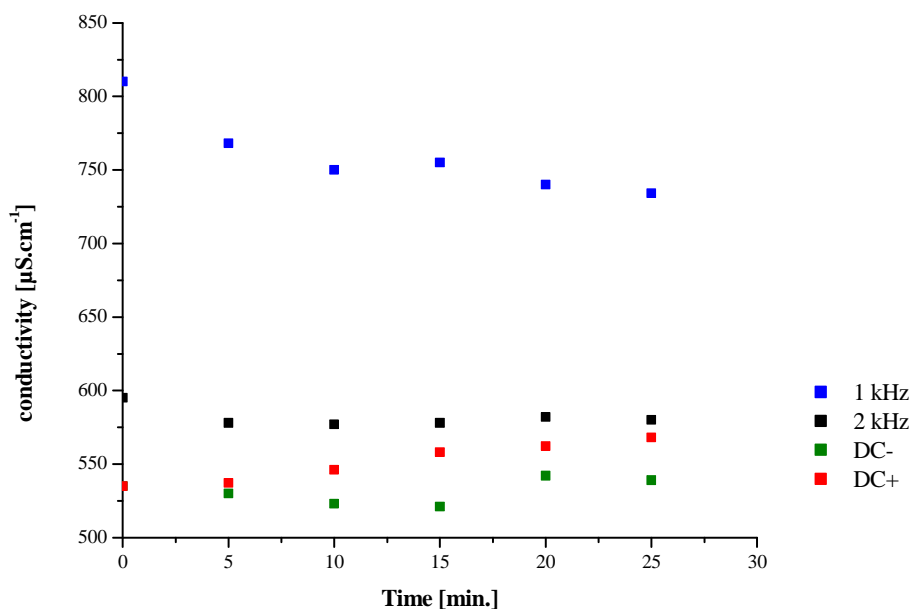


Figure 23 Time evaluation of the liquid conductivity.

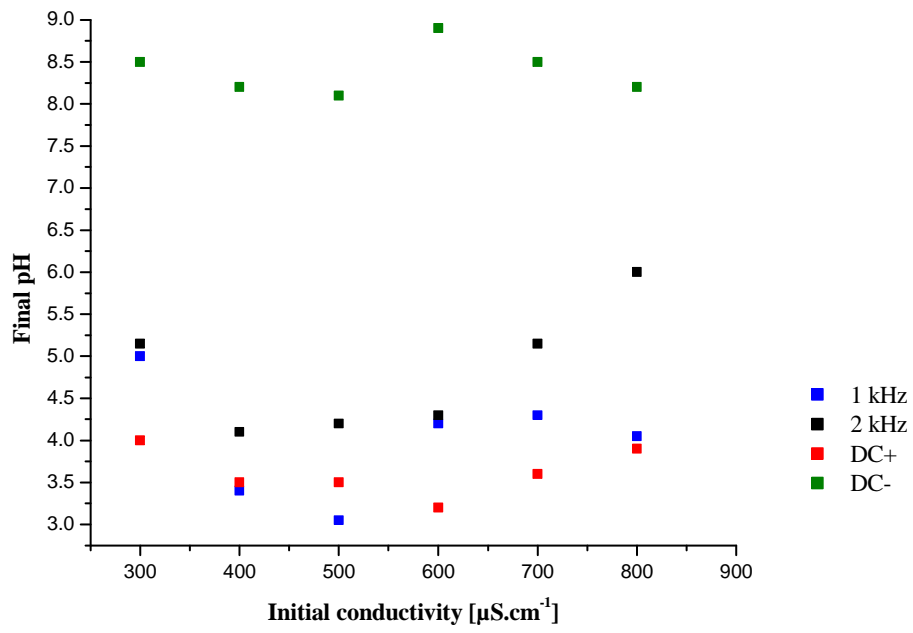


Figure 24 Final pH value after one hour discharge operation. The initial pH value of the solution has been 6.5.

5 UNDERWATER ELECTRIC DISCHARGE IN GASEOUS BUBBLES

The results presented in this part of my thesis have been taken at the Ghent University in Belgium where I was working as a visitor researcher. I have worked at the Department of Applied Physics with an experimental device which has been specially designed at the local department and which has fully suited my specific measurement requirements. The plasma has been generated in selected low conductivity saline solutions and in some solutions with a small additional of organic dyes. The plasma generation has been supported by bubbling system using selected gases. The detailed description and conditions of my experiments are given in the next paragraphs.

5.1 Experimental technique

The scheme of the set-up for the underwater discharge generation in gas bubbles is presented in the figure 25. The discharge reactor has been consisted of glass discharge chamber (volume of 1 l), on the bottom of which a glass capillary (the inner diameter of 1.2 mm, length 50 mm) has been placed as it can be seen at the photography on figure 26. Liquid has been grounded by stainless steel electrode placed at the upper part of the chamber. The plasma-solution reactor has been cooled in order to avoid thermal destruction of hydrogen peroxide because temperatures has reached at the experiment end above 70°C without cooling. A positive high voltage electrode has been made from stainless steel (the outer diameter of 0.5 mm) and it has been placed inside a glass capillary mounted from the bottom of reactor. The gas (Ar, He, Air and N₂) have been applied through this tube in order to produce bubbles. The gas flow in the system has been regulated by mass flow control system (MKS 4000). Flow rate of gases has been fixed at 200 sccm in all experiments.

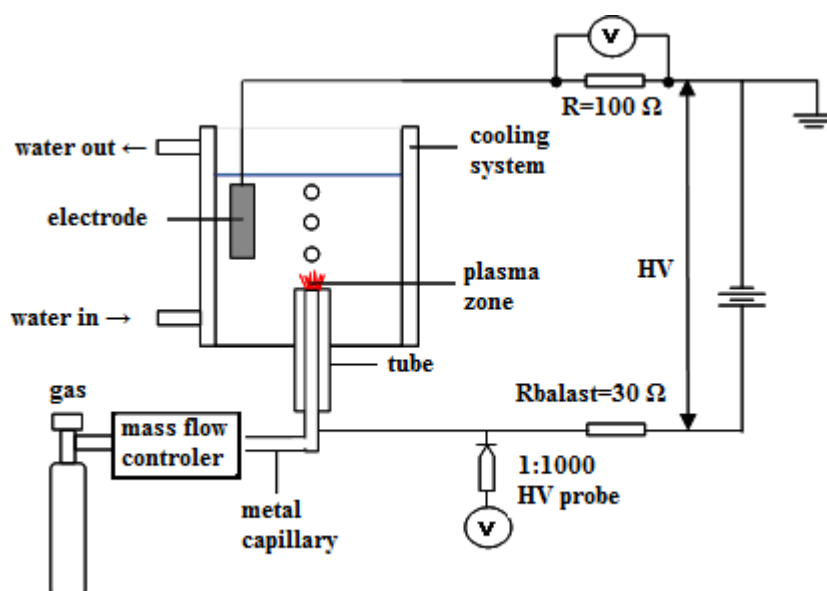


Figure 25 The scheme of the experimental set-up for the discharge generation in gaseous bubbles.

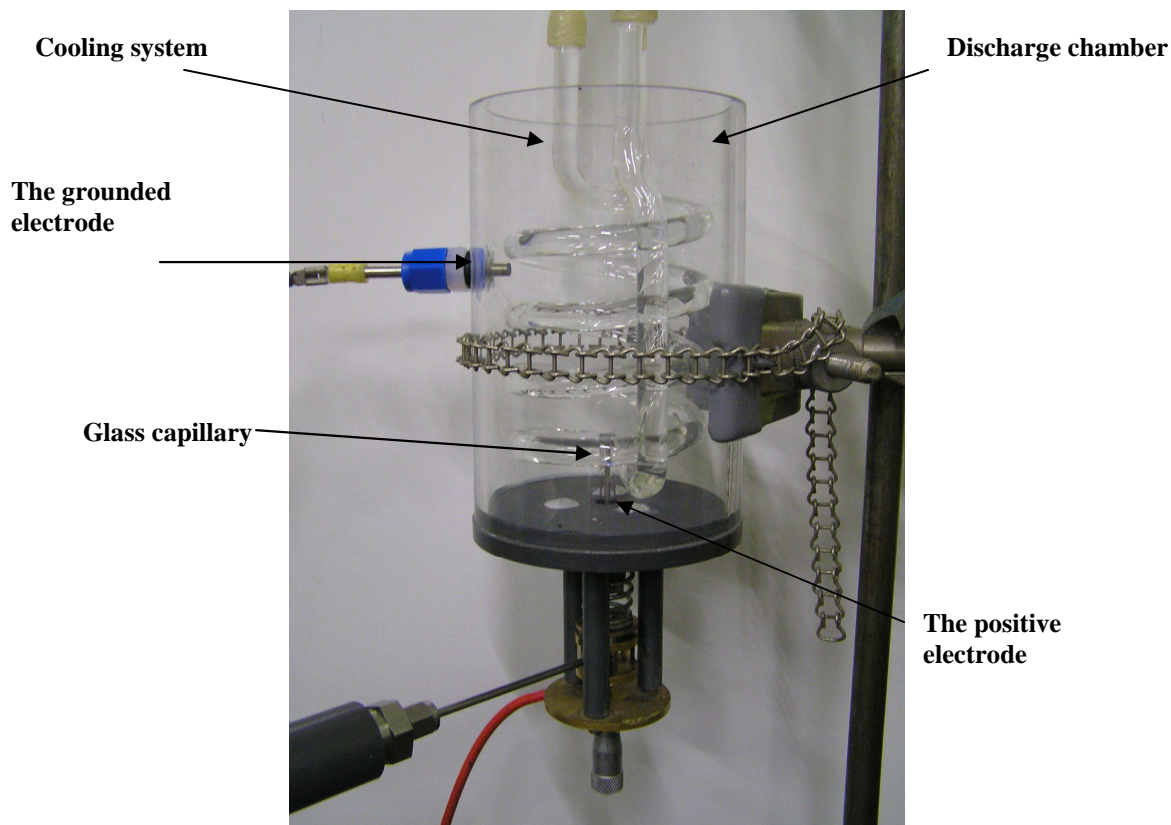


Figure 26 The photo of discharge chamber.

The electric discharge has been started directly on the surface of the metallic tube inside of bubbles and propagated into the liquid by streamers as it can be seen from photography presented by figure 18. The DC power supply has been connected to the reactor through a ballast resistor of 30 k Ω for the discharge stabilization. The applied positive voltage has been varied from 0.2 to 6 kV. The electrode placed in the liquid has been grounded through a small shunt resistance of 100 Ω .

5.2 Examined solutions

The examined solutions have also been poured directly in the discharge chamber and both of the electrodes have had to be submerged under the water. The solution has been basically prepared by mixing distilled water and always the same amount of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was added. As well as NaCl , this type of salt can be dissolved very easily in the distilled water. According the process conditions, the main claim for studied solution has been as low initial conductivity as possible. Due to this fact, the initial value of the conductivity of the solution has reached only 5 $\mu\text{S}\cdot\text{cm}^{-1}$ in all cases. This work has been focused on hydrogen peroxide generation in the solution with a bubble system. Four different types of gas have been utilized for making a bubble environment during plasma discharge process – air, argon, helium and nitrogen and just the influence of the bubble gas on the hydrogen peroxide production has been investigated. All plasma treatment of the studied solutions have taken twenty minutes.

In the case of measurements of organic dyes, the distilled water with a synthetic dye with no salt addition has been mixed. The initial concentration of the solution has been 20 $\text{mg}\cdot\text{l}^{-1}$.

Two organic dyes have been chosen for these studies – Direct Blue 106 (figure 27) and Direct Red 79 (figure 28). These azo dyes are very often used as some sample dyes due to their structures [88, 89]. They have only one absorption maximum in the UV-VIS area and they are very often used as some model dyes which subsequently allows a comparison of their determined properties. These two dyes with different organic structure have been chosen to compare the plasma influence on the organic structure decomposition. The bubble system has been also used during the plasma generation. As well as plasma treatment to gain hydrogen peroxide generation, the plasma has also been generated for twenty minutes in the solution.

The last experimental part was carried out in water solutions containing a small amount of ethanol, so the solution has been composed of distilled water, organic dye and this alcohol.

The concentration of hydrogen peroxide, such as organic dyes decomposition, has been also determined spectroscopically. It has been utilized the reaction of hydrogen peroxide with metavanadate ammonium and the absorptions maxima of the organic dyes. The detailed explanation has been given in the theoretical part 3.2.

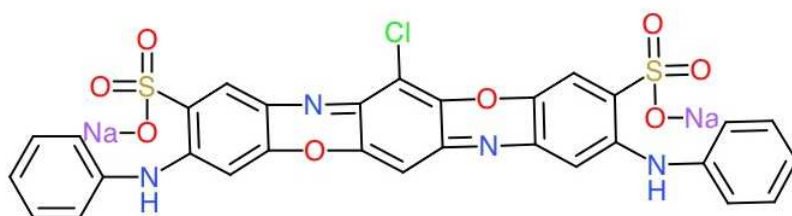


Figure 27 Direct blue 106 chemical structure.

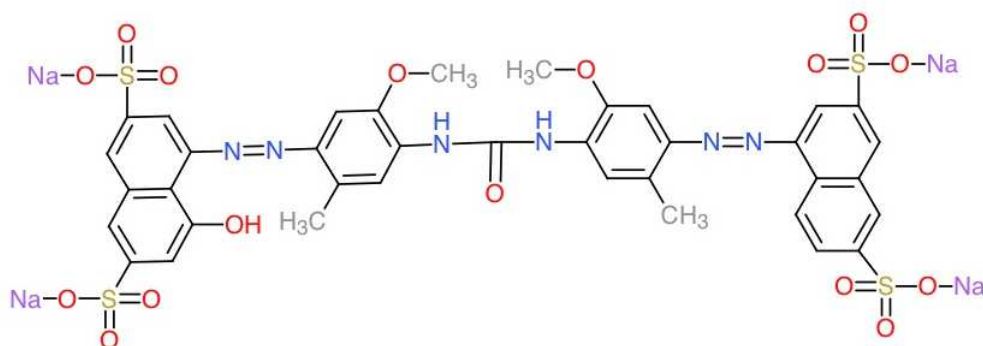


Figure 28 Direct Red 79 chemical structure.

5.3 Results

5.3.1 Hydrogen peroxide generation

The hydrogen peroxide generation has been studied in saline solutions with the addition of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ by using different discharge currents. The influence of the applied current on the hydrogen peroxide concentration have been determined such as an influence of the used gas. In the first measurement, the current of 10 mA has been applied in the system. A maximum of the current has reached 30 mA. All four gases have been flown through the investigated liquid.

The hydrogen peroxide generation at the discharge current of 10 mA in different gases is shown by figure 29. Here, a strong oscillations of hydrogen peroxide production during the

discharge operation have been registered. The reason for that is the plasma instability that was partially observable also visually. The supplied current probably has not provided enough energy into the system and the discharge has not been created at all time, so only low concentration of hydrogen peroxide (about 0.38 mmol/l) has been observed after twenty minutes of the process. Due to this fact an increase of the current has been desirable.

The kinetic curves for hydrogen peroxide generation at 15 and 20 mA are demonstrated in figures 30 and 31. It is seen that the increase of the current has definitely supported the hydrogen peroxide production. It practically means that there has been enough energy input to the solution which has led to high stability of plasma operation.

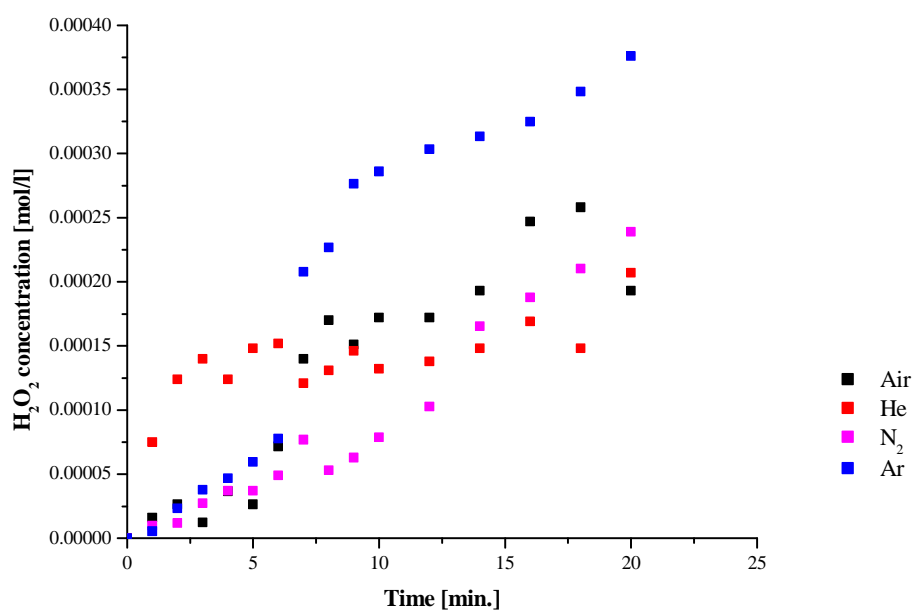


Figure 29 The hydrogen peroxide generation at the discharge current 10 mA.

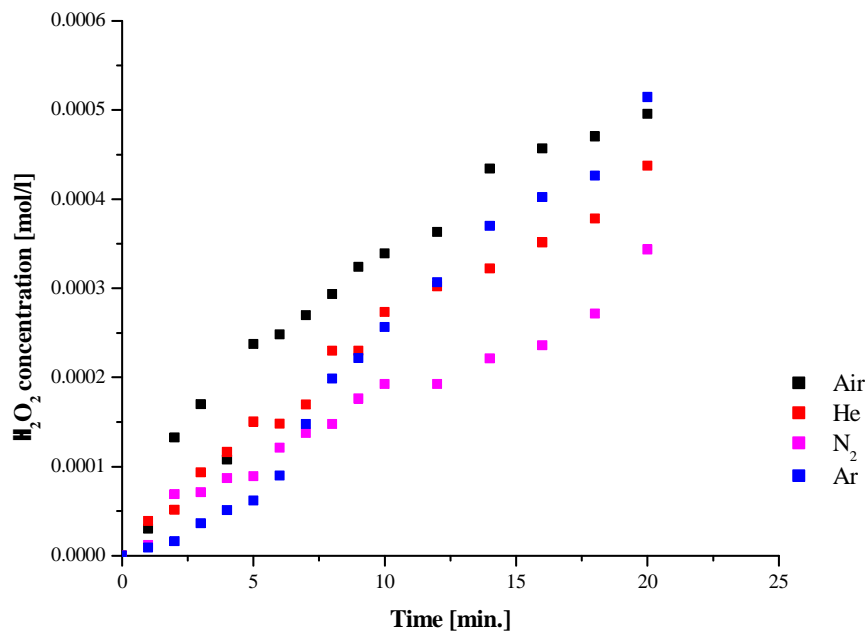


Figure 30 The hydrogen peroxide generation at the discharge current 15 mA.

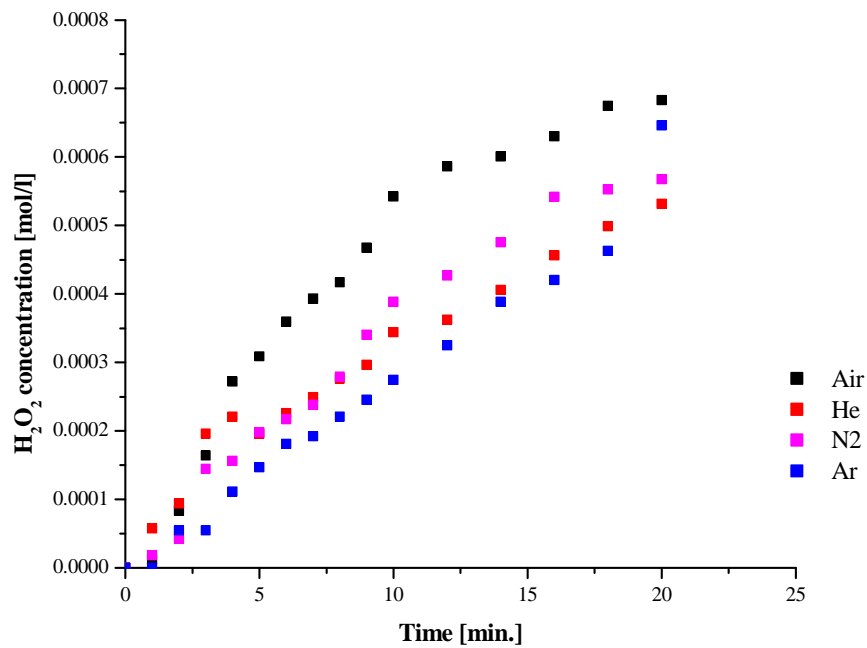


Figure 31 The hydrogen peroxide generation at the current 20 mA.

The last two figures 32 and 33 present the hydrogen peroxide generation by using the highest currents - 25 and 30 mA. Both of them confirm the trend that an increase of discharge current makes the plasma operation stable. Because the higher current has been applied, the higher hydrogen peroxide concentration has been determined.

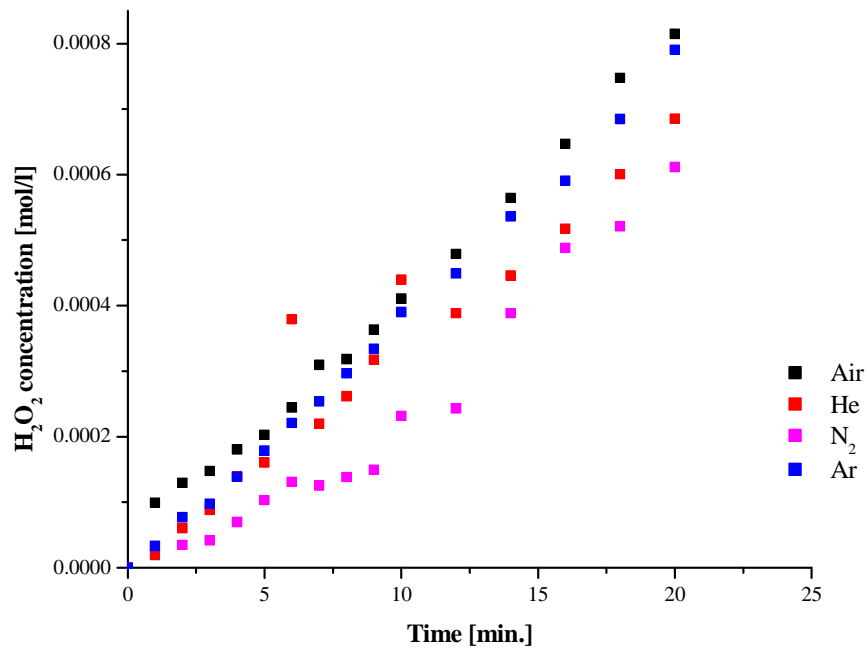


Figure 32 The hydrogen peroxide generation at the current 25 mA.

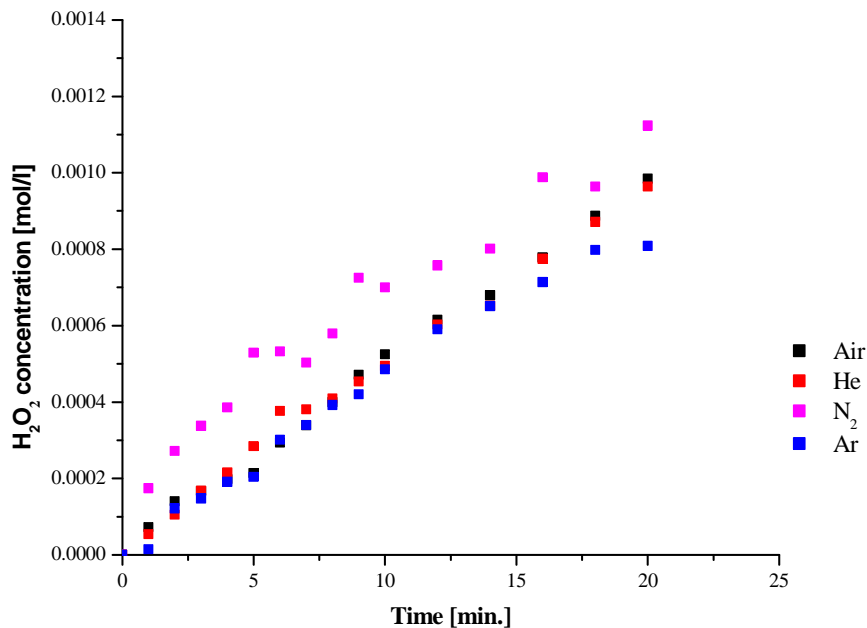


Figure 33 The hydrogen peroxide generation at the current 30 mA.

This tendency has been observed for all four gases. There has not been found a pronounced different among their influences on hydrogen peroxide formation. Almost the same values about $1 \text{ mmol} \cdot \text{l}^{-1}$ has been gained after twenty minutes of the process. The initial rates of hydrogen peroxide production are presented in table 4. Generation of the hydrogen peroxide in the reactor is characterized by almost linear kinetic plots during twenty minutes without

reaching of steady-state regime. This practically means the thermal destruction of hydrogen peroxide and catalytic decomposition (as for example Fenton's reaction) do not play any important role in the investigated system.

Table 4 Initial rate of hydrogen peroxide formation as function of discharge current.

Current [mA]	Initial rate [mmol/l.s] x 10 ⁻⁴			
	He	Ar	N ₂	Air
15	3.3	3.6	3.8	4.2
20	4.2	3.7	5.0	5.8
25	5.8	6.1	6.3	6.7
30	8.3	8.3	8.3	8.3

5.3.2 Decolorization of organic dyes

The kinetic plots of Direct Blue 106 dye destruction for discharge currents from 10 to 15 mA are presented bellow in figures 34 and 35. As there can be seen, the discharges generated at these currents have not been stable again which has caused a low efficiency of hydroxyl radicals production in the solution that could have disrupted a complex organic structure of examined dyes. These currents have been practically too low and (except in nitrogen) there has been no remarkable decomposition of the solution determined. It can be concluded that too low currents are not suitable to the complex structure decomposition.

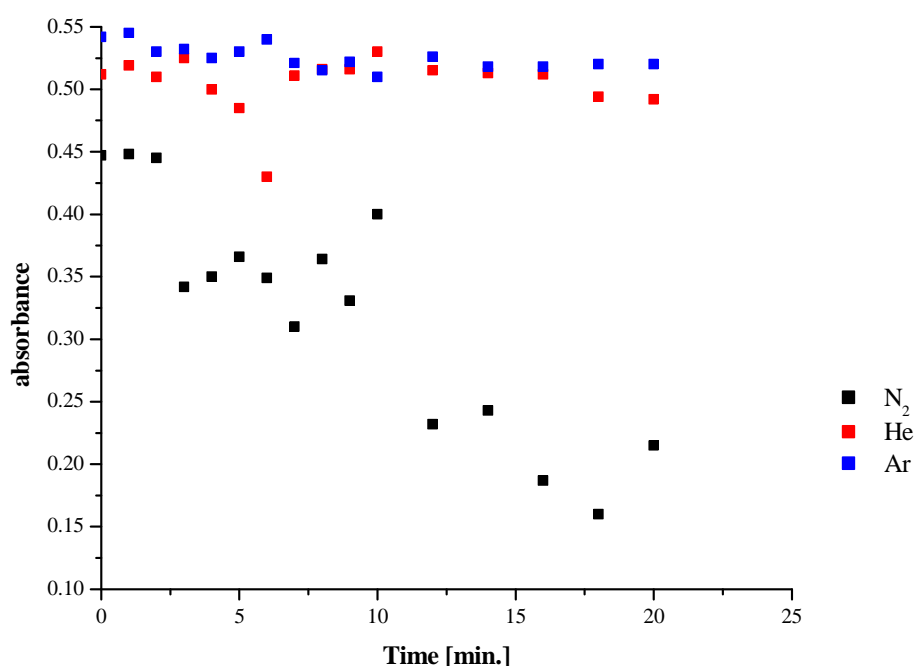


Figure 34 Kinetic plot of Direct Blue 106 dye destruction at the current 10 mA.

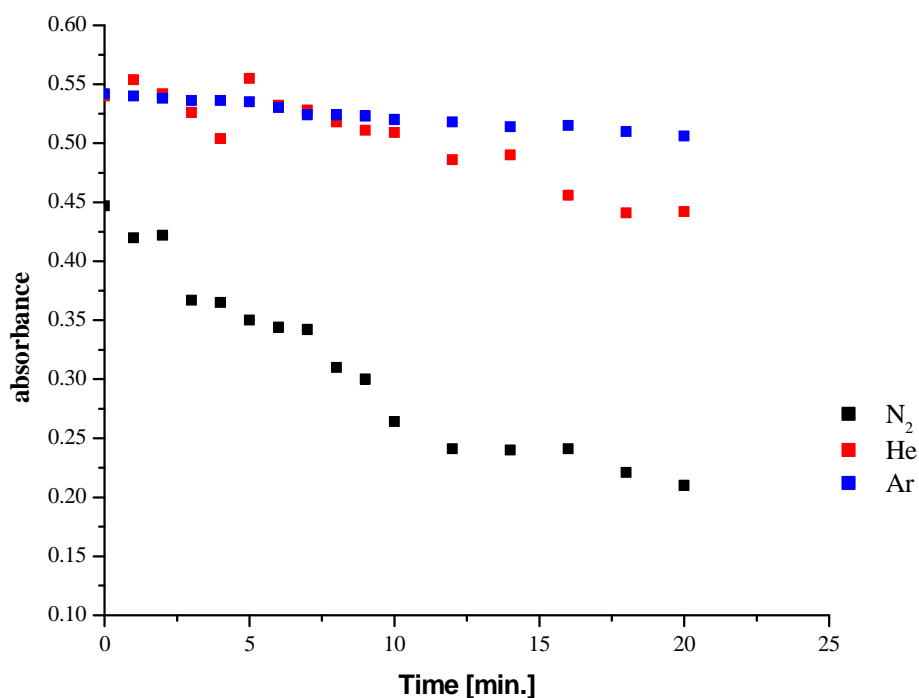


Figure 35 Kinetic plot of Direct Blue 106 dye destruction at the current 15 mA.

The next three figures (figures 36-38) show the obtained results when the higher currents have been applied. As is was expected, the higher efficiency has been gained by applying higher current which leads to the detection the direct proportionality between the applied current and destruction of organic dye. Basically, the best results have been detected by using current of 30 mA when the plasma discharge has been stable due to higher applied voltage and could produce enough hydroxyl radicals into the studied solution. Also, by the application of the higher current, streamers can penetrate directly inside the solution which cause this mentioned increased OH radicals production and besides that, streamers can interact with the dye. These hydroxyl radicals have been strong enough and could break the very stable structure of organic dyes as for example double bonds. Unfortunately, a detailed study of the products composition could not been implemented due to an absence of a suitable analytical technique at the department.

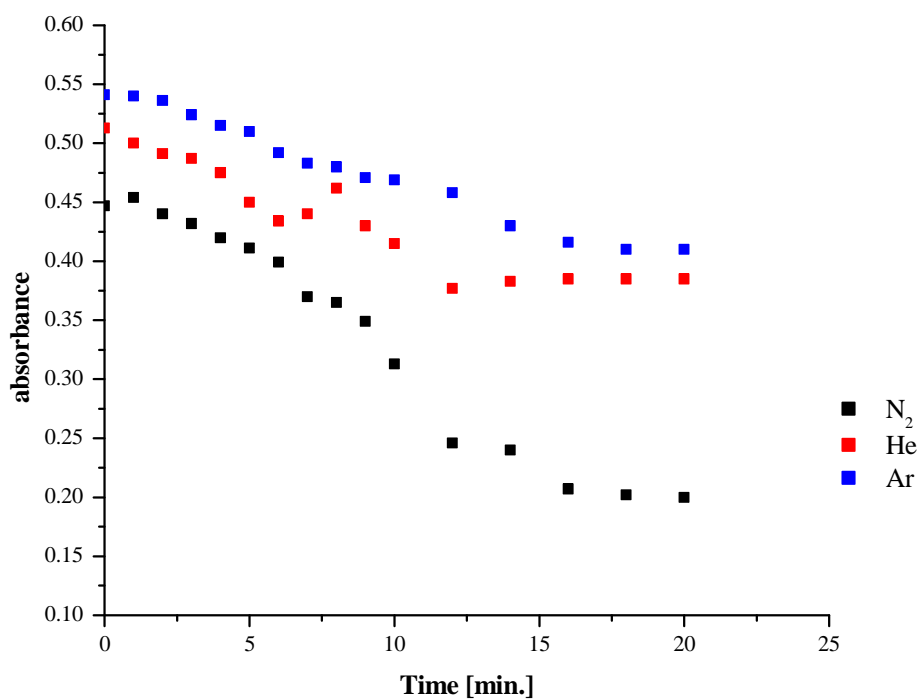


Figure 36 Kinetic plot of Direct Blue 106 dye destruction at the current 20 mA.

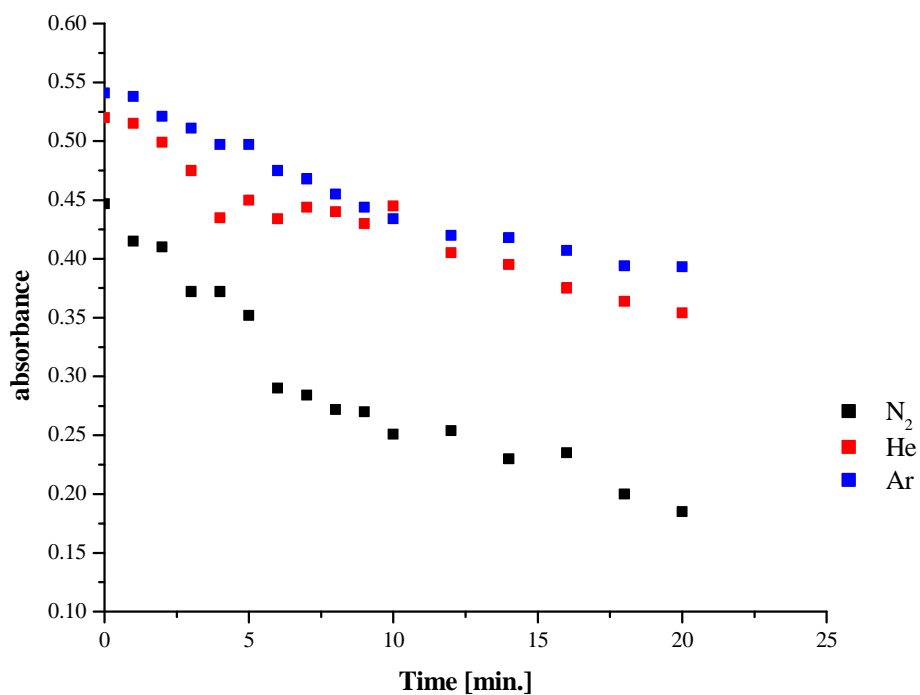


Figure 37 Kinetic plot of Direct Blue 106 dye destruction at the current 25 mA.

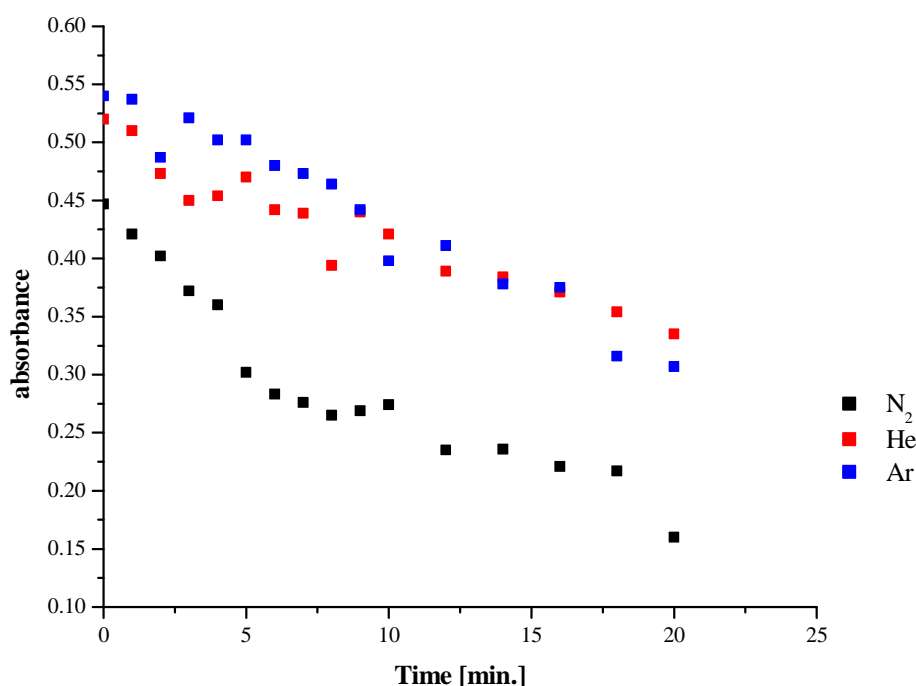


Figure 38 Kinetic plot of Direct Blue 106 dye destruction at the current 30 mA.

The general conclusion of the Direct Blue 106 dye discoloration is shown by table 5. One can see that in the case of He and Ar plasmas the destruction efficiency of the direct blue dye molecules has been much lower than in the case of N₂. The maximal destruction of about 64 % was achieved in N₂ plasma at the highest applied current. We suppose that this effect is connected to the formation of HNO₃ in case of N₂ due to oxidation of N₂ that leads to the decrease of solution pH down. To confirm this theory, pH of the solution has been measured which has really shown strong acidic environment (pH=2). Used dye has lower stability in acidic solutions with pH<6 and the oxidative ability of plasma is stronger in acidic conditions (e.g. the oxidative potential of the hydroxyl radical is 2.70 V at pH 3.0 and 2.34 V at pH 9.0).

Table 5 Efficiency of the Direct Blue 106 destruction after 20 minutes plasma treatment.

Current [mA]	Decomposition of the dye [%]		
	He	Ar	N ₂
10	4	4	52
15	6	15	53
20	21	24	55
25	32	30	59
30	36	43	64

As it has been already said, two different dyes have been studied. The destruction of the second one (Direct Red 79) by plasma treatment is demonstrated in the three charts bellow (figures 39-41).

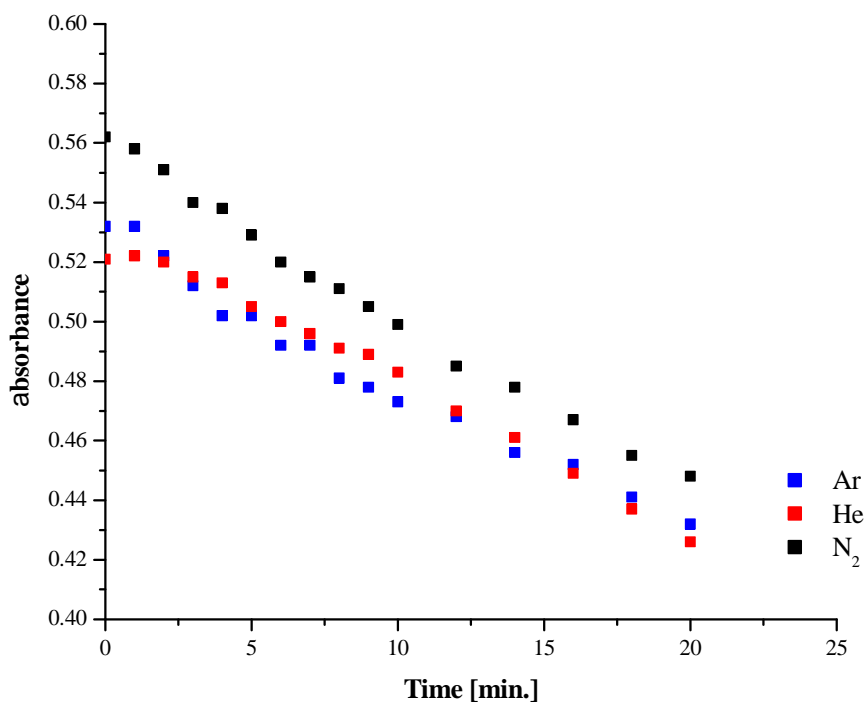


Figure 39 Kinetic plot of Direct Red 79 dye destruction at the current 10 mA.

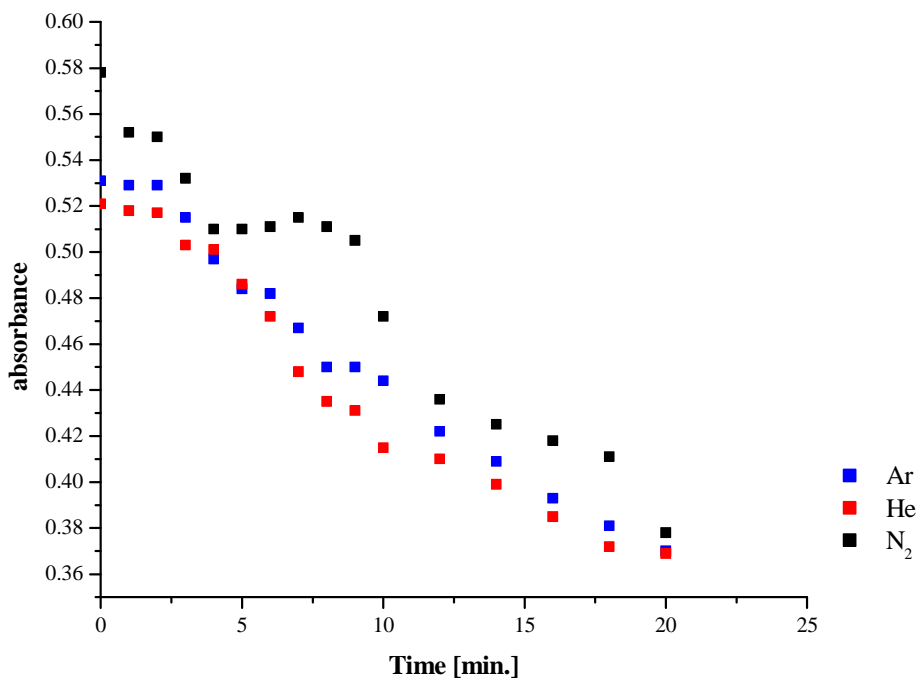


Figure 40 Kinetic plot of Direct Red 79 dye destruction at the current 15 mA.

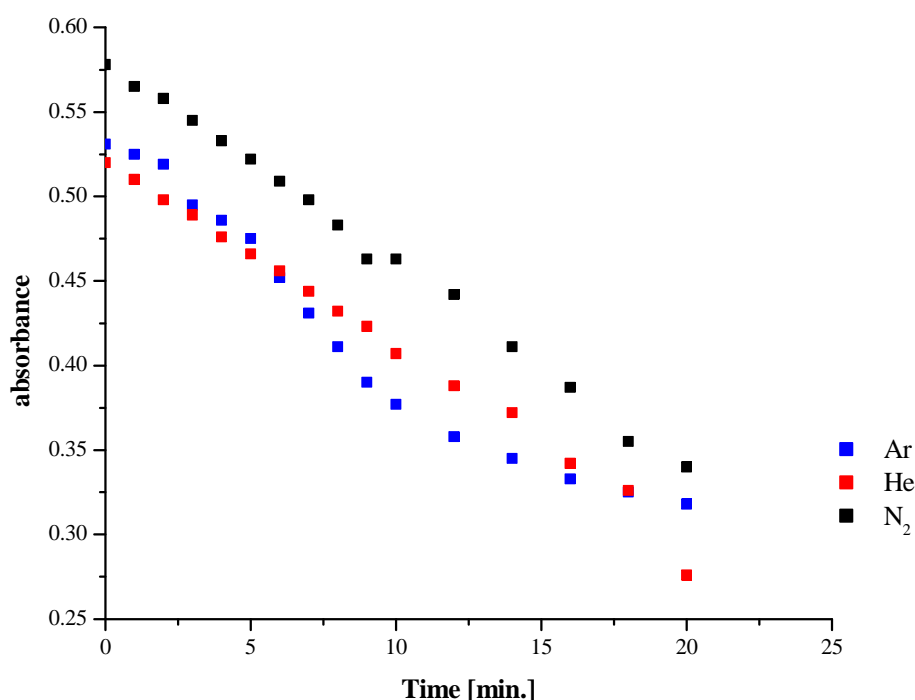


Figure 41 Kinetic plot of Direct Red 79 dye destruction at the current 20 mA.

By evaluation of the obtained data, there is possible to notice the same destruction trend. By lower current such as 10 or 15 mA the plasma has not been stable again, there has not been enough of hydroxyl radicals presented in the examined solution and thus the organic dye could not been decomposed. A first noticeable countable decrease of the dye is seen in case of use current 20 mA. The absorbance values are not exactly the same as in case of Direct Blue 106 decomposition, however the destruction dependence on discharge current has been confirmed. Thus, it can be concluded again, that the higher current has been applied the more organic dye has been decomposed. The resume shows table 6. Looking at the data it is possible to see that nitrogen has been the most effective gas again but the difference is much less than in the Direct Blue 106 dye.

Table 6 Efficiency of the Direct Red 79 destruction after 20 minutes plasma treatment.

Current [mA]	Decomposition of the dye [%]		
	He	Ar	N ₂
10	18	19	20
15	29	30	35
20	37	40	42

Decomposition of the Direct Blue 106 organic dye in the air

As an additional experiment, a decomposition of the Direct Blue 106 organic dye using the Air bubbles has been carried out. A goal of this extra experiment had been an idea to compare

the dye destruction by the plasma created in the Air to plasma created in the nitrogen gas. It has been considered that the Air, such as the gas consisted of 78 % nitrogen, should have a very similar influence on the organic dye decomposition as clear nitrogen gas. A confirmation of this idea would bring a significant reduction of operating costs because using the air is much more cheaper than the use of nitrogen. The obtained results are shown in the figures 42 and 43. While in the figure 42 there has been a difference between these two gases obtained, the figure 43 shows a similar decomposition of organic dye. Due to the previous investigation, the system where 30 mA current has been applied, it has been considered to make a conclusion of this experiment because here the generated plasma has the most effective. It means, the Air shows similar behaviour by organic dye destruction. Thus it can be said, that the main part of dye decomposition has been affected by nitrogen, the nitrogen acid generation respectively. As it has been already explained, the generation of this acid in the solution creates the acidic environment which the OH radicals have a higher oxidation potential in.

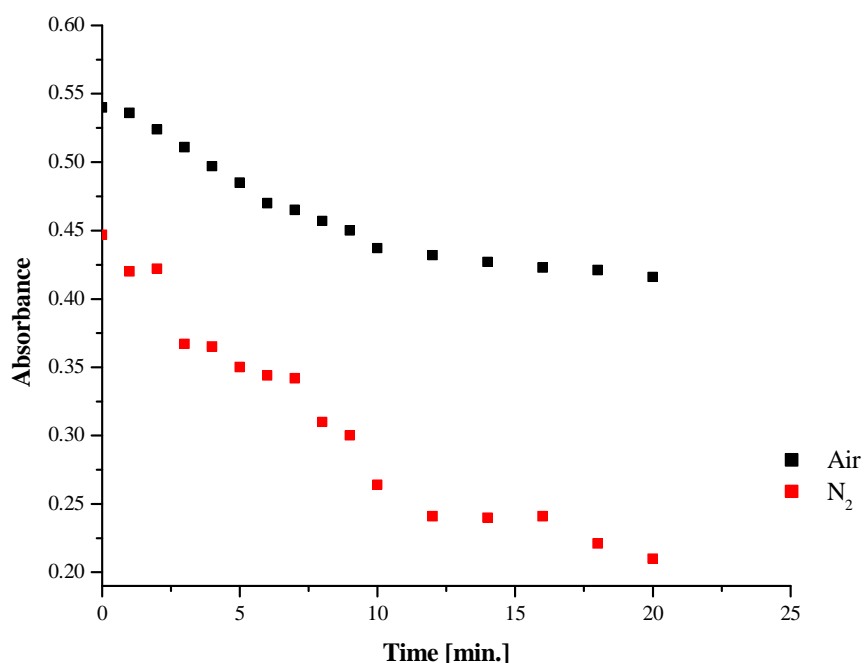


Figure 42 Kinetic plot of Direct Red 79 dye destruction at the current 15 mA to compare air and nitrogen gas.

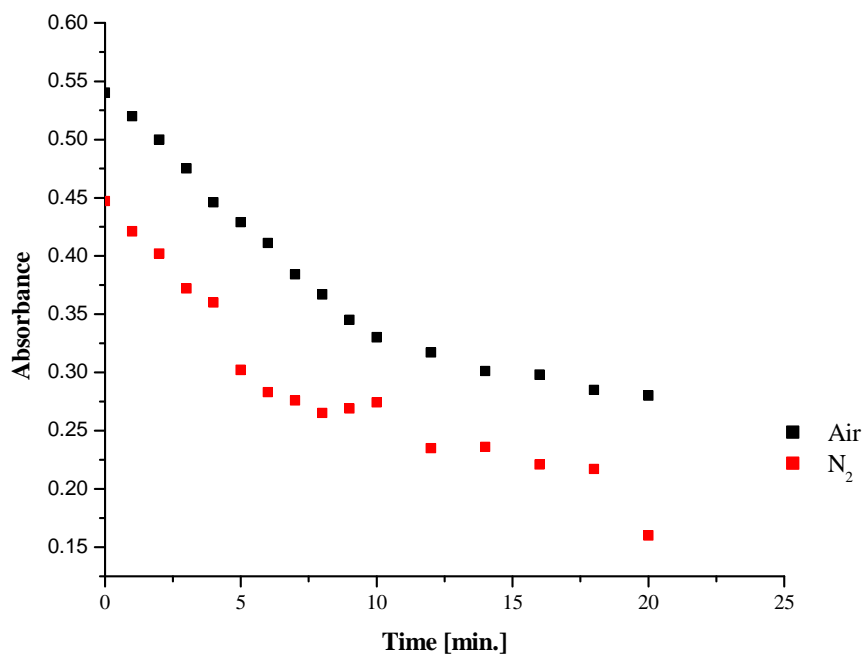


Figure 43 Kinetic plot of Direct Red 79 dye destruction at the current 30 mA to compare air and nitrogen gas.

The additional investigation has been made to verify the possibility of dye structure decomposition via thermal dissociation. Because of that a scavenger of OH radicals has been added into the solution to estimate an importance of different mechanisms in chemical decolorization of organic dye. Ethanol, C₂H₅OH has been chosen as scavenger agent in this experiment. The organic dye decomposition has been studied in the solution with the additional of ethanol. Nearly no decolorization of the dye has been obtained with 0.1 % of alcohol in the reactor using Ar or Air plasma. Thus the thermal destruction of the dye and reactions the dye with other reactive particles (for example O₃) have had negligible role in the liquid plasma treatment. It can be deduced that the main mechanism responsible for the purification in the underwater discharge is the oxidation of the dye by hydrogen peroxide. More detailed investigation of the alcohol addition in the liquid medium is going to be given in the next chapter using another experiemntal set up.

6 HIGH FREQUENCY UNDERWATER ELECTRIC DISCHARGE

This part of my thesis has been realized during my studies at the Queen's University in Belfast in Northern Ireland where I was working as the visitor research as well. During my stay at the university, there have been interesting results taken by a special experimental system which has produced an electric underwater discharge and which starts to be commonly used in surgery at the present time. The properties of this kind of discharge have been examined. The plasma has been created in two different saline solutions. The detailed description of the technique and discussion of the results are given below.

6.1 Experimental technique

Plasma has been created by special device which is called Arthrocare [90]. The principal scheme of this experimental set-up is shown in the figure 44. It is a high-performance surgery instrument which is commonly used in biomedicine at the present time. This system allows direct contact with a targeted soft tissue without any side effects on undesired places in surrounding. The thermal effect on surrounding tissue is also minimal. This device has ability to perform tissue ablation, tissue removal, tissue shrinkage and hemostasis. It is quit easy and fast way how to treat a small place in a human body. Besides the application of plasma medicine, it can be, of course, used also for the fundamental research in the field of discharges generated in liquids.

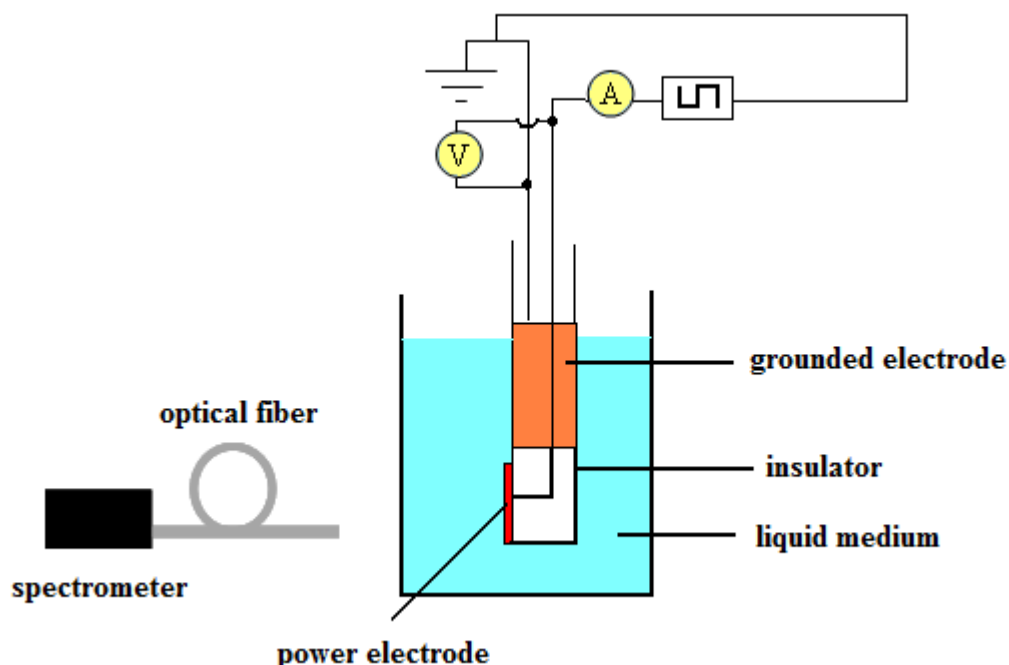


Figure 44 The scheme of experimental set-up.

The specific area of tissue can be hit due to small multi-electrode system (figure 45) where there is a plasma on the surface of this electrode system generated at the same time as treatment process. Following figure shows the electrode head under operation (figure 46).

In principle, this system operates as a multi-electrode setup with driving circuitry producing 100 kHz RF bipolar square wave voltage signals. The current is determined via the various impedance influencing factors dependent on the environment in which the plasma is formed. The main factor is obviously the solution conductivity which in turn depends on temperature and concentration. Also, the presence of other dissolved or suspended particles, or nearby physical structures have a significant influence. Naturally, the discharge chemistry in each specific instance also affects the applied current. Electrical characteristics are measured on a cable supplying one of the four electrodes mounted in the device active head, and for the purposes of power calculations it is assumed that the characteristics of all four electrodes are equivalent. The power applied into the system can be adjusted at eight levels in this system. It can be ranged from low-voltage conditions to higher-voltage conditions. While low-voltage conditions are basically used for tissue coagulation, the higher-voltage conditions are used for cutting or excising tissue rapidly.

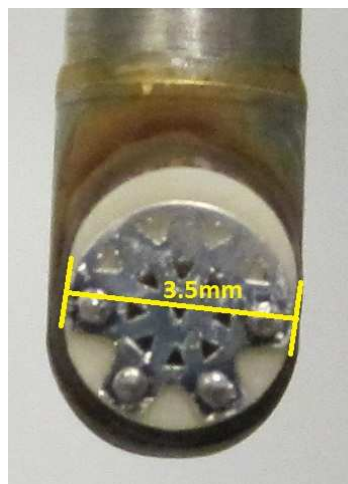


Figure 45 The detail of powered electrode structure.



Figure 46 The detail of power electrode structure with plasma under liquid (yellow area).

6.2 Examined solutions

The plasma was generated in four different 0.15M distilled water solutions of NaCl, KCl, BaCl₂ and Na₂CO₃. The volume of liquid was 20 ml, contained in a 25 mm diameter glass cyclinder. The sodium chloride solution has been later chosen to subjected to a detailed examination due to its biomedical character.

NaCl has been chosen as one of the isotonic solutions which are commonly utilized in biomedicine due to the fact that it has the same osmotic pressure as a blood. This allows its to be in contact directly with an injured human tissue. This practicaly means that it can be used as a disinfection for an opened injury. The studied fluids were easily prepared by mixing distilled water and pure solid compounds bought at Sigma Aldrich company.

Some of the solutions have consisted also a small additional of alcohol. There is a few reasons why the alcohol was added. The first one is an approach to electric discharges which are generated in organic liquids because a majority of previous measurements are focused on plasmas generated in inorganic solutions, only, but perspectives of discharges in liquids are probably in organic solutions. That situation has occured due to a low conductivity of organic fluids which practicaly means that the discharge generation in the laboratory is very hard in such kind of liquids. So the first step to approach organic discharges could be the addition of small amounts of an organic compounds into the inorganic solution. The second reason is a hydrogen atoms production. It is known that addition of ethanol will produce free molecular hydrogen in a solution exposed to the plasma [91]. This knowledge can provide an idea about using ethanol as a hydrogen donor in case it is exposed to electron impact.

The importance of hydrogen

Some previous studies have focused on hydrogen gas production since it is considered to be one of the foremost prospective energy sources for the future. The demand for hydrogen energy has increased in recent years because of the increase in world energy consupcion, as well as recent developments in the fuel cell technologies. At this work, the hydrogen has been considered as one of the easiest ways how to support hydrogen peroxide generation in the examined solutions once the hydrogen peroxide concentration is one of the main goals of this work. The importance of hydrogen peroxide has been explained in the previous chapter 2.2.2.

Here, methanol and ethanol have been chosen as representatives of the simplest organics compounds. The physical properties of the solutions such as a conductivity, temperature and pH have been studied, especially their changes evoqued by the plasma treatment. The changes were recorded before the operation, after every minute during the operation and at the end of the plasma treatment. Also, the hydrogen peroxide generation, optical emission spectra of discharge and electrical characteristics have been studied.

All these properties of the studied solutions were measured when the system was set up to give a maximum power to avoid a very unstable plasma generation. The value of power moved between 3 – 4 W. The minor probe (multi – electrode head) was immersed into the solution (the volume of treated liquid was 20 ml for these experiments) and plasma was continuously generated for three minutes.

6.3 Analysis of the examined solutions

All physical properties of the studied solutions have been determined by Hanna instruments. A multi-range conductivity meter HI 9033 and HI 9124 pH meter have been utilized to determination of pH and conductivity changes.

The hydrogen peroxide generation has been determined by titanium reagent again. The detailed description of this method has been already given in the previous chapter 3.2

Two Ocean Optics spectrometers have been utilized to acquire discharge emission spectra over several spectral ranges. As the first, the BRB spectrometer (with spectral range from 300 nm to 900 nm) has been used for a plasma generated species overview. The other spectrometer with range of 293 – 393 nm was used mainly for the detailed observation of OH radical emission.

6.4 Results

6.4.1 Determination of hydrogen peroxide concentration by test sticks

Initially, two other different solutions have been considered as a conductive medium to hydrogen peroxide production - BaCl_2 and Na_2CO_3 . Unfortunately, there has been a white precipitate formed in these solutions during plasma operation. Because of this fact, the hydrogen peroxide concentration could not been determined spectroscopically and another method has had to be found. An alternative solution has been provided by Quantofix peroxides test sticks which are supplied by Sigma Aldrich company [77]. These sticks generally consists of a plastic strip with attached sealed test paper which is immersed into the solution to detect the hydrogen peroxide. The principle of H_2O_2 detection is a reaction of hydrogen peroxide with peroxidase and the organic redox indicator in the test field to form a blue colored oxidations compound. These sticks are used for many different applications. For example, in chemical laboratories, they are utilized to check organic solvents because hydrogen peroxide presented in the organic solvents can cause an explosion when the solution is warmed up [92]. The obtained results are shown in the table 7 where the last row shows hydrogen peroxide concentrations determined by using titanium reagent. Comparing these concentrations with the test sticks concentrations there has been a very significant difference found. Generally, all of the test sticks values have reached lower concentration. It has been approximately even 12 times lower in the NaCl and KCl solutions. This can be considered as a provement of the titanium reagent importance which is able to detect even the lowest concetrations in the studied liquid systems while the test sticks do not provide trustable results at the low peroxide concentrations.

Table 7 The hydrogen peroxid concentrations measured by test sticks.

	NaCl	KCl	BaCl ₂	Na ₂ CO ₃
Exposure time [min.]	2	2	2	1
H ₂ O ₂ conc. [mg/l]	4 ± 1	5 ± 1	6 ± 1	0
Mr [g/mol]	58.4	74.6	208.24	105.99
H ₂ O ₂ conc. [mmol/l]	0.07	0.07	0.03	0
H ₂ O ₂ conc. [mmol/l] determinated by titanium reagent	0,87	0,78	-	-

Another unwanted phenomenon has been observed during the measurements. The preeliminary results have shown that there is a white particulate formed in the BaCl₂ and Na₂CO₃ solutions during the plasma process which naturally does not allow to use a titanium reagent to hydrogen peroxide determination. For this reason and the fact that test sticks do not provide trustable results, the BaCl₂ and Na₂CO₃ solutions have been excluded from the further investigation.

6.4.2 Hydrogen peroxide generation

An influence of the used kind of electrolyte on the hydrogen peroxide generation has been investigated in the NaCl and KCl liquid solutions. The obtained results are shown in the figure 47. As it can be seen there, the hydrogen peroxide concentrations have reached higher values in the solutions with the small additional of alcohol. Comparing KCl and NaCl solution it can be observed that values of hydrogen peroxide concentrations are very similar and it can not be surely said which solution has given better conditions to hydrogen peroxide generation.

H₂O₂ production has been studied in detail using the 0.15 M NaCl solution and in the solutions with the additional of alcohol. The kinetic curve for hydrogen peroxide generation is presented in the following figures 47 and 48. As it was expected, the hydrogen peroxide concentration increases in time. This can be considered as a prevention of no undesirable effects decomposing hydrogen peroxide as for example iron losing from the electrode (see 0.) Thus, the initial purity of the examined solutions has been kept during the operation. As there is seen, the highest concentration has been observed in the solution with 0,05 ml (0,25 %) of ethanol and the lowest in the solution without any additional of alcohol. It practically means that methanol and ethanol definitely support hydrogen peroxide generation and ethanol seems to be even more effective. However, there is only a slight difference between these two alcohols and the confirmation of this conclusion would require a detailed chemical analysis.

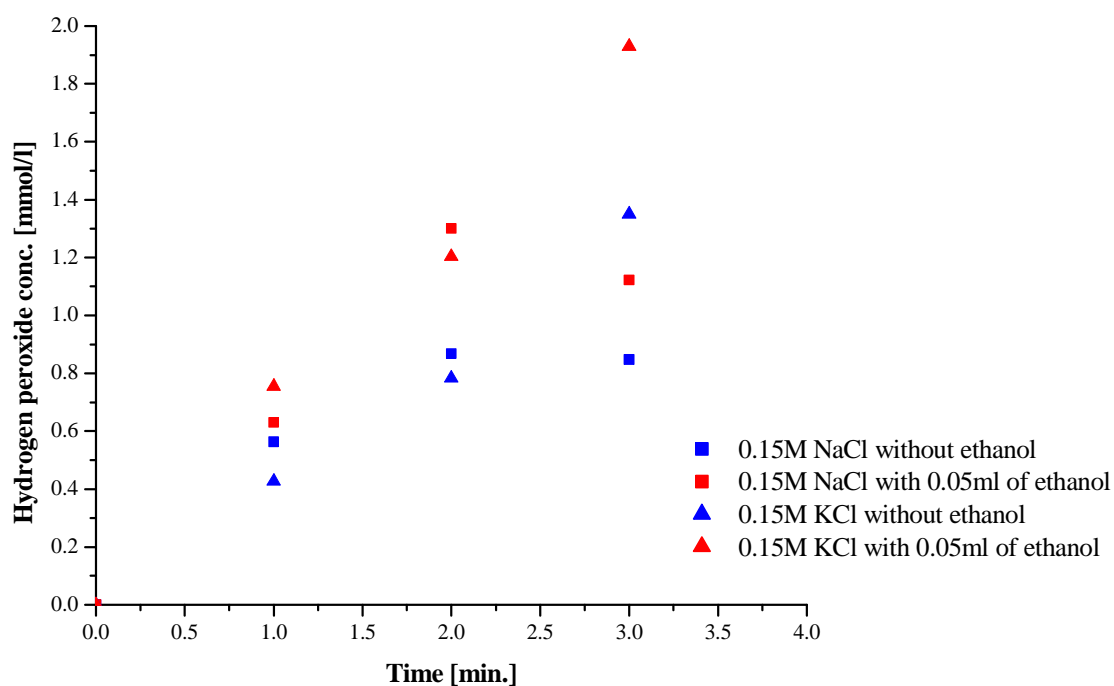


Figure 47 Hydrogen peroxide generation in the time in four different solutions.

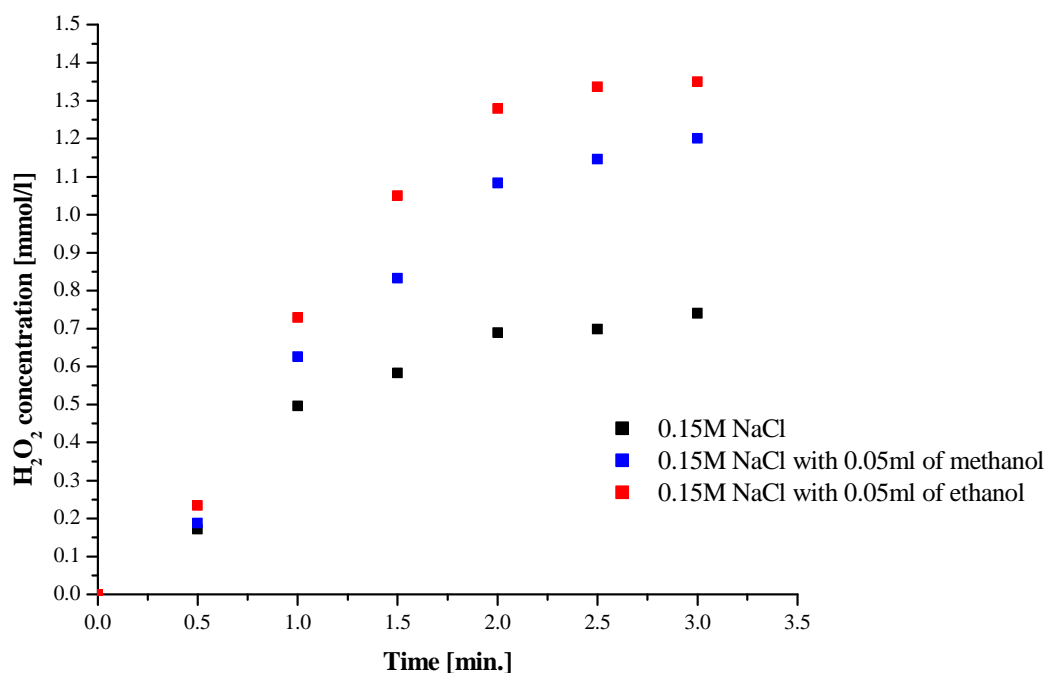


Figure 48 Hydrogen peroxide generation in the time in three different solutions.

Theoretically, there are two ways how these alcohols could support hydrogen peroxide generation. The first is based on the fact that hydrogen atoms are provided by alcohols in the solutions once they are treated by plasma. This means that hydrogen atoms, before they

recombine to hydrogen molecule, could react according bellow schemes which would lead to the increase of hydrogen peroxide production:



The second way could be an OH radical generation because this group is contained in the alcohol molecule structure and it can be separated easily by plasma treatment. Organic molecules destruction by plasma in a liquid system has been observed by *K. R Stalder at all* in 2005 [93]. This study shows a complete decoposition of the copound structure except the parts with double bonds. Due to this knowledge both of the above-mentioned processes have probably had an influence on the hydrogen peroxide generation. An exclusion or confirmation one of them brings a next idea for a specific individual project. Here, it can be concluded that alcohols generally cause the increase of hydrogen peroxide concentration in the liquid solution during the plasma operation.

The next part of this examination has been focused on an amount of the alcohols added into the solutions. The obtained results are shown in the figure bellow (figure 49). For the methanol, the red points represent the solution where there has been put ten times more amount of the alcohol than in previous experiment. Compare to blue curve, showing only 0,05 ml of the alcohol, it can be sawn that the higher additional of the alcohol has caused a lower increase of hydrogen peroxide concentration as it has been expected. This trend has been observed in the case then ethanol was used, too. The lowest hydrogen peroxide concentration has been measured once 0,5 ml of ethanol has been put in the solution. The concetration has been even lower than in the clear solution at this time. The reason is an oxidation process between alcohol and hydrogen peroxide. The produced hydrogen peroxide from the interaction of plasma with water oxidises alcohol to form an acid and water. The low amount of alcohol does not cause the hydrogen peroxide to turn to water immediately because there is not enough of alcohol molecules to accept the oxygen atoms from the hydrogen peroxide. Thus, it can be concluded, that alcohols such as simple organic molecules can be efectively utilized to increase the hydrogen peroxide production in the solution. They seem to be a good and cheaper alternative for gases which are now used to manage the same effect. Indeed, the quantity of the alcohol added in the liquid is strictly limited and had to be controlled. Based on the obtained data, it can be concluded that an ideal volume is just trace amount of alcohol (0,05 ml in 20 ml of the solution ~ 0.25 %).

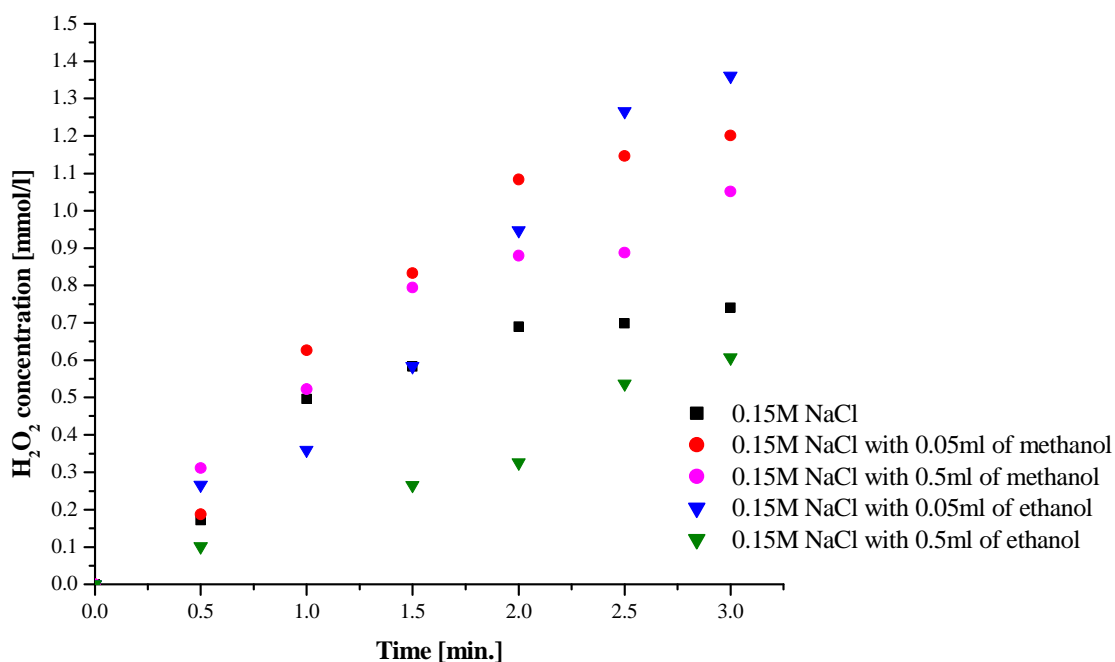


Figure 49 *Hydrogen peroxide concentration generated in the solution with different amount of the methanol and ethanol.*

6.4.3 The pH of the treated solution

There is one more advantage of the alcohol additional in the treated water solution. As it has been said, alcohols succumb to the oxidation process which naturally brings a wanted change in the pH of the solution. The obtained results are shown bellow in the figures 50 and 51. In the figure 50, the blue marks represent solutions without the additional of the alcohol. It can be seen that the pH values have not decreases distinctly after the plasma operation in this case. The red marks show the solutions with the small additional of alcohol and here the pronounced difference between initial and final pH values has been obtained. The same phenomenon has been observed in the figure 51. Here, the black points represent the 0.15 M clear NaCl solution. As there is distinct, there has been only slightly decrease in pH values obtained. The negligible difference between initial and final pH values means that there has not been any HCl acid formed in the solution during the operation or it was synthesized in negligible amount which has not had influence on the pH. Normally, these little changes are caused by hydrogen peroxide due to its weak acidic character. The opposite trend, which is shown by other curves, presents the solutions with a small addition of the alcohols. In this case, there has been obtained a pronounced decline in pH values. The initial pH values have decreased by a few units and so the final pH values have reached an acidic environment. This phenomena can be evaluated as satisfying result because the OH radicals generated by plasma operation have a higher oxidation potential under these conditions. Obviously, this acetic environment of the investigated solution is caused by acids formation from the alcohols. The ethanol turns to an acetic acid and methanol oxidizes to formic acid.

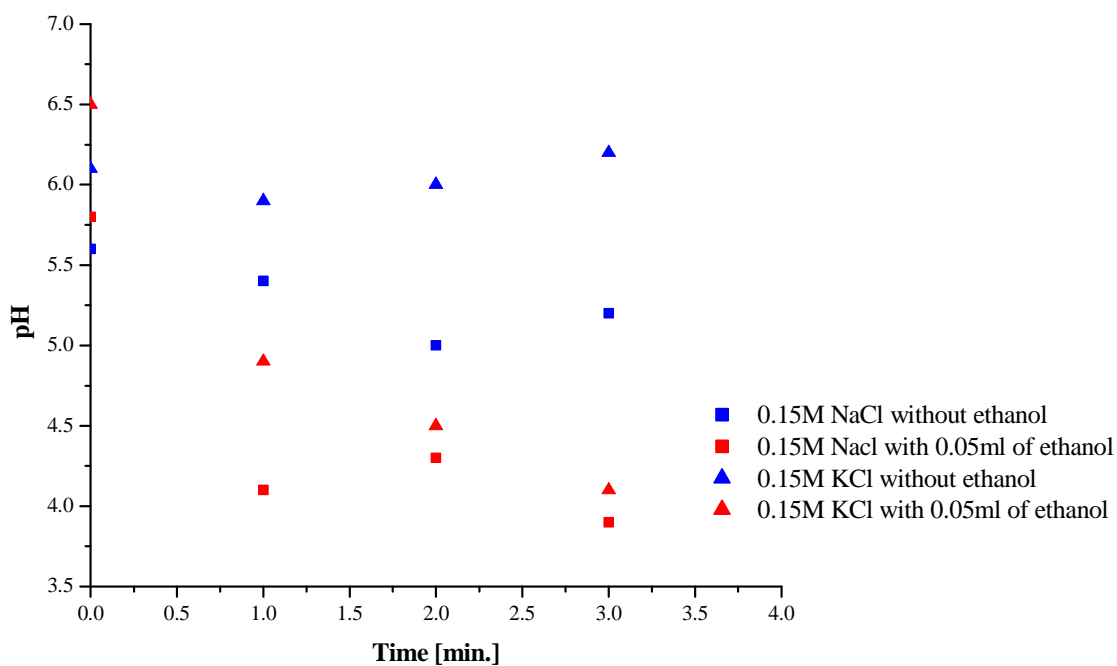


Figure 50 Final pH values after three minutes of the discharge operation in the 0,15 M NaCl and KCl solutions.

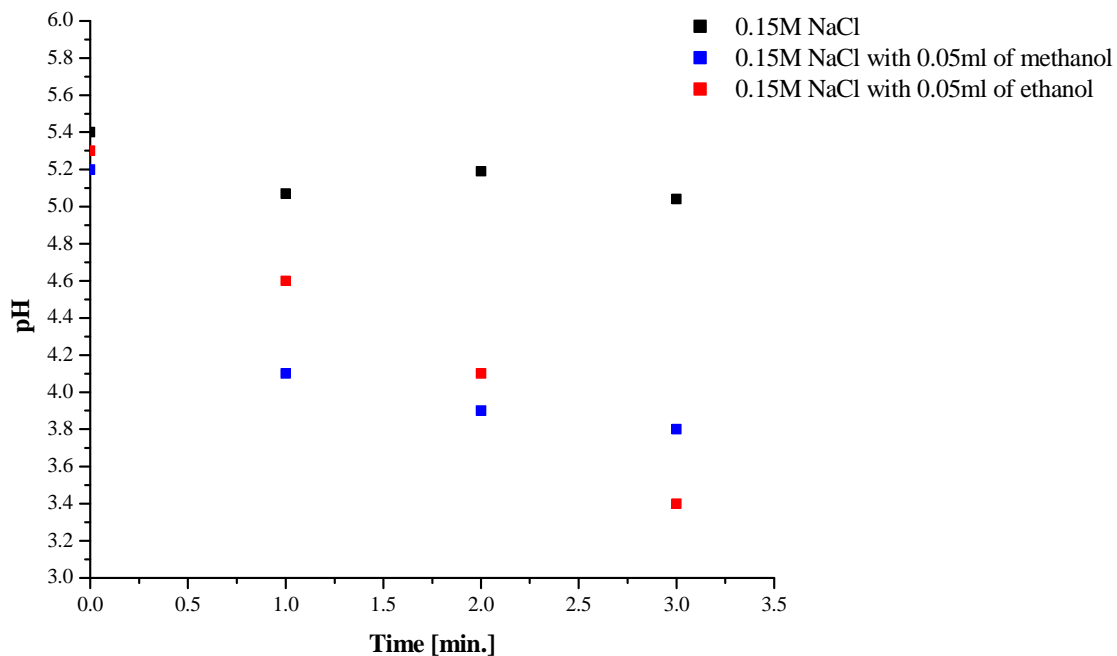


Figure 51 Final pH values of the examined solutions after three minutes of discharge operation.

To confirm the conclusion that ethanol and methanol are oxidized during plasma treatment an additional study has been carried out. The same amount of isopropanol has been added into the 0.15 M NaCl solution to observe the changes of pH values. It had been considered before experiments that isopropanol as the simplest secondary alcohol can not turn to an acid because the last level of its oxidation is a ketone. The obtained results are shown in the figure 52. The black points represent the solution with the additional of isopropanol. As there is possible to observe the pH values were changing only slightly during the plasma operation and the difference between initial and final value is just insignificant. This means the consideration has proved as correct. While methanol and ethanol can provide quite stable acidic environment in the treated solution, pH values of the solutions with isopropanol or just NaCl solution are kept nearly without change.

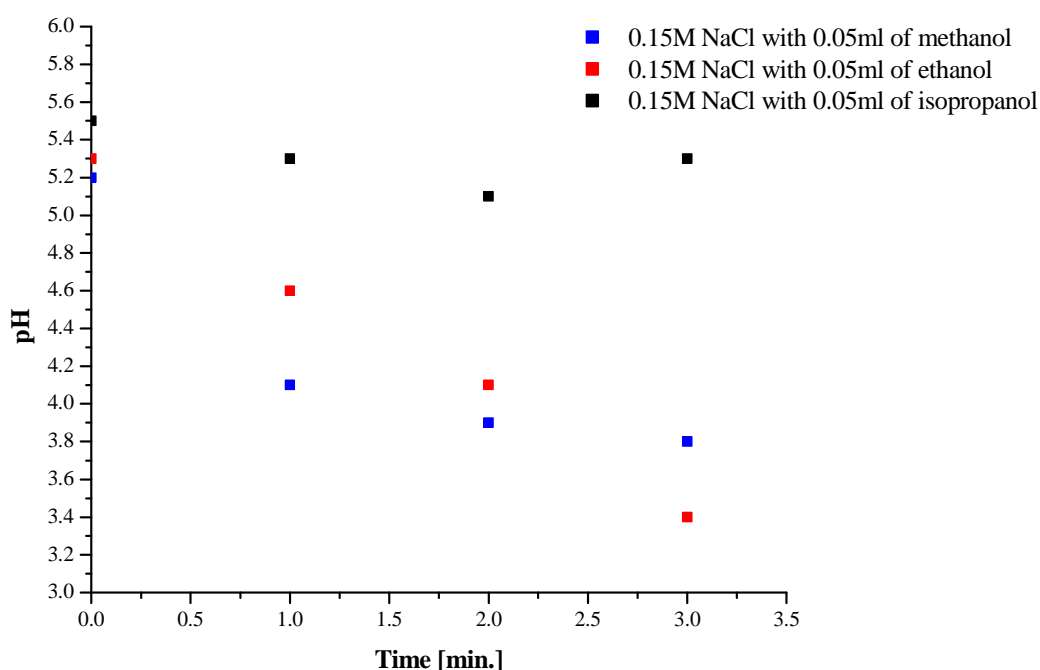


Figure 52 Final pH values of the examined solutions after three minutes of discharge operation.

6.4.4 The temperature of the solution

Another also important physical property of the system, which has been studied, is the temperature and its changes during the plasma operation. The kinetic curves are presented in the figure below (figure 53). As there is seen, the values of the temperature were constantly increasing during the discharge operation in all solutions. The highest value (80 °C) has been obtained in the solution with the additional of methanol, and the lowest value (77 °C) has been noticed in the solution with the addition of ethanol.

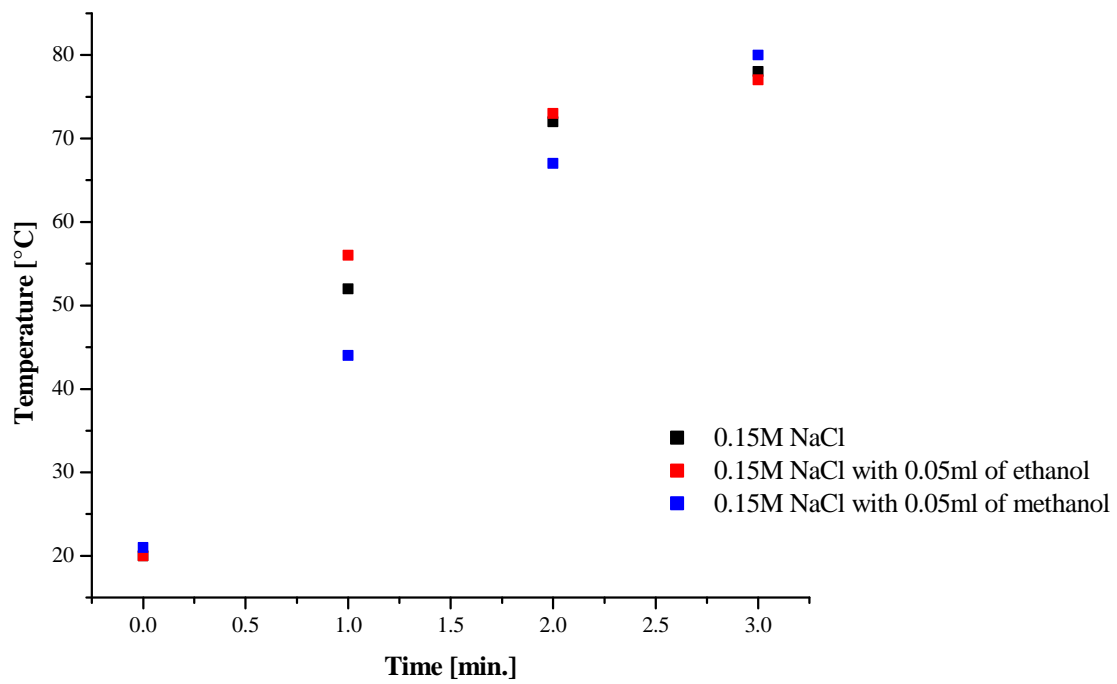


Figure 53 Final temperature values of the 0.15 M NaCl solution after three minutes of discharge operation.

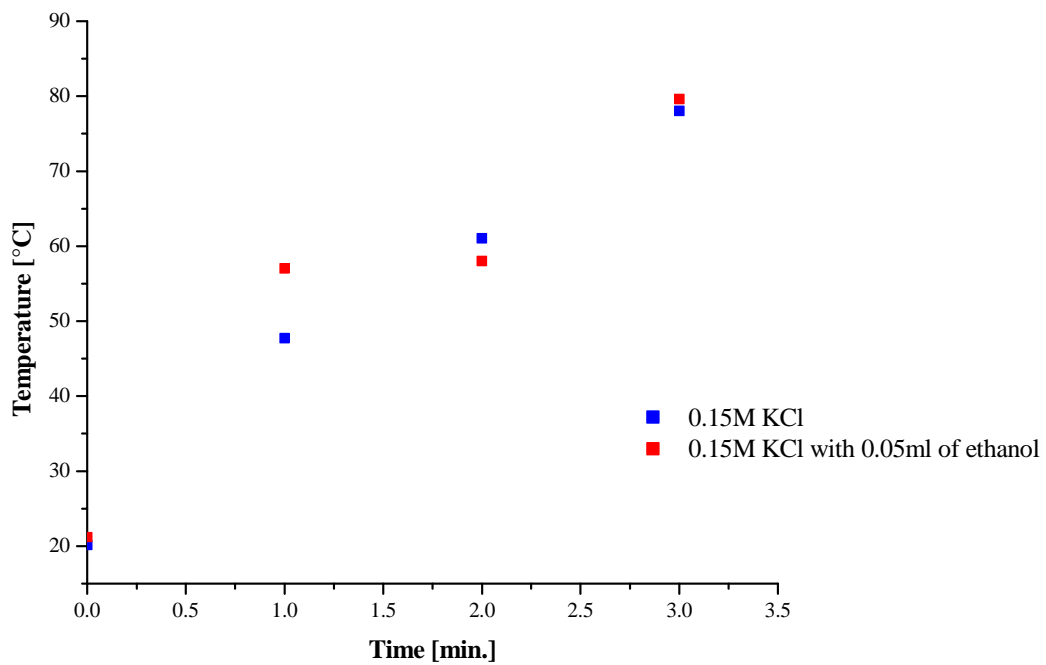


Figure 54 Final temperature values of the 0.15 M KCl solution after three minutes of discharge operation.

However, the difference between these two numbers has not been pronounced which practically means that each investigated system could accept approximately the same amount of energy in the same period time (3 min). Thus, alcohols such as organic compounds have not had any considerable influence on the energy acceptance from the source. The same trend of the temperature evolution has been observed in the KCl solution. The result is shown in the figure 54.

6.4.5 The conductivity of the solution

As it has been mentioned in the previous chapter 6.2, there is generally low conductivity of organic fluids and so it had been expected that an addition of alcohol could have caused a problem with plasma generation in the liquid system. Fortunately, this trace amount of alcohols have not had any influence on the initial conductivity of the solution and the experiment could be carried out. The points showing the evolution of the initial conductivity of the studied solutions are shown in the figures 55 and 56. As there is seen, the initial conductivity values of the solutions with the additional of alcohol have been almost identical as the initial values of the clear NaCl solution. Thus plasma could be generated in every studied system without any unwanted interruptions during all operation. The final conductivity values differ only slightly which practically says that there have not been an excess of charge carries and the current could be easily applied in the examined solution. Again, the trace additional of the alcohols have not influenced the required plasma generation.

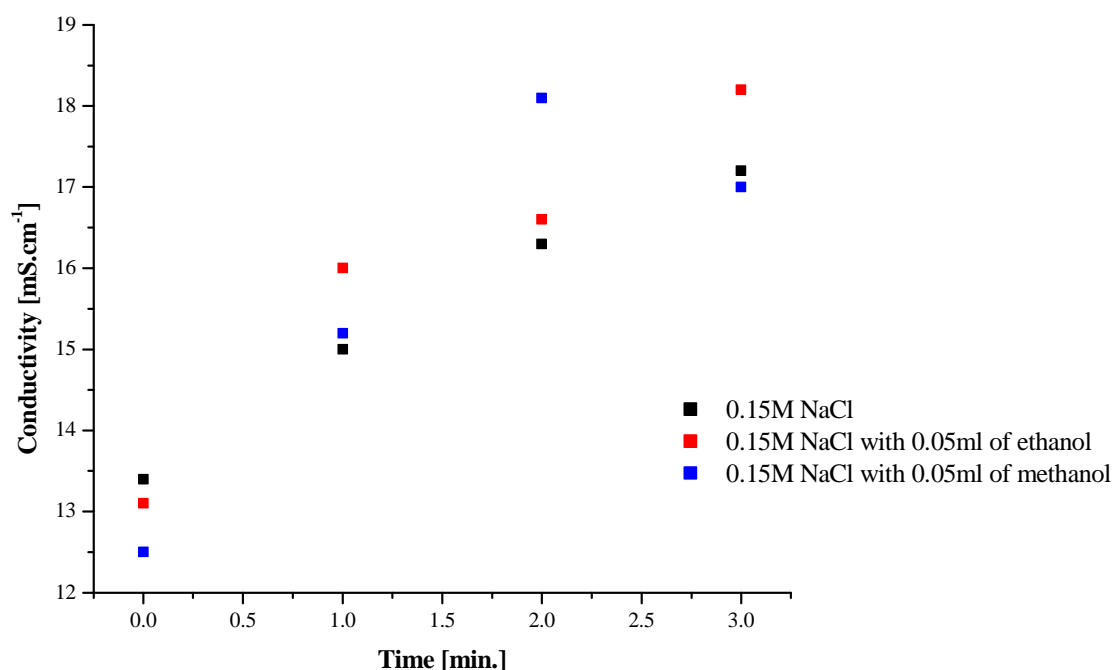


Figure 55 Final conductivities values of the 0.15M NaCl solutions after three minutes of discharge operation.

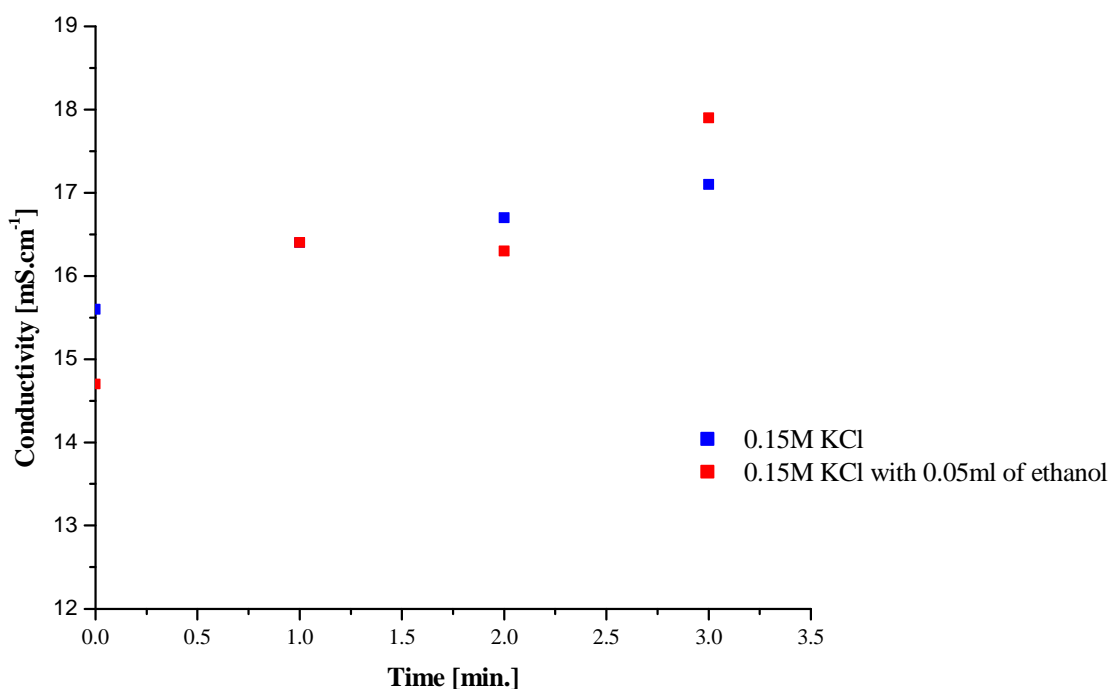


Figure 56 Final conductivities values of the 0.15 M KCl solutions after three minutes of discharge operation.

6.4.6 Spectra analysis

To get more information about species produced in the solution, the optical emission spectroscopy has also been utilized as another method to make a detailed analysis of the plasma generated in the liquid systems.

As the first, the spectrum of discharge generated in BaCl₂ solution has been taken to observe namely OH radicals peaks area. Basically, these radicals are one of the most wanted particles generated by plasma because they are understood as precursors of the hydrogen peroxide and also, they can oxidize undesirable compounds in the solution (see 2.2.1). Their presence in the system has been proven by a typical wide peaks area located between 300 and 350 nm.

As there has been shown in the previous paragraph 6.4.1, there has been some hydrogen peroxide generated in the solution. Unfortunately, these results are due to determination method not trustable so the spectrum has been considered as an additional method useful to confirm OH radicals generation. The obtained spectrum is shown by figure 57. As there is seen, the OH radicals have been generated in this solution during plasma treatment. It practically means that hydrogen peroxide has been also generated in the liquid and BaCl₂ solution is suitable medium for its production.

The next figure 58 shows the spectrum of discharge generated in Na₂CO₃ solution. The early results have shown no hydrogen peroxide concentration in the solution after two minutes of plasma operation. But there is seen quite pronounced OH peaks area in the spectrum which means that hydrogen peroxide should be generated in the solution. Due to the other results proving that the test sticks method to H₂O₂ determination is not trustable, it can be concluded

that Na_2CO_3 is probably also suitable medium for H_2O_2 production but it is impossible now to make any correct quantification.

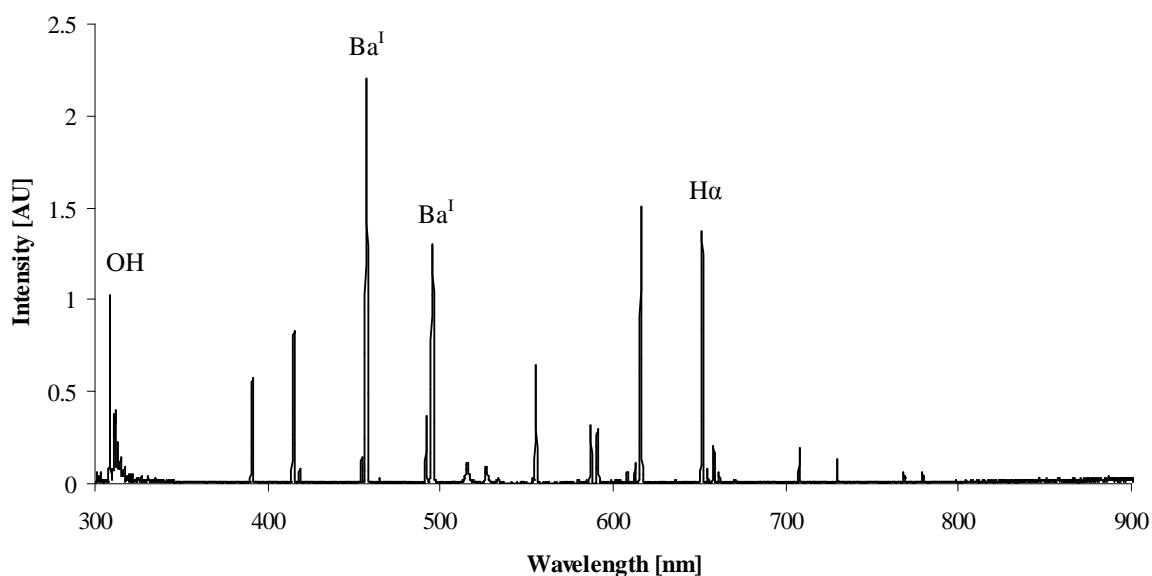


Figure 57 The spectrum of discharge generated in 0.15 M BaCl_2 .

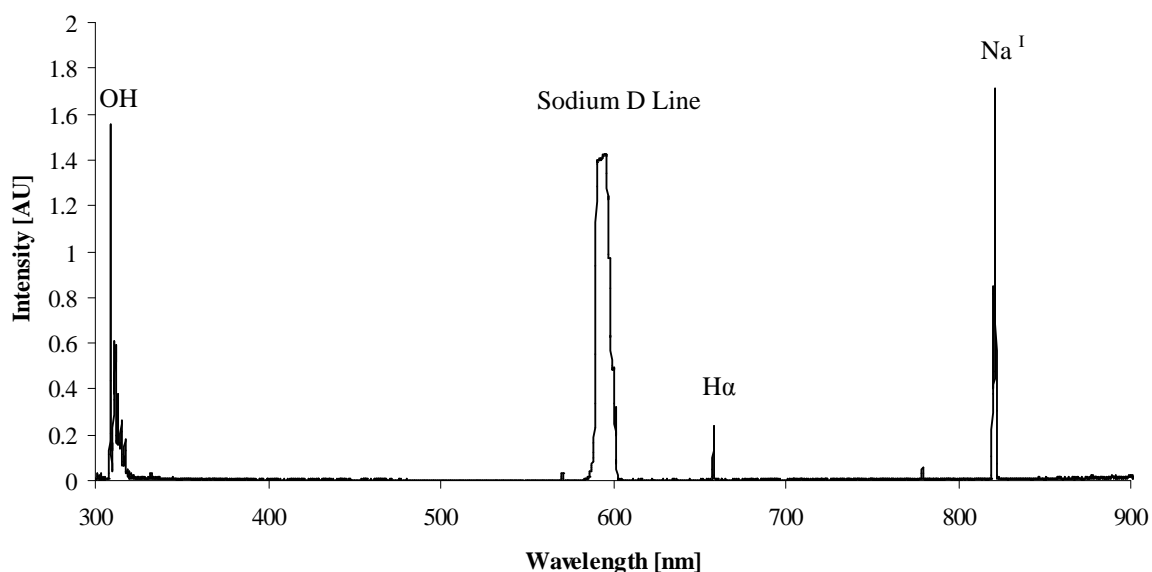


Figure 58 The spectrum of discharge generated in 0.15 M Na_2CO_3 solution.

The figure 59 shows another spectrum representing the obtained result of the 0.15 M KCl solution without addition of alcohol. Again, the main species have been observed. Here a very pronounced potassium peak has been noticed while the maximal intensity of the OH radicals molecular band has been very low. The ratio between the maximal OH radicals intensity and $\text{H}\alpha$ peak intensity has been approximately 2:1. The next spectrum in the figure 60 shows the obtained results in the 0.15 M KCl solution with the addition of alcohol. As there is seen, the same elements have been measured – a pronounced potassium peak (769 nm), $\text{H}\alpha$ peak

(656 nm) and OH radicals peaks area. The main difference has been observed by counting the ratio between the maximal intensity of OH radicals band and the H α peak intensity. The 5:1 ratio has been determined. This phenomenon has been probably caused by the addition of the alcohol. Unfortunately, the absolute values of the intensities are non-comparable because it was impossible to fix the optical geometry during all experiments.

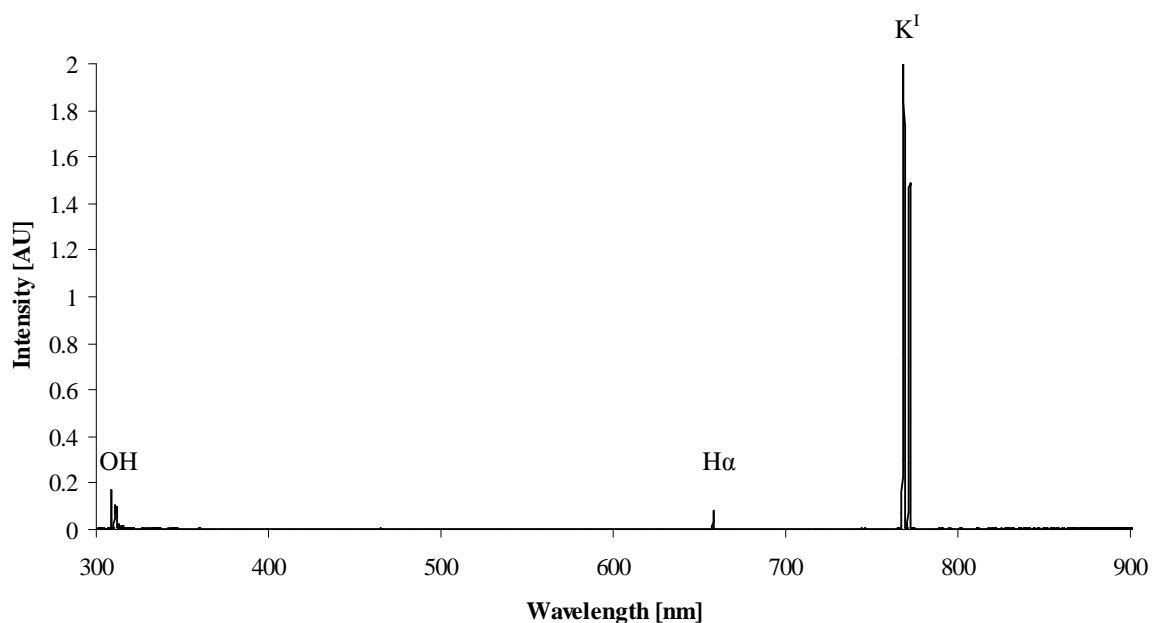


Figure 59 The broadband spectrum of discharge generated in the clear 0.15 M KCl solution.

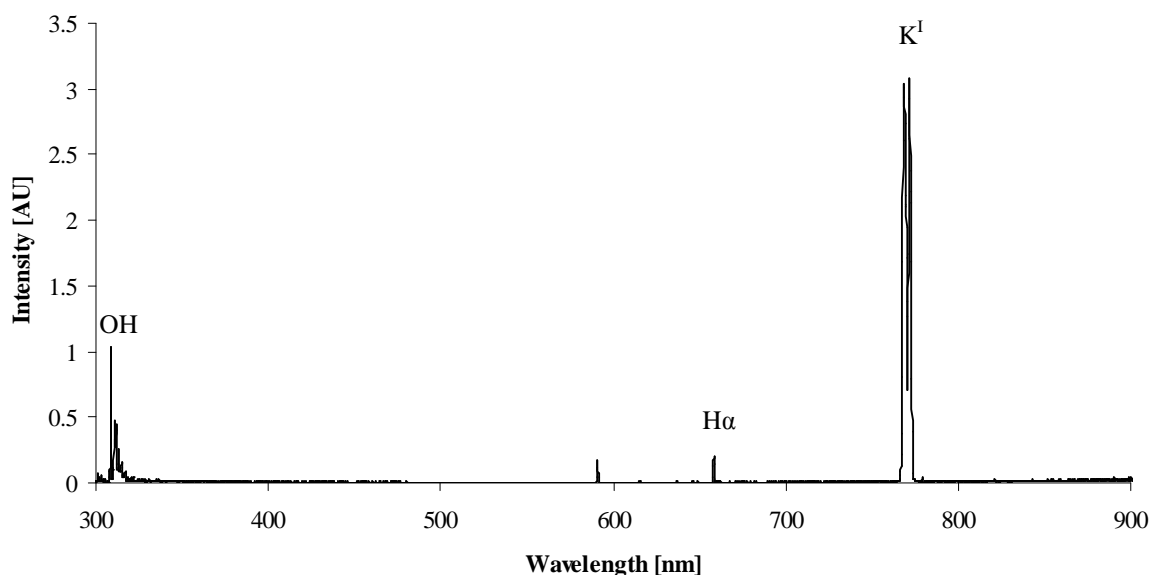


Figure 60 The broadband spectrum of discharge generated in the 0.15 M KCl solution with the addition of ethanol.

The spectrum of the clear NaCl solution has been evaluated. The gained result is shown by figure below (figure 61). This obtained optical spectrum has provide a complete summary of

the atoms or molecules which have been generated in the solution during the plasma operation. As it has been expected, there have been OH radicals generated in the investigated solution. The next figure (figure 62) represents the spectrum of the 0.15 M NaCl solution with the small additional of ethanol. As there is seen, this spectrum is nearly identical. As in the previous case the peaks representing sodium (589 and 819 nm) are dominant, following the peaks area of the OH radicals. Calculating the ratio between H α peak (656) and sodium peak (780) nm there has been found a slight increase of the intensity of the H α line in the solution with the additional of the alcohol. It can be considered as the results of some extra hydrogen atoms which are caused by plasma treatment of the ethanol during the operation.

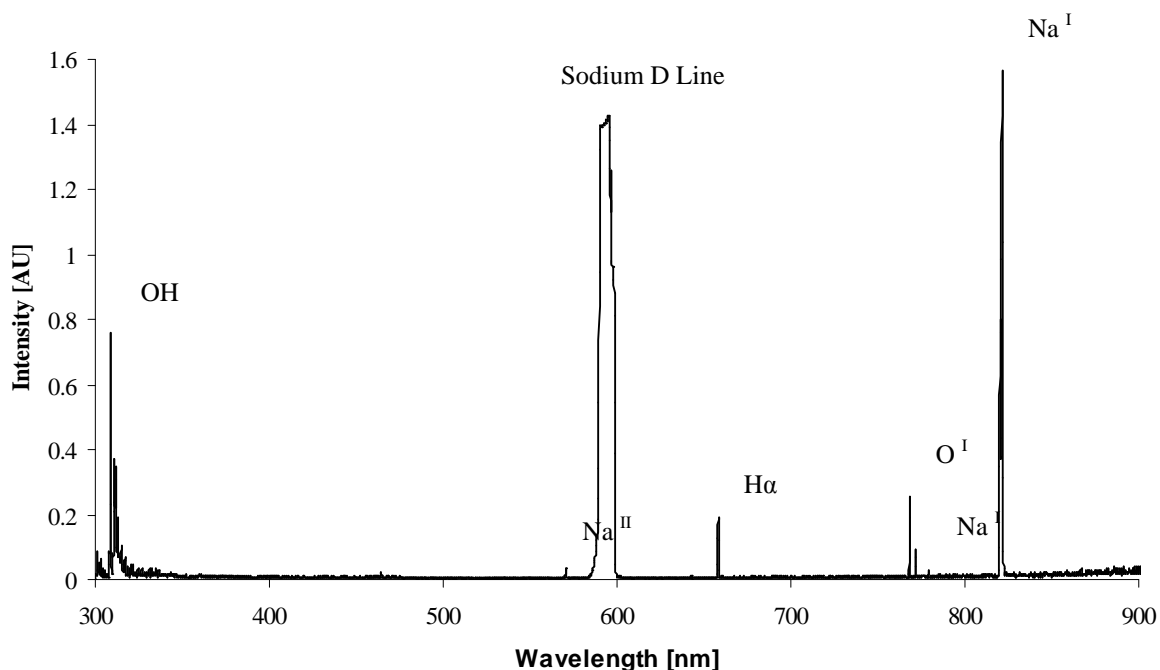


Figure 61 The spectrum of discharge generated in clear 0.15 M NaCl solution.

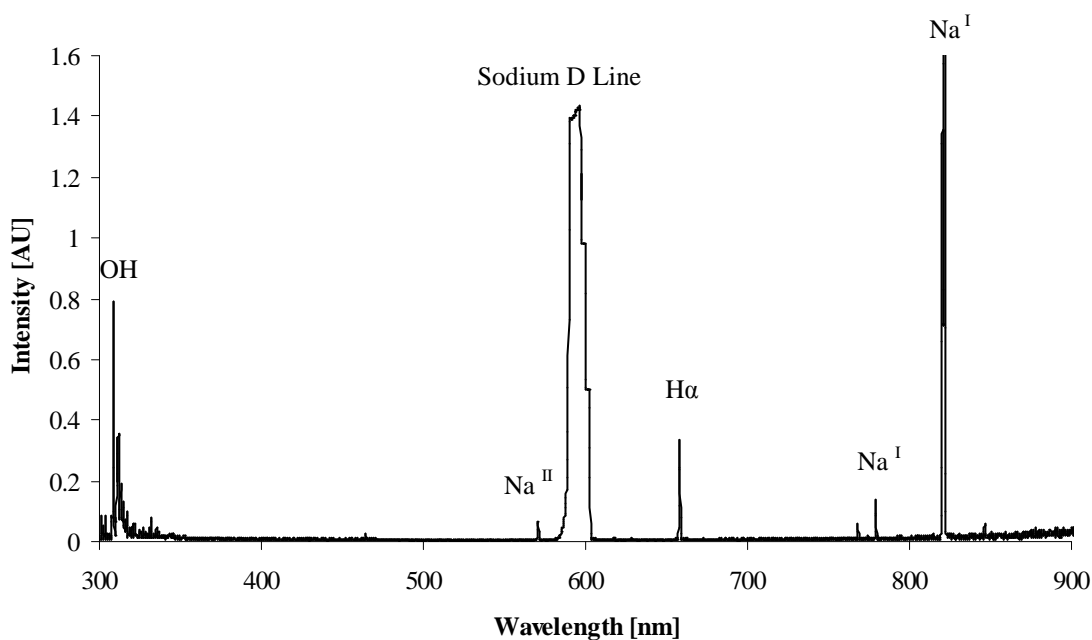


Figure 62 The spectrum of discharge generated in 0.15 M NaCl solution with the additional of ethanol.

6.4.7 Electrical characteristic

Some electrical properties of the KCl and NaCl solutions have been recorded to make a detailed analysis of the electric energy applied into these liquid systems. In this part of investigation, the influence of the small addition of ethanol on the supplied power has been studied. As it has already been mentioned, ethanol is the organic liquid with too low conductivity and so it had been considered that it could make impossible the electric current flow in the solution. The electrical characteristics have been taken during plasma operation in the first, the second and the third minute in each solution to gain a detailed data which could subsequently guarantee a trustworthy results. The schemes of the electrical characteristics for the 0.15 M NaCl solution with and without addition of ethanol are presented by figure 63 - 68. Due to high similarity with the records for KCl solutions electrical characteristics for this examined solution are not displayed. The results for the 0.15 M NaCl solution without addition of the ethanol are shown by figures 63, 64 and 65, analogical the results of the solutions with the addition of the ethanol are shown by figures 66, 67 and 68. As there can be seen, all these curves presented in the figures report regular processes without any unexpected deflections. Even in the solution with the addition of the ethanol, it has not been any strange effect observed which means that this addition has not had a pronounced influence on the energy that has been applied into the solution.

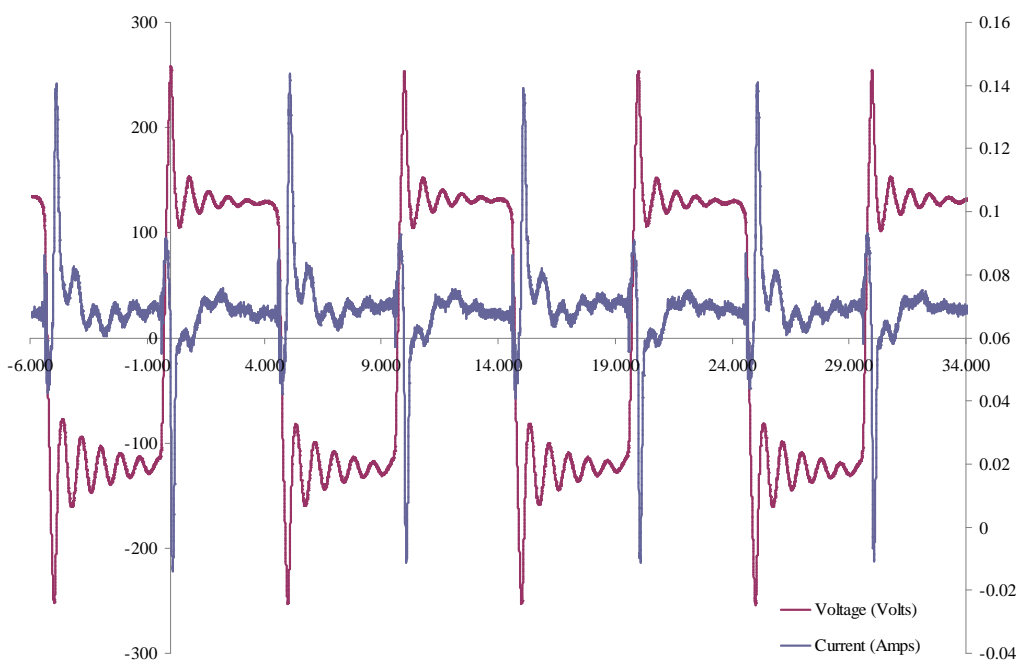


Figure 63 The scheme of electrical characteristics for 0.15 M NaCl solution without addition of ethanol in the first minute of the discharge operation.

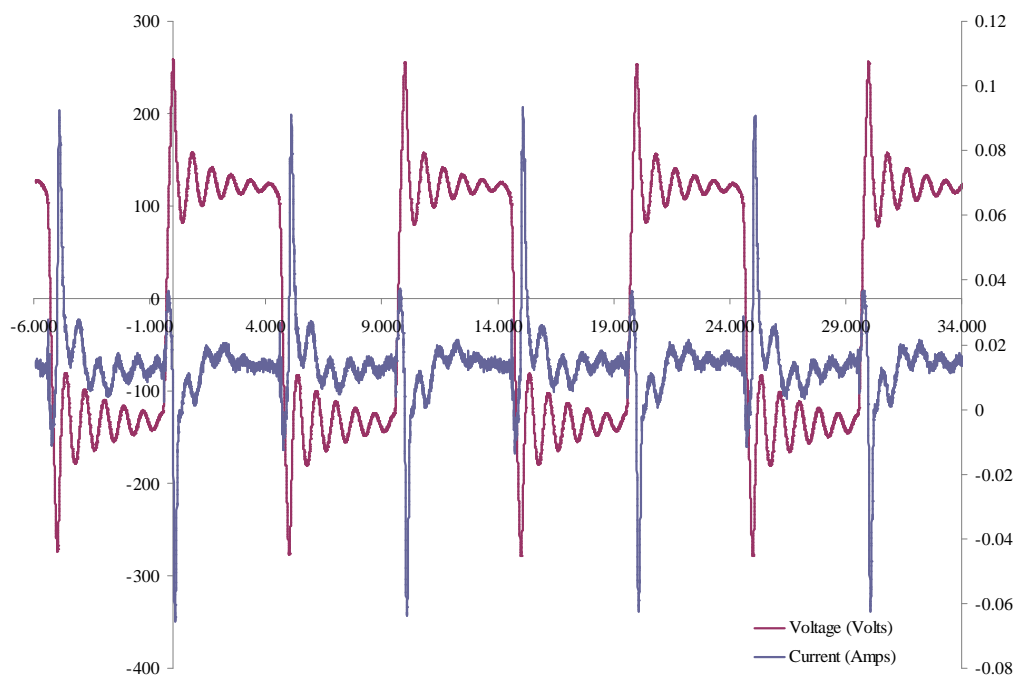


Figure 64 The scheme of electrical characteristics for 0.15 M NaCl solution without addition of ethanol in the second minute of the discharge operation.

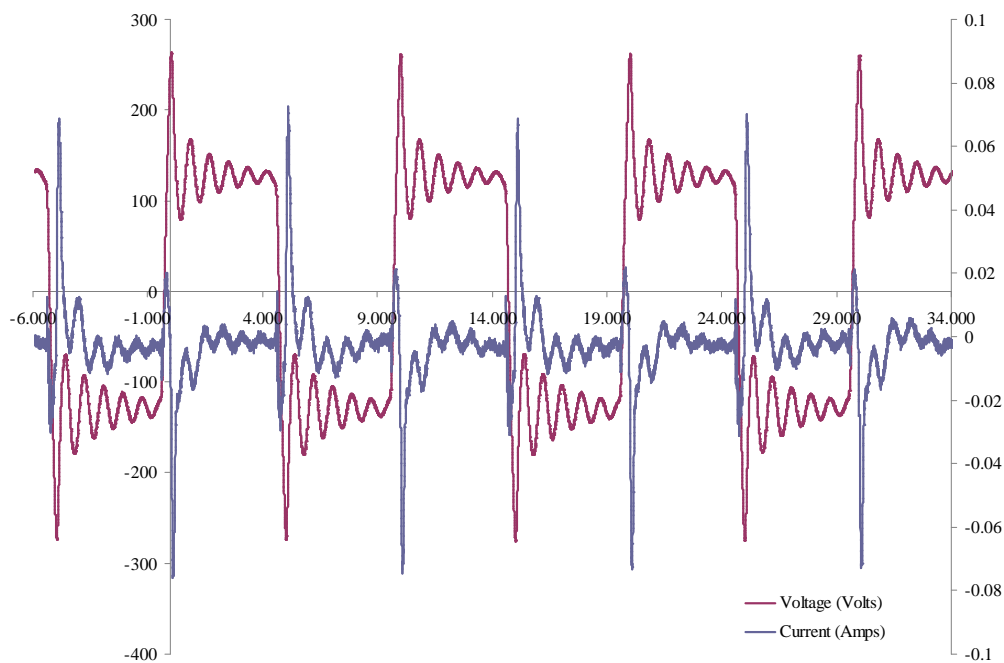


Figure 65 The scheme of electrical characteristics for 0.15 M NaCl solution without addition of ethanol in the third minute of the discharge operation.

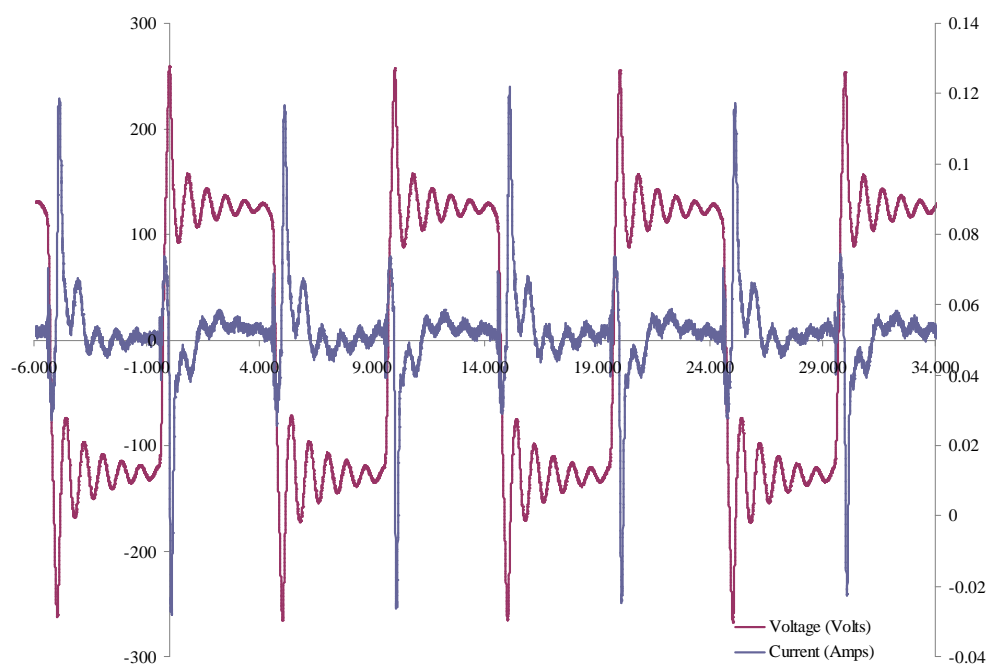


Figure 66 The scheme of electrical characteristics for 0.15 M NaCl solution with addition of ethanol in the first minute of the discharge operation.

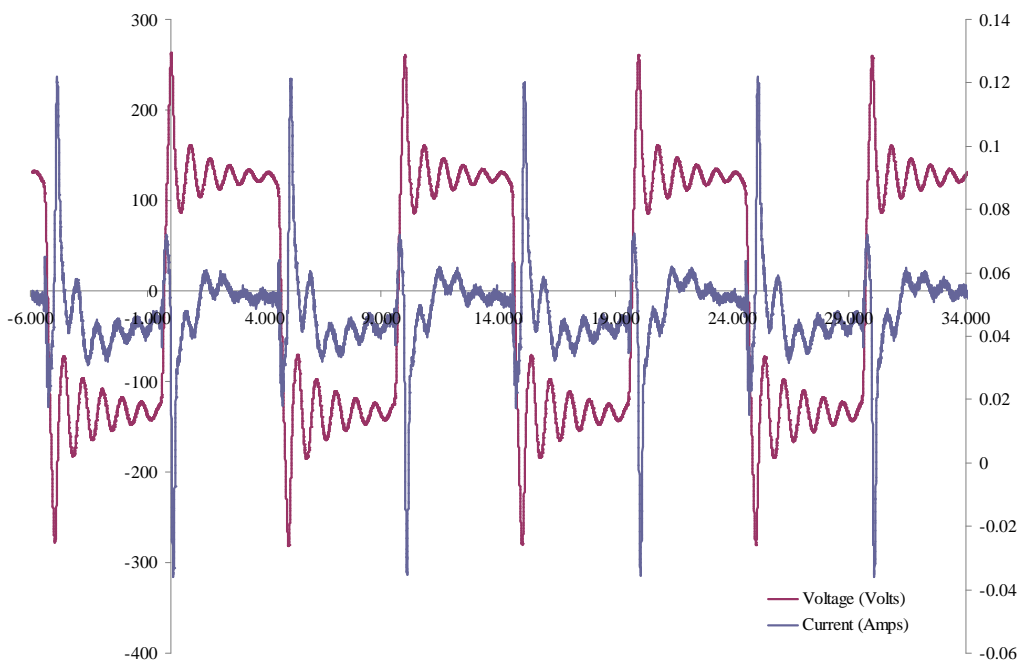


Figure 67 The scheme of electrical characteristics for 0.15 M NaCl solution with addition of ethanol in the second minute of the discharge operation.

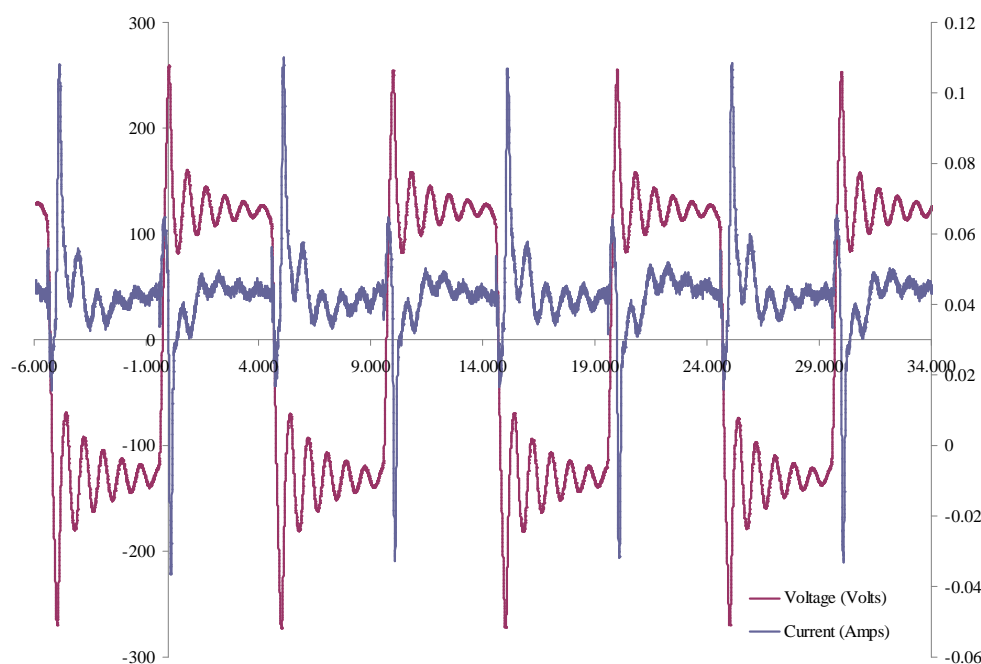


Figure 68 The scheme of electrical characteristics for 0.15 M NaCl solution with addition of ethanol in the third minute of the discharge operation.

As it has been mentioned in the previous paragraph, according the studied records, the addition of the ethanol has not had any influence on the energy which has been applied into the solutions. To confirm this detection, the exact values of the current, voltage and power have been determined based on gained electrical characteristics. The results for all of the investigated solutions are shown in the table 8.

Table 8 The counted current, voltage and power values of the examined solutions.

Solution	Max/Min. current (Amps)	Max./Min. voltage (Volts)	Averaged power (Watts)
NaCl 1 min.	0.08/-0.08	257.9/-253.9	3.8
NaCl 2 min.	0.08/-0.08	259.1/-278.6	3.9
NaCl 3 min.	0.08/-0.07	263.4/-275.6	3.8
NaCl with ethanol			
NaCl 1 min. with the addition of ethanol	0.07/-0.08	259.1/-273.2	3.8
NaCl 2 min. with the addition of ethanol	0.07/-0.08	263.0/-281.5	3.4
NaCl 3 min. with the addition of ethanol	0.07/-0.08	259.1/-273.2	3.8
KCl			
KCl 1 min.	0.07/-0.08	258.9/-264.7	3.7
KCl 2 min.	0.07/-0.07	259.3/-269.2	3.6
KCl 3 min.	0.06/-0.06	268.7/-276.2	3.8
KCl with ethanol			
KCl 1 min. with the addition of ethanol	0.07/-0.08	256.9/-257.5	3.3
KCl 2 min. with the addition of ethanol	0.07/-0.08	257.7/-262.9	3.3
KCl 3 min. with the addition of ethanol	0.08/-0.09	260.7/-266.0	3.1

Generally, the measured values are very similar for all types of the solutions. The maximal value of the applied current has been obtained in the 0.15 M NaCl solution without ethanol in the second minute of the operation, the minimal value of the applied current has been observed in the 0.15 M KCl solution without ethanol in the second minute of the operation. Similarly, the maximal voltage has been found in the 0.15 M KCl solution without ethanol in the third minute of the operation and the minimal voltage in the 0.15 M NaCl solution without ethanol in the first minute of the process. However, all of these numbers have reached approximately the same values which practically means that the difference among them is within an acceptable deviation. The same trend has been obtained evaluating at power data.

Thus it can be concluded that the ethanol such as organic molecule has not had any influence on the current, voltage or power applied in the studied systems.

7 ATMOSPHERIC PRESSURE MICROPLASMA JET IN INTERACTION WITH LIQUIDS

The last part of my thesis presents some preliminary but very interesting results which have been taken during my short visitor stage at the University of Ulster, Newtonabbey, UK. Here, the electric discharge micro jet in touch with liquid phase is used for gold nanoparticles synthesis. The experimental technique has been constructed at that department and the plasma discharge has been utilized to induce the liquid chemistry. My role in this applied research was mainly in the study of hydrogen peroxide generation because it was supposed that it radicals plays significant role in hte proces of nanoparticles formation.

7.1 Experimental solution

A solid powder of gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) has been bought from Sigma Aldirch, UK. Six selected solutions with different initial conductivity have been prepared (2.5 μM , 0.05 mM, 0.1 mM, 0.2 mM, 0.6 mM and 1 mM) by dissolving this gold salt in the distilled water. The plasma treatment of each solution has taken ten minutes. The hydrogen peroxide has been determinated by using titanium reagent again and also the gold nanoparticles were determined by spectroscopy method which is described in the previous chapter 3.2.

7.2 Experimental technique

The principal scheme of the experimental technique is shown bellow in the figure 69. An atmospheric microplasma jet has been generated over the surface of a gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) aqueous solution. The interactions of plasma and liquid phase have initiated some reactions inside the solution which have led to a reduction of the gold-chloride-trihydrate. After that, the nucleation and growth of gold nanoparticles have started. The capillary which has produced the microplasma has been made form stainless steel (1 mm external diameter and 0.25 mm internal diameter). Helium has been flown at the fixed flow rate of 25 sccm through this capillary. The microplasma has been substained by a high DC voltage (2 kV) which has been applied at the carbon rod (anode) while the stainless steel capillary has been grounded through a ballast resistor of 100 k Ω . The processing current has reached a values 1 – 5 mA. The photo of microplasma is given by figure 70.

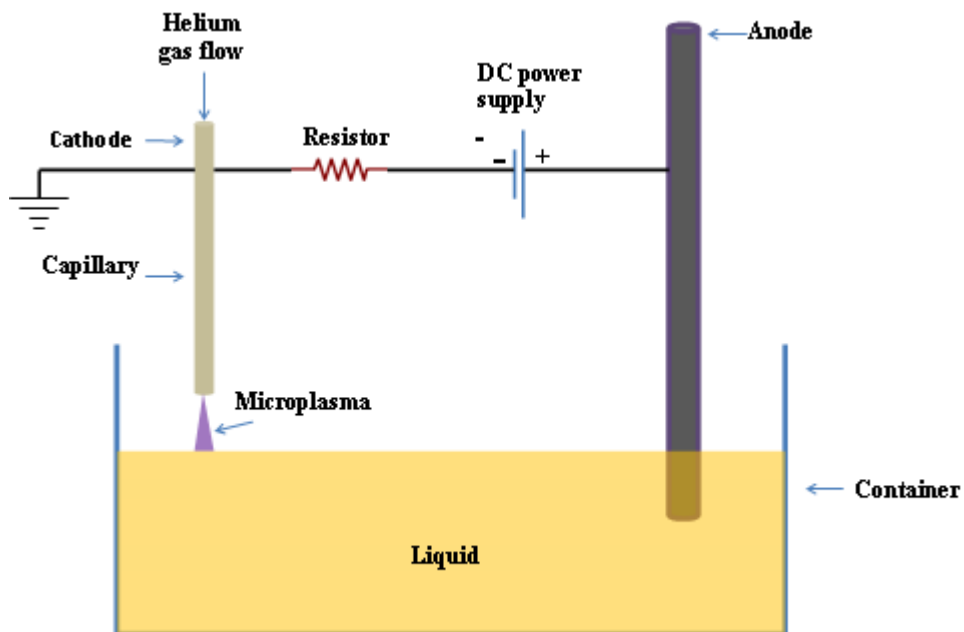


Figure 19 Atmospheric pressure microplasma experimental set up.

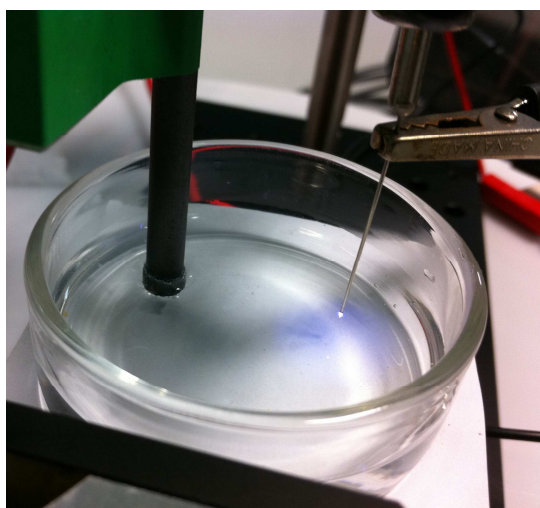


Figure 70 The photo of microplasma generated on the surface of the liquid system.

7.3 Synthesis of gold nanoparticles

As the first basic experiment which should prove a presence of the nanoparticles, the electric discharge has been generated in the 0.2 mM HAuCl_4 for 10 minutes. As there is seen in the figure 71, the typical purple color of the resonance peak has been obtained after plasma operation. Subsequently, the microplasma has been generated in all solutions and the gold nanoparticles dependence on the initial concentration of the solution has been measured. The processing current during this plasma treatment has been kept at 5 mA. Next figure 72 compares the color of the solutions after ten minutes of plasma processing. It has been clearly observed that the different precursors concentrations form a different amount and size of gold nanoparticles. Thus, in the solutions with higher concentrations of the gold salt, there is still not excess of charge carriers and the electrons provided by microplasma can penetrate in the liquid system to form the gold nanoparticles.

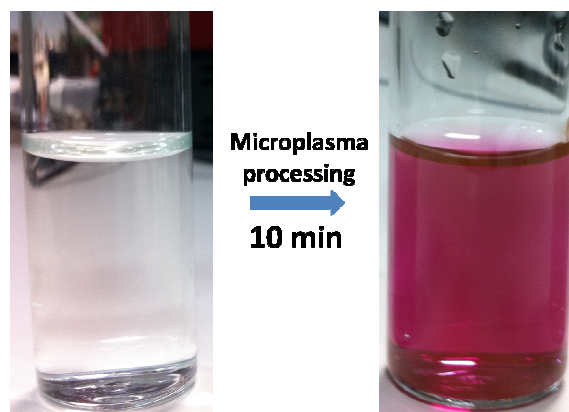


Figure 71 Colour change of the 0.2 mM HAuCl₄ aqueous solution after 10 minutes of microplasma treatment.

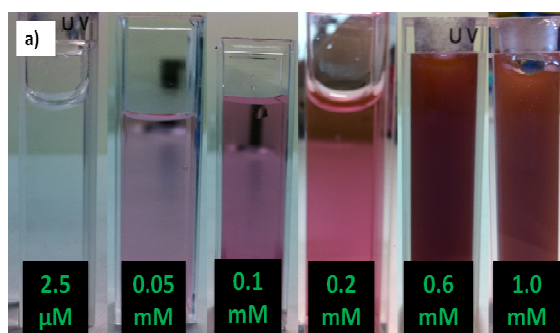


Figure 72 The colour changes in the solutions with different initial concentration after 10 minutes of plasma treatment.

7.4 Hydrogen peroxide measurements

The formation of H₂O₂ is key to understanding this hybrid plasma-chemical synthesis process because hydrogen peroxide has been reported as a reducing agent for the gold precursor [94]. Also, because hydrogen peroxide is not formed in a standard electrochemical approach with both electrodes immersed in solution, we have to deduce that plasma electrons “injected” in the solution are responsible for the formation of H₂O₂. The contribution of the other radicals, ions and photons from the plasma can be neglected in this specific configuration as it has been previously demonstrated [95-96]. A complete qualitative analysis of the possible reactions [95-96] leads to the following chemical pathways:



where the first reaction represents dissociative electron attachment to the water/vapor interface by gas-phase electrons from the plasma; the second reaction occurs in the bulk liquid phase whereby with bulk we mean far from the interface. Electrons may also reach the bulk

of the liquid without reaction (33) occurring, becoming hydrated electrons in the process. However, if that was the case for the majority of electrons, there would not be any energetically favorable chemical pathway for the formation of hydrogen peroxide given that hydrated electrons and water could only produce OH^- and H^\bullet . It follows that reactions (33) and (34) above are the most probable mechanism that lead to hydrogen peroxide formation. Therefore this hypothesis indicates that electrons do not directly reduce the gold salt: electron-induced reactions at the plasma-liquid interface promote cascaded chemistry leading to hydrogen peroxide (via equation (33) and (34) above) and that the latter reduces the gold precursor via following reaction 35. A schematic model of reaction mechanisms, which is considered based on obtained results, is shown by figure 73.

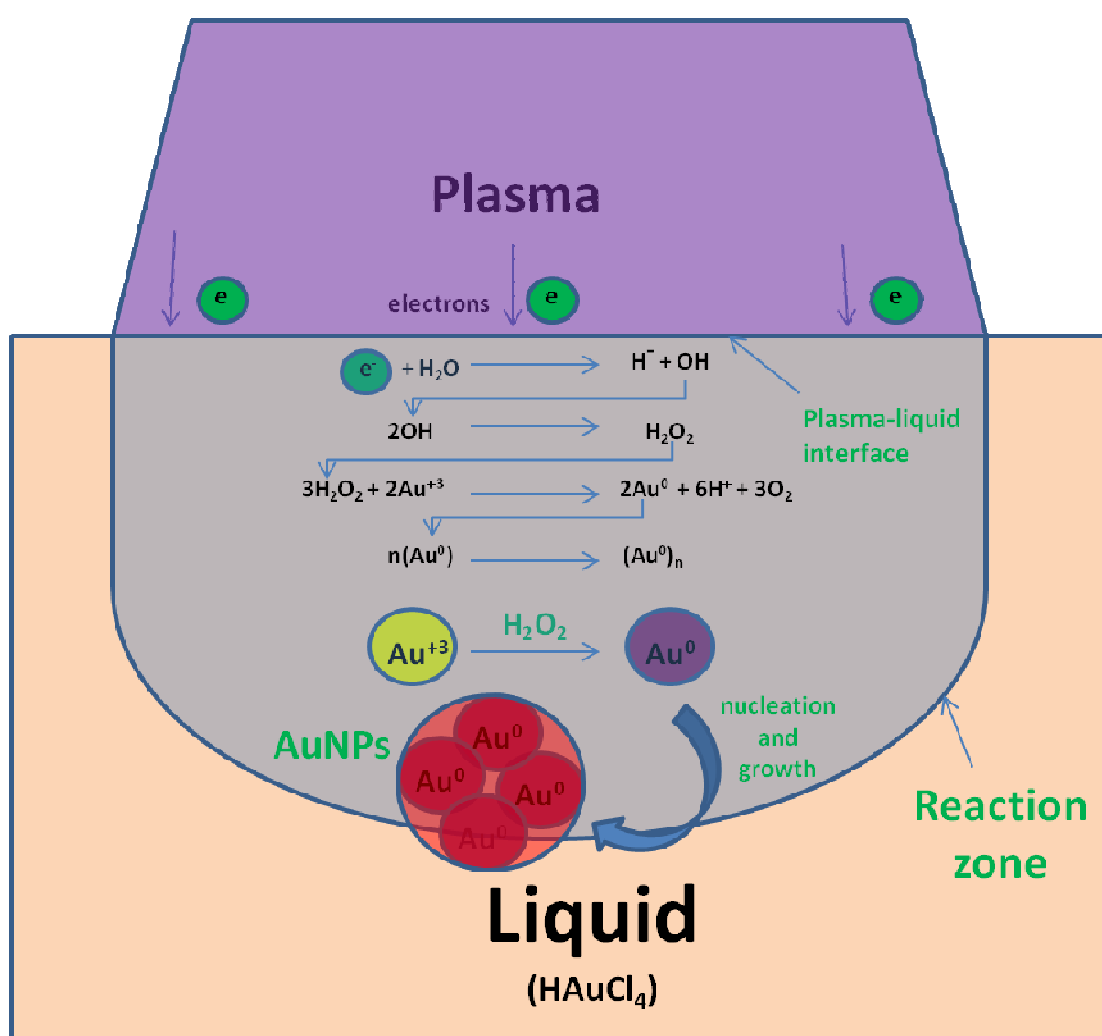
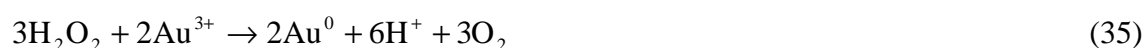


Figure 20 A schematic model of reaction mechanisms for the gold nanoparticles synthesis [97].

Two different measurements have been carried out to find an influence of the HAuCl_4 solid powder on the hydrogen peroxide production. Generally, this type of compound dissolves very easily in the distilled water and provides enough charge carries in the studied solution

which makes a higher conductivity of the examined system. The first, only distilled water has been examined. There has been 0.03 mmol/l of hydrogen peroxide determined after 10 minutes of plasma operation. The second, 0.1 mM HauCl_4 has been subjected to the same plasma treatment. As expected, the compound has positively affected the hydrogen peroxide production. There has been 0.51 mmol/l obtained after the same time period. Thus, the solution with solid powder has provided seventeen more hydrogen peroxide than only distilled water under the same conditions.

As another very important property of the studied system, the current and its influence on the hydrogen peroxide generation has been examined. The obtained results are shown by following table 9. As there is seen, the hydrogen peroxide concentration has increased at the increased discharge current. A very interesting fact has been observed during this experiment, even a very low current (0.05 and 0.2 mA) could generate stable plasma and cause the hydrogen peroxide production. Thus, it can be concluded that the microplasma produced by this equipment is very effective. Also, this hydrogen peroxide concentration has proven that the microplasma has had an influence on the studied solution which practically means that it can affect all processes occurring inside the examined system.

Table 9 The hydrogen peroxide concentration as a function of the applied current. The plasma treatment time 10 minutes.

The applied current [mA]	The hydrogen peroxide concentration [mmol/l]
0.05	0.04
0.2	0.06
2.5	0.22
5	0.46

8 CONCLUSION

This studium has been focused on various systems generated plasma in the liquids with the respect to the reactive particles production and their further application in different industry areas. As the liquid medium a few different type of solutions have been used and mainly the hydrogen peroxide generation has been examined. Besides this, the other important properties of the solutions, such as conductivity, pH, temperature or electrical characteristics have been investigated to gain a detailed description about electric discharges generated in the liquids. In addition, some spectra have been taken as a very important property of the examined solutions. They can provide many useful information which lead to determination of physical and chemical properties of the studied liquids.

In the first part of this work, the diaphragm discharge has been generated using audio-frequency power supply in the NaCl solutions with different initial conductivity (from 100 μS to 800 μS). The different voltage (DC as well as high frequency AC) have been applied in the system to create plasma. DC voltage has been used to create the electric discharge in the previous study (Diploma thesis of the same author) were the values of the current has moved between 62 and 110 mA, the value of the applied voltage has reached approximately 1.5 kV and the maximum value of the power has achieved 140 W. Unfortunately, a problem with remarkable overheating of the studied solution has been obtained at this study. Due to this unwanted fact, the time for plasma operation has been limited which has brought an idea about using HF power supply. Therefore HF voltage of 15 kV and the frequency of 1 and 2 kHz have been utilized at this work to discharge operation and peroxide production, temperature and conductivity changes have been monitored to investigate chemical processes initiated by this type of energy. With respect to the results, which have been obtained during the plasma generation in this type of discharge reactor, it can be concluded that the utilize of HF voltage leads to the quality particles production without undesirable overheating of the solution. Based on these results, a new optimized high frequency source has been constructed at the BUT Brno, Faculty of Chemistry, which allows to initiate the HF electric discharge without any unwanted effects. The device with this type of source can be used in the industry and in the laboratory as well. Together with this result, optimal conditions for plasma generation have been found. The best values of initial conductivity of the studied solution belong in the interval 500 and 800 $\mu\text{S}\cdot\text{cm}^{-1}$ where the maximal hydrogen peroxide concentration has been obtained. At this initial conductivity, the plasma is generated at all time of the treatment process and the discharge can be evaluated as stable.

Next part of this work has dealt by underwater electric discharge in gaseous bubbles and the investigation could be realized due to colaboration with Ghent University in Belgium, Department of Applied Physics. The plasma has been generated in the special chamber where the small glass capillary (the inner diameter of 1.2 mm, length 50 mm) has been placed. Due to this innovation the gas (Ar, He, Air and N_2) could be applied through this tube inside the solution (200 sccm) and so directly support the initiation and propagation of the discharge which has been created by DC power supply. The applied positive voltage has varied from 0.2 to 6 kV and the applied current has moved in the interval from 10 – 30 mA. One of the very important properties of this device has been a cooling system that has been built in the chamber. Two different types of solutions have been subjected to the examination, the first

$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ($5 \mu\text{S}\cdot\text{cm}^{-1}$) when the hydrogen peroxide production has been investigated, and the second organics dyes solution with the initial conductivity $20 \text{ mg}\cdot\text{l}^{-1}$ were an influence of the plasma on the complex organic structure destruction has been obtained. It has been obtained that the most important discharge parameter influencing H_2O_2 generation has been the applied current. The increasing applied current significantly has enhanced the H_2O_2 concentration and the dependence its generation on the time has been found as linear. There has not been obtained a pronounced different by using four various gases. Destruction of the organic dyes structure in the reactor has been characterized by almost linear kinetic plots during twenty minutes operation. The maximal decrease of the organic dyes concentration in the solutions has been achieved by applying current of 30 mA. While in case of hydrogen peroxide studies the kind of gas has not influenced its concentration, here the different behaviour of supplied gases has been found. In the case of He and Ar plasmas the destruction efficiency of the direct blue dye molecules has been much lower than in the case of N_2 . This effect has been connected to the formation of HNO_3 in case of N_2 due to oxidation of N_2 that leads to the decrease of solution pH down to 2. Used dye has lower stability in acidic solutions with $\text{pH} < 6$ and also, the oxidative ability of plasma is stronger in acidic conditions due to oxidative potential of the hydroxyl radical which is 2.70 V at pH 3.0 and 2.34 V at pH 9.0). This, together with the fact that there has been only slightly increase of temperature noticed, leads to the conclusion that the constructed device is suitable for industrial applications. The cooling system, used during the investigation, has been fully satisfied, the solution has not become overheated and there is no more need to use special type of energy source. The bubble system has been found as a very helpful in this studied problem, mainly use of nitrogen because it has been able to destruct even 62 % of organic dye in the solution. The configuration of the technique makes its versatile to variety of practical useage, mainly in the waste water industry.

The third part of this work has been implemented at the Queen's University in Belfast in Northern Ireland. The electric discharge has been generated by a special medical device Arthrocare that is widely used in biomedicine at the present time. The most important part of this technique is a plasma scalpel which the plasma has been created in four different 0.15M distilled water solutions of NaCl, KCl, BaCl_2 and Na_2CO_3 . The volume of liquid was 10 ml, contained in a 25 mm diameter glass cylinder. The sodium chloride solution has been later chosen to subjected to a detailed examination due to its biomedical character. It is one of the isotonic solutions which are commonly utilized in biomedicine due to the fact that it has the same osmotic pressure as a blood which allows its to be in direct contact with an injured human tissue. After taking first results, it has been found that there has been a precipitate formed in the BaCl_2 and Na_2CO_3 solutions which has not allowed to determine hydrogen peroxide spectroscopically. As an alternative solution Quantofix peroxides test sticks has been considered. Unfortunately, they have not pass the detailed test examination which has been carried out. They have shown very often different values of the H_2O_2 concentration than another analysis or sometimes, they even could not detect low concentrations. From this detection it can be concluded that these Quantofix peroxides test sticks are not suitable for quantitative hydrogen peroxide determination. For this reason the BaCl_2 and Na_2CO_3 solutions have been excluded from the next investigation. Two other solutions (NaCl and KCl) have

been subjected to a detail examination. The clear solutions have compared to the solution with a small additional of alcohol. There is a few reasons why the alcohol has been added. The first one is an approach to electric discharges which are generated in organic liquids because a majority of previous measurements are focused on plasmas generated in inorganic solutions, only, but perspectives of discharges in liquids are probably in organic solutions. That situation has occurred due to a low conductivity of organic fluids which practically means that the discharge generation in the laboratory is very hard in such kind of liquids. So the first step to approach organic discharges could be the addition of small amounts of an organic compounds into the inorganic solution. The second reason is a hydrogen atoms production. It is known that addition of ethanol will produce free molecular hydrogen in a solution exposed to the plasma. This knowledge provides an idea about using ethanol as a hydrogen donor to increase hydrogen peroxide production. The taken results have shown that in the solutions with the small additional of alcohol the hydrogen peroxide concentrations have reached higher values. Comparing KCl and NaCl solution it can be observed that KCl has provided a better conditions to H₂O₂ generation. Kinetic curves for hydrogen peroxide concentration in the time have been linear, as it has been expected, the hydrogen peroxide concentration has increased in the time. From the next analysis of NaCl solution it can be concluded that the higher hydrogen peroxide concentration has been reached in the NaCl solution with 0.25 % of ethanol and the lowest in the solution without any additional of alcohol. It practically means that the alcohols generally support hydrogen peroxide generation and ethanol seems to be even more effective than methanol. Besides H₂O₂ production, physical properties of the liquid system such as temperature, conductivity and pH have been studied. A remarkable result has been obtained in the NaCl solution with the additional of ethanol when the pH of the solution has decreased in the acidic environment (due to ethanol oxidation) and mainly, it has been stable during all plasma operation. As has been already said, the acidic plasma is a desirable phenomenon because OH radicals have higher oxidation potential. The values of the temperature have been constantly increasing during the discharge operation in all solutions. The highest value (80 °C) has been obtained in the NaCl solution with the additional of methanol, and the lowest value (77 °C) has been noticed in the KCl solution with the addition of ethanol. However, the difference between these two numbers has been evaluated as weak, which practically means that each investigated system could accept approximately the same amount of energy in the same period time (3 min.). Thus, alcohols such as organic compounds have not had any considerable influence on the energy acceptance from the source. As the last physical property of the solution conductivity has been evaluated. As it has been expected that an addition of alcohol could have caused a problem with plasma generation in the liquid system. Fortunately, this trace amount of alcohols have not had any influence on the initial conductivity of the solution and the experiment could be carried out. Plus, the final conductivity values differ only slightly which practically says that there have not been an excess of charge carriers and the current could be easily applied in the examined solution. Again, the trace additions of the alcohols have not influenced the required plasma generation. To get more information about elements produced in the solution, the optical emission spectroscopy has also been utilized as a suitable method. All spectra have shown OH radicals peaks area which are understood as a precursors of hydrogen peroxide. Thus all

of examined solutions are suitable medium for H_2O_2 production. In addition in some spectra other elements such $\text{H}\alpha$, $\text{Na}^{\text{I}}, \text{Na}^{\text{II}}$, Ba, K or O^{I} have been obtained. During this all this examination, electrical characteristics have been recorded to make a detailed analysis of the applied electric energy into these liquid systems. The electrical characteristics have been taken during plasma operation in the first, the second and the third minute in each solution. All of them have been presented without any unwanted deflections. Even in the solution with the addition of ethanol has not been any strange effect observed which means that this addition has not had a pronounced influence on the energy that has been applied in the solution.

The last part of this work presents some results which have been at the University of Ulster, Newtonabbey, UK. Here, the microplasma which has been in direct touch with the liquid medium has been studied. The experimental technique producing this type of discharge has been constructed at the local department. A solid powder of gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) with different initial conductivity (0.05 mM, 0.1 mM, 0.2 mM, 0.6 mM) has been used as the liquid medium. The microplasma has been sustained by a high DC voltage (2 kV) and the processing current has reached a values 1 – 5 mA. Subsequently, the microplasma has been generated in all solutions and from the taken results it can be concluded that the gold nanoparticles concentration depended on the initial concentration of the solution. Two different measurements have been carried out to find an influence of the HAuCl_4 solid powder on the hydrogen peroxide production. While there has been 0.03 mmol/l of hydrogen peroxide determined after 10 minutes of plasma operation, there has been 0.51 mmol/l obtained in the 0.1 mM HAuCl_4 solution after the same time period. Thus, the solution with solid powder has provided seventeen more hydrogen peroxide than only distilled water under the same conditions.

The presented results have clearly shown a great application potential of various discharge configuration in and with liquids. The key role of the hydrogen peroxide generated in these systems has been confirmed. New experimental devices with advanced properties have been constructed based on the obtained results.

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