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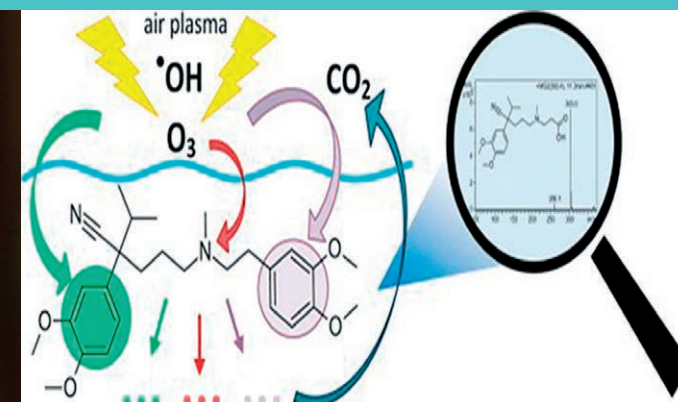in České Budějovice

2017

Degradation of organic pollutants in water by non-thermal plasma based advanced oxidation processes

Degradace organických znečišťujících látek ve vodě nízkoteplotním plazmatem na bázi pokročilých oxidačních procesů

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Czech Republic, Vodňany, 2017

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14th September 2017, at 14:00, in USB, FFPW, RIFCH, Vodňany, Czech Republic.

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Title of thesis:
Degradation of organic pollutants in water by non-thermal plasma based advanced oxidation processes
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CONTENT

CHAPTER 1

GENERAL INTRODUCTION

ORGANIC POLLUTANTS IN AQUATIC ENVIRONMENT

Aquatic environment is being contaminated by chemical components, such as organic pollutants, eutrophication agents (nitrates, phosphates), metal cations and others. Major organic pollutants arise from chemical and pharmaceutical industries, food technologies, petrochemical plants, oil refineries, dye and textile production units, agro-industrial activities and others. Petrochemical wastewaters often contain oils and greases, phenolic compounds, aromatics and halogenated organic compounds. Wastewaters from paper mills, sugar mills, olive mills and leather tanneries are other important sources of organic pollutants (Daud et al., 2010). Organic wastes originating from industrial and urban sewages also contain hazardous compounds such as aromatic hydrocarbons, petroleum products, halogenated solvents, pesticides, detergents, phenolic compounds, and require adequate treatments before being discharged (Beltran et al., 2005; Giordano et al., 2007; Nidheesh and Gandhimathi, 2012).

Phenolic compounds are an important family of organic pollutants. They usually arise from industries manufacturing pesticides, pharmaceuticals, synthetic dyes (Nidheesh and Gandhimathi, 2012), and food processing industries (Giordano et al., 2007). Most pesticides are resistant to chemical or photochemical degradation under typical environmental conditions (Grover and Cessna, 1991). Organic dyes and their azo derivatives present in the textile wastewaters are carcinogenic and mutagenic, and are too difficult to eliminate. They are extensively used in different industries such as rubber, textiles, cosmetics, paper, leather, pharmaceutical and food (Aksu and Donmez, 2005). Special attention is given to pharmaceutical compounds, due to their large variety and high consumption over the past decades. Moreover, most of the pharmaceuticals are non-biodegradable due to their metabolic stability.

Organic pollutants enter the aquatic medium in several different ways, either dumped directly, such as hospital and industrial effluents, or from wastewater treatment plants (WWTPs) that do not fulfils their obligations. They may also enter the water indirectly through the use of plant health products, such as biocides and fertilizers, in agriculture. In general, highly water-soluble substances can be transported and distributed more easily in the water cycle.

Most of the above mentioned compounds are recalcitrant and non-biodegradable, showing a high stability under environmental conditions (Hernandez et al., 2002; Ternes et al., 2002; Jurado et al., 2012; Luo et al., 2014). The presence of these organic pollutants in water can have potential health effects on humans and aquatic vertebrates. Therefore, it is necessary to treat the effluents containing these compounds adequately before discharging them (Espulgas et al., 2007; Grabowski et al., 2007; Benotti et al., 2009; Chelme-Ayala et al., 2010).

CONVENTIONAL WATER TREATMENT TECHNOLOGIES

Currently available water treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, but still remain and not being completely removed (Padmanabhan et al., 2006). Other conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary pollutants into the ecosystem (Gaya and Abdullah, 2008). Chlorination is still the most widespread conventional treatment for disinfecting drinking waters. Various studies on the chlorination of aromatic compounds revealed that the chlorine reaction rate can be strongly affected by the presence

of different functional groups in the benzene ring. For instance, the reaction is usually rapid in pharmaceutical compounds containing amines, giving chlorinated products (Pinkston and Sedlak, 2004). Thus, oxidation of metropolol and sulfamethoxazole give rise to chloramines. Studies on the removal of acetaminophen, the active compound of paracetamol, showed that it reacts with chlorine to form numerous by-products, two of which have been identified as toxic compounds (Glassmeyer and Shoemaker, 2005; Bedner and MacCrehan, 2006).

The main natural routes for destroying toxic compounds in water are biodegradation and photodegradation. Photodegradation, which is an important method for degrading organic pollutants, may be by direct or indirect photolysis. It depends on the photosensitizers, such as nitrate and humic acids present in the natural water. Biological degradation of a compound refers to the elimination of the pollutant by the metabolic activity of living organisms, usually microorganisms and in particular bacteria and fungi that live in natural water and soil. In this context, conventional biological processes do not always provide satisfactory results, especially for industrial wastewater treatment, since many of the organic substances produced by the chemical industry are toxic or resistant to biological treatment (Steber and Wierich, 1986; Bowers et al., 1989; Adams et al., 1996; Pulgarin and Kiwi, 1996; Gracia et al., 2001; Munoz and Guieysee, 2006; Lapertot et al., 2006). Therefore, the only feasible option for such biologically persistent wastewater is the use of advanced technologies such as advanced oxidation processes or non-thermal plasma based treatments.

Generally, WWTPs comprise a primary system of physicochemical treatments and a secondary system that consists of a biological reactor formed by active sludge. These conventional plants have a limited capacity to remove pollutants like pharmaceutical products from urban wastewaters, since most of the compounds cannot be metabolized by microorganisms as source of carbon and may even inhibit the activity of the microorganisms or produce their bioaccumulation in the food chain. Although further research is required on this issue, it is known that conventional WWTPs do not remove all pharmaceuticals from wastewaters. In primary treatments, some pharmaceuticals can be removed by adsorption, whereas others remain in the water, e.g., ibuprofen, naproxen, sulfamethoxazole, and iopromide. Subsequent biological treatments remove 30–75% of anti-inflammatories and antibiotics (Carballa et al., 2004). There have been various reports that carbamazepine is not appreciably removed by WWTPs (Ternes, 1998; Heberer, 2002; Strenn et al., 2004; Clara et al., 2005).

In short, conventional treatment systems are unable to completely remove a large amount of the organic pollutants present in urban wastewaters. More effective and specific treatments are required to reduce the environmental and potential impact of industrial effluents. Tertiary water treatments include: biological systems to remove nitrogen; ionic exchange to remove ions; chemical precipitation to remove phosphorus; distillation to remove volatile organic compounds; liquid-liquid extraction; adsorption on activated carbon to remove organic and inorganic pollutants; and advanced oxidation processes to remove toxic biorefractory organic compounds.

ADVANCED OXIDATION PROCESSES

The destruction of organic pollutants in wastewater can be achieved through the use of advanced oxidation processes (AOPs). In AOP, the highly reactive hydroxyl radicals ($\bullet$OH) are responsible for the destruction of the pollutants in water. Having a high standard reduction potential of 2.8 V vs NHE in acidic media, hydroxyl radicals should be are able to oxidize almost all organic compounds to carbon dioxide and water (Bigda, R.J., 1995). The most attractive

feature of AOPs is that this highly potent and strongly oxidizing radical allows the destruction of a wide range of organic pollutants with no selectivity. Furthermore, due to an unpaired electron, hydroxyl radical has many advantages:

1. It has very high reaction kinetic (around 10^8 M s^{-1}).

2. It is non-selective opposed to ozone (Hoigne and Bader, 1983).

3. It reacts with a wide range of organic and non-organic pollutants (Hoigne and Bader, 1976).

4. No persistence or residues in aqueous phase (short life of 10^{-9}s).

However, the lifetimes of these radicals are so short to utilize them effectively. Therefore, the direct radical generations are widely researched.

The most widely used AOPs include heterogeneous photocatalysis (Coleman et al., 2000; Ohko et al., 2002; Doll and Frimmel, 2004; Baran et al., 2006; Gonzalez et al., 2010; Mahmoodi and Arami., 2010; Affam and Chaudhuri, 2013), the Fenton's reaction (Munoz et al., 2006; Shemer et al., 2006; Catalkaya and Kargi, 2008), ozonation (Huber et al., 2003; Mantzavinos and Psillakis, 2004; Irmak et al., 2005; Dantas et al., 2007 and 2008; Luis et al., 2011), ultrasound and wet air oxidation, while less conventional but evolving processes include ionizing radiation, the ferrate reagent, microwaves and non-thermal plasma.

Ozonation

Ozone is a strong oxidizing agent that can decompose in water to form hydroxyl radicals (•OH), which are stronger oxidizing agents than ozone itself. It can also induce indirect oxidation by attacking selectively certain functional groups of organic molecules through an electrophilic mechanism (Mantzavinos and Psillakis, 2004; Dantas et al., 2007, 2008). Depending on the type of the substrate and the operating conditions, ozonation is usually favoured at higher pH values due to the increased production of hydroxyl radicals. Moreover, the treatment efficiency is usually enhanced when ozone is combined with light irradiation (Irmak et al., 2005), hydrogen peroxide (Zwiener and Frimmel, 2000; Balcioglu and Otker, 2003; Huber et al., 2003; Arslan-Alaton and Dogruel, 2004; Arslan-Alaton and Caglayan, 2006) or with iron or copper complexes as catalysts (Skoumal et al., 2006). Compared to other oxidizing reagents, ozonated water is more efficient in pollutant degradation and it is not harmful for most of the organisms, because no strange chemicals are added to treated waters.

Ozonation has been widely used for drinking water treatment for odor and taste control, disinfection and organic compound degradation (Gottschalk et al., 2000), but its application to wastewater treatment is limited due to its high energy demand. Owing to its oxidizing power and the absence of hazardous decomposition products, ozonation could be used as a potential pre-treatment technology to transform refractory compounds into substances that could be further removed by conventional methods (Hu and Yu, 1994; Baig and Liechti, 2001).

During ozonation, the pollutants can be degraded by two different pathways: direct reactions with O_3 and indirect reactions with hydroxyl radicals. At high pH values, there is a high concentration of hydroxide ions that enhances the decomposition of O_3 by a complex chain mechanism into hydroxyl radicals that can react faster and less selectively than O_3 (Ikehata and El-Din, 2004). In fact, hydroxyl radicals can react 10^6–10^9 times faster than ozone, since the latter is a selective oxidizing agent that preferentially attacks electron-rich

organic moieties (Munter, 2001). Thus, the oxidation of organic compounds by OH radicals at high pH is often more efficient than at low pH where the amount of OH radicals is lower and not enough to cause the decomposition of dissolved ozone (Luis et al., 2011). Ozonation has been widely used for the degradation of organic contaminants in water (Andreozzi et al., 2005; Catalkaya and Kargi, 2009; Fan et al., 2014).

PLASMA BASED ADVANCED OXIDATION PROCESSES

Plasma

Plasma is a gas containing charged and neutral species such as electrons, ions, radicals, atoms and molecules. Plasma is often referred to as the fourth state of matter, since it occurs by adding energy or heat to a gas. Plasmas comprise the majority of the matters in the universe. However, the most common occurrences of plasma in the Earth's atmosphere are lightning and auroras. Lightning is the most frequently observed form of a spark discharge occurring at near-atmospheric pressure accompanied by an acoustic phenomenon, thunder. This kind of discharge, together with arc discharge, is called thermal plasma because all the energy density is solely in the discharge channel, thus resulting in very high temperatures. Thermal plasma is close to thermodynamic equilibrium because of high collision frequency caused by high number density of electrons and ions around 10^{23} m^{-3} and temperature of the order of 1 eV. Temperatures of electrons, ions and neutrals in thermal plasmas are approximately the same.

Non-thermal plasma (NTP) on the other hand results from the application of a short-duration pulsed power to a gaseous gap at atmospheric pressure or the application of electric field to a gaseous gap at a low pressure (from tenths to hundreds pascals). The surrounding gas is kept at room temperature because the ionization degree is low and the electrons do not heat up the heavy particles such as molecules or ions efficiently. When an intense electric field is applied, a discharge is formed which causes the formation of self-propagating electron avalanches, also known as streamers within the gas volume. Plasma technologies have been applied for several industrial applications including microelectronics industry, coating industry, surface property modifications for different polymer materials, and for the development of sterilization or disinfection techniques.

The plasma chemistry is driven by high energy electrons causing ionization, molecule excitation, and production of reactive radicals. It is for this reason that the application of NTP for chemical reactions in environmental applications has been continuously developed. Direct application of plasma on contaminated water effectively combines the contribution of UV radiation, active radicals, and high electric fields are considered, therefore, an alternative to the conventional water treatment methods (Locke et al., 2006). By producing highly reactive hydroxyl radicals, plasma technique is able to degrade pollutants non-selectively, without needing high temperatures or low pressures.

Plasma discharges for water treatment

NTPs are initiated and sustained by electric fields which are produced by either direct current or alternating current power supplies. These plasmas are also referred to as electrical discharges, gaseous discharges, or glow discharges, and are another type of AOPs. NTPs represent an effective plasma abatement technology because of its high reaction rate and lower power consumption. In processes of NTP only very small part of energy is lost in heating the surrounding fluid, which allows the energy to be focused on the excitation and acceleration of electrons. As the electrons in NTP can reach temperatures of 10,000–100,000 K, while

the gas temperature can remain as low as ambient temperature, the chemical processes are determined by this high electron temperature. In atmospheric NTPs, most of the electrical energy is consumed to produce free radicals with a much greater reactivity than atoms and molecules in the ground state.

The primary benefit of the non-thermal plasma advanced oxidation process (NTP AOP) is the ability to generate UV light, ozone, and hydroxyl radicals without chemical addition or the use of UV lamps. It has been found that electrical discharges in liquids initiate various physical and chemical effects, such as high electric fields, intense UV radiation, shock waves, as well as the formation of chemically active species: radicals (•H, •O, •OH) and molecules (H_2O_2, H_2, O_2, O_3) which are effective for the removal of pollutants. NTP generated in electrical discharges at the gas-liquid interface also produces these strong oxidants, which can diffuse into the liquid. The most known wastewater treatment techniques allowing operation at NTP conditions are dielectric barrier discharge (DBD), pulsed corona discharge (PCD) and gliding arc discharge (GAD).

Dielectric barrier discharge

Dielectric barrier discharge (DBD) also referred to as barrier discharge or silent discharge is a specific type of AC discharge, which provides strong thermodynamic, non-thermal plasma at atmospheric pressure, and at moderate gas temperature. It is generated in an arrangement consisting of two electrodes, at least one of which is covered with a dielectric layer placed in their current path between the metal electrodes. The presence of one or more insulating layer on/or between the two powered electrodes is one of the easiest ways to form non-thermal atmospheric pressure discharge. Due to the presence of capacitive coupling, time varying voltages are needed to drive the DBD. An AC voltage with amplitude of 1–100 kV and a frequency from line frequency to several megahertz is applied to DBD configurations. DBD cold plasma can be produced in various working mediums through ionization by high frequency and high voltage electric discharge. The DBDs unique combination of non-thermal and quasi-continuous behavior has motivated a wide range of applications. For several years DBD has been used to degrade organic contaminants in water (Bubnov et al., 2006; Magureanu et al., 2008a; Tang et al., 2009; Marotta et al., 2012).

Pulsed corona discharge

Pulsed corona discharge (PCD) is another technique to produce non-thermal discharges utilizing high voltage pulses. Streamer properties in PCD are almost similar to those in DBD but the inter-electrode distance is bigger in PCD. It exists in several forms, depending on the polarity of the field and the electrode geometrical configuration. This type of discharge is the characteristic of an asymmetric electrode pair and results from the electric field that surrounds inhomogeneous electrode arrangements powered with a continuous or pulsed DC voltage. In a highly non-uniform electric field e.g. point plane gap or wire cylindrical gap, the high electric field near the point electrode or wire electrode far exceeds the breakdown strength of the gas and weakly ionized plasma is created. Coronas are thus inherently non-uniform discharges that develop in the high field region near the sharp electrode spreading out towards the planar electrode. This phenomenon of local breakdown is called corona discharge.

The characteristics of the ions producing the plasma depend on the polarity of the discharge and the characteristics of the gas mixture, specifically on the electron attaching species. A positive corona develops when the electrode with the strongest curvature is connected to the positive output of power supply and a negative corona develops when this electrode

is connected to the negative terminal of power supply (Chang, 1991). Researchers have investigated the influence of corona discharge on the degradation of organic contaminants in water (Sano et al., 2002; Faungnawakij et al., 2004; Grabowski et al., 2006 and 2007; Magureanu et al., 2008b).

Gliding arc discharge

The gliding arc discharge (GAD) belongs to the group of non-thermal plasmas, although it is formed from an electric arc. The gliding arc consists of a high voltage generator (up to 10^3 V) used to ignite the discharge and a second power generator (with a voltage up to 1 kV, and a total current J up to 60 A). The initial breakdown of processed gas starts at shortest distances of electrodes (several mm), then after forming stable plasma channel quasi-equilibrium stage is established and, when arc exceeds certain critical length transits into non-equilibrium stage which is fast. The electron temperature is around 1 eV whereas temperature of gas is around 0.1 eV (Fridman et al., 1999).

The energy transfer from the electric field to the ambient gas leads to the formation of activated species which are raised to some excited energy levels, and this induces vibrational, rotational and electronic transitions. The activated species are radicals, atoms or excited molecules. The nature of the activated species depends on the feeding gas. Emission spectroscopy studies on a gliding arc plasma in humid air revealed that OH and NO radicals are simultaneously present in the discharge with a much higher density for •OH than NO• (Benstaali et al., 2002). GAD has emerged as an important destructive technology leading to the degradation of the organic pollutants in water (Lesage et al., 2013; Ghezzar et al., 2013; Hentit et al., 2014; Horakova et al., 2014).

Electrohydraulic spark discharge

The application of strong electric fields in water (Electrohydraulic spark discharge, ESD) containing organic contaminants has been studied for several years. Studies showed that electrical discharge could dissociate water into hydroxyl (•OH) and hydrogen (•H) radicals and that higher energy discharge could lead to the dissociation of •OH into oxygen atom and hydrogen radical (Clements et al., 1987; Sun et al., 1997; Sun et al., 1998; Sunka et al., 1999). Studies have also demonstrated the production of hydrogen peroxide, molecular oxygen and hydrogen, hydroperoxyl and other radicals. In addition, depending upon the solution conductivity and the magnitude of the discharge energy, shock waves and UV radiation may also be formed (Tezuka, 1993; Joshi et al., 1995; Sato et al., 1996; Kirkpatrick and Locke, 2005). Though these discharges can be created using various electrode geometries, the majority of the work is conducted in a point-to-plane electrode geometry. It has been suggested that electrical discharges with shorter pulse duration result in the formation of non-thermal whereas those with longer pulses more thermal-like plasmas. These discharges have been used to degrade organic contaminants present in water (Tezuka and Iwasaki, 1998; Sun et al., 1999; Tezuka and Iwasaki, 2001).

AIMS OF THE THESIS

1. Determination of degradation kinetics and degradation mechanism of model organic pollutants in water under DBD. Pharmaceuticals such as verapamil and hydrocortisone and a pesticide atrazine will be used as model pollutants.
2. Determination of degradation kinetics and degradation mechanism of selected model pollutant in water under GAD.
3. Determination of degradation kinetics of verapamil and atrazine in water during ESD and ozonation.
4. Comparison of degradation kinetics of verapamil and atrazine in water under DBD, GAD, ESD and ozonation.

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CHAPTER 2

DEGRADATION OF ATRAZINE AND HYDROCORTISONE IN WATER BY DIELECTRIC BAR-RIER DISCHARGE TREATMENT

Krishna, S., Ceriani, E., Marotta, E., Spatenka, P., Paradisi, C., 2016. Degradation of atrazine and hydrocortisone in water by non-thermal plasma (dielectric barrier discharge) treatment (Manuscript).

My share on this work was about 50%.

DEGRADATION OF ATRAZINE AND HYDROCORTISONE IN WATER BY DIELECTRIC BARRIER DISCHARGE TREATMENT

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ABSTRACT

Aqueous solutions of atrazine and hydrocortisone were subjected to oxidative degradation in a dielectric barrier discharge (DBD) reactor. Both of them were completely degraded in water according to an exponential decay as a function of treatment time at constant voltage. After 90 min treatment almost complete removal of the pollutants were achieved. The transformation products and CO_2, the final product of pollutant decomposition, were detected and identified by HPLC-MS and FT-IR analysis. Plausible mechanisms of the degradation were discussed.

Keywords: *Water pollutants removal; non-thermal plasma; transformation products; degradation kinetics; reaction mechanisms.*

INTRODUCTION

Most of the organic contaminants such as pesticides, synthetic dyes, pharmaceuticals and personal care products (PPCPs) are toxic and non-biodegradable. Water pollution with organic compounds can be attributed to several sources, such as emission from production sites, direct disposal of unused medicine, accidental discharge of farm wastes from silage manufacture and from intensive livestock rearing, which contain very high concentrations of oxidizable organic matter. Also, strong organic wastes from food manufacture such as, milk products, sugar refineries and olive mills can be accidentally discharged directly to watercourses, or via sewage treatment plants which may be unable to cope with the massive additional load. The presence of these compounds and their transformation products in surface waters have been detected, clearly indicating that some of them cannot be eliminated during wastewater treatment (Perez-Estrada et al., 2001).

Traditional wastewater treatment processes such as coagulation, flocculation, sedimentation, microfiltration or ultrafiltration are unable to completely remove a large amount of the organic pollutants present in industrial effluents and urban wastewaters. Advanced oxidation processes (AOPs) have been introduced as an efficient and environmentally friendly treatment technology for the degradation and mineralization of organic pollutants in water. Generally, AOP relies on the *in situ* generation of highly reactive and non-selective hydroxyl radicals (•OH), which plays key role in the destruction of organic pollutants present in the wastewater (Deng and Ezyske, 2011). AOPs such as ozonation, UV/H_2O_2, UV/TiO_2 and photo-Fenton are alternative to conventional treatment and have recently received considerable attention for the degradation of organic compounds in water (Espulgas et al., 2007; Trovo et al., 2008; Yang et al., 2008; Benotti et al., 2009; Yang et al., 2010). The UV/H_2O_2 and O_3/H_2O_2 processes are relatively conventional and most studied AOPs for their powerful oxidation ability. But these processes require significant chemical addition and residual H_2O_2 quenching, which represents a significant portion of their operational costs (Pekarek, 2003; Locke et al., 2006).

Among the alternatives, we considered non-thermal plasma (NTP) discharges as green sources of reactive species able to degrade organic pollutants. NTPs can be generated in large volumes and combine the advantages of gas-phase discharge (i.e., for ozone (O_3) and oxygen radical (O•) formation and ultraviolet radiation generation) and liquid-phase discharge (i.e., for hydroxyl radical (•OH) and hydrogen peroxide (H_2O_2) formation) makes them very attractive for various water treatment applications (Sun et al., 1998; Hayashi et al., 2000). NTP can be regarded as highly efficient because there is no energy loss in heating the surrounding liquid, which allows the energy to be focused on the excitation of electrons (Pekarek, 2003). In NTP, electrons can reach temperatures of 10,000–100,000 K while molecule remains at ambient temperature (Petipas et al., 2007). NTPs, such as dielectric barrier discharge (DBD), corona discharge and glow discharges are highly potential alternatives for the degradation of organic compounds (Gao et al., 2003; Magureanu et al., 2008; Marotta et al., 2012). Recently, the degradation of several organic compounds in water using NTP has been reported (Sano et al., 2002; Bubnov et al., 2006; Grabowski et al., 2007; Ghezzar et al., 2007; Krause et al., 2009; Tang et al., 2009; Magureanu et al., 2010; Magureanu et al., 2011; Drobin et al., 2013).

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is a member of the s-triazine group of herbicides. For decades atrazine has been widely used all over the world to control pre- and post-emergence of a variety of broadleaf and grassy weeds in corn, cotton, sorghum and sugarcane crop fields. Atrazine is an endocrine-disrupting compound and is harmful for human health. Due to its high mobility and widespread use in huge quantity, atrazine has been frequently detected in surface and ground waters, and its use has been banned by many European countries (Acosta et al., 2004; Chen et al., 2011). It is classified as a possible

human carcinogen by the United States Environmental Protection Agency (USEPA). Therefore, it is necessary to develop efficient atrazine removal methods from aquatic environments. Hydrocortisone is a corticosteroid hormone. It has also been widely used as an anti-inflammatory drug.

Among NTP discharges, one of the most promising and efficient device is certainly the dielectric barrier discharge (DBD) reactor. This study presents an investigation of the atrazine and hydrocortisone degradation in water in a dielectric barrier discharge reactor. Also, their degradation by-products are identified and the degradation pathway is discussed.

MATERIALS AND METHODS

Chemicals

Atrazine (99%) and hydrocortisone (99%) were purchased from Labor Dr Ehrenstorfer and used as received. MilliQ water was obtained by filtration of deionized water with Millipore system. Pure air used in the experiments was a synthetic mixture (80% nitrogen and 20% oxygen) from Air Liquide with specified impurities of H_2O (< 3 ppm) and of C_nH_m (< 0.5 ppm).

Instrument and analytical conditions

The experimental apparatus used for water treatment by dielectric barrier discharge is shown in Fig. 1. Briefly, the reactor is a glass vessel (internal dimensions 95 × 75 mm^2 and 60 mm height) closed by a teflon cover with four passing electrodes of stainless steel which support two parallel stainless steel wires of 75 mm length and 0.15 mm diameter fixed upon their tips. The wires are placed at a distance of 38 mm between each other and are kept above the test solution. The outside surface of the reactor base is covered with a film of silver and connected to a grounded plate. The reactor is powered with an AC high voltage transformer with 16.5–18 kV and a frequency of 50 Hz. During the experiments the voltage was maintained constant. Current and voltage profiles were monitored with a digital oscilloscope (TDS5032B, bandwidth 350 MHz, sample rate 5Gs/s) to assure the reproducibility of the electrical conditions. A flow of air of 30 mL min^{-1} was allowed through the reactor and the discharge occurred in the gas phase above the liquid surface. The air was humidified by passing it through a water bubbler placed before the reactor. It would help to minimize the evaporation from the test solution during discharge.
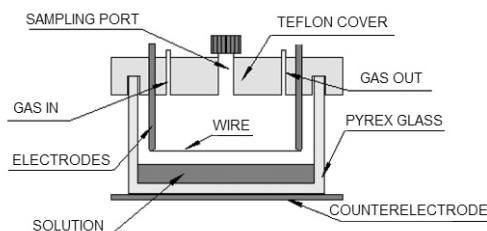

Figure 1. *Schematics of DBD reactor.*

The HPLC-UV analyses were performed using the chromatograph by thermo separation products comprising a pump system P2000 Spectra System and a diode array detector UV6000LP. The column used was Kinetex 5u C18 100A 150 × 4.6 mm. The eluents used were 0.1% formic acid in water and 0.1% formic acid in acetonitrile. The gradient started with 5%

acetonitrile, increasing to 50% within the first 16 min, and to 100% acetonitrile from 16 to 21 min. From 21 to 23 min, the acetonitrile content remains constant and decreases to 5% from 23 to 33 minutes.

The HPLC/MS analyses were done on an Agilent Technologies 1100 series HPLC with binary pump model G1312A coupled to an ion trap MSD Trap SL model G2245D operated under positive ion electrospray (ESI) conditions in the full scan, MS^n mode. The nebulizer pressure was kept to 65 psi and the dry gas temperature to 350 °C, while 4 kV were applied to the nebulizing capillary. Full mass spectra were acquired by scanning the mass range of m/z 50–1000. The collision induced dissociation (CID) spectra were obtained from the protonated molecules $[M+H]^+$. The eluents, column and chromatographic conditions were same as in the case of HPLC-UV analysis. The FT-IR analyses were done on a Nicolet 5700 spectrometer.

Plasma treatment experiments

A 5×10^{-5} M aqueous solution of the target pollutant (70 mL) was transferred into the reactor. The discharge was then applied and the efficiency of the decomposition process determined by measuring pollutant conversion as a function of treatment time. Samples were taken out at various time intervals (0, 5, 10, 20, 30, 45, 60, 90, 120, 180, 240 & 300 min), so that the discharge was briefly interrupted to allow for the withdrawal of 0.5 mL of the treated solution. The fraction of residual pollutant, $[Pollutant] / [Pollutant]_0$ was plotted against treatment time and the data were fitted by equation (1) to obtain k, the rate constant of the decomposition process.

$$[Pollutant] / [Pollutant]_0 = e^{-kt} \qquad\qquad (1)$$

Where $[Pollutant]_0$ and $[Pollutant]$ are the concentrations at time zero and t, respectively.

The half-life time of pollutant was thus calculated by equation (2)

$$t_{1/2} = 0.693/k \qquad\qquad (2)$$

The gas exiting the reactor was subjected to on-line FT-IR analysis using a 10 cm long flow cell with CaF_2 windows.

Results and discussion

Atrazine degradation

Atrazine degradation kinetics and mineralization yield

The atrazine degradation by atmospheric pressure DBD at room temperature is shown in Fig. 2, where 98% of atrazine was removed within 90 min. A pseudo-first order kinetics was observed for the plasma based degradation of atrazine at rate constant 0.029 min^{-1} and the corresponding half-life time was 24 min. Fig. 3 shows the chromatograms corresponding to the pure atrazine initial solution and the atrazine solutions treated in DBD reactor for durations of 30, 45, 60, 90 min, respectively. The chromatograms recorded for the solutions exposed to discharge showed ten chromatographic peaks, which corresponds to atrazine and its transformation products (M1, M2a, M2b, M3a, M3b, M4, M5, M6 and M7). Mass spectra

and retention data regarding to these peaks are summarized in Table 1. It is clear from the UV chromatograms that the atrazine is almost completely disappeared after 90 min discharge. But the concentration of the transformation products formed in the beginning of the discharge was increased after 90 min DBD treatment, except the products M4 and M7.
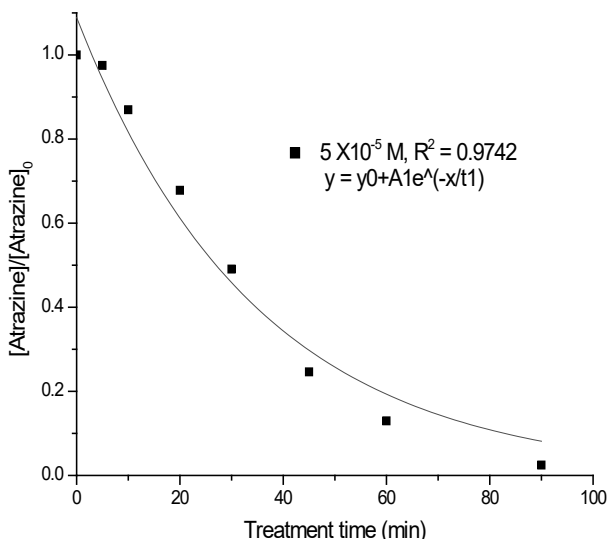

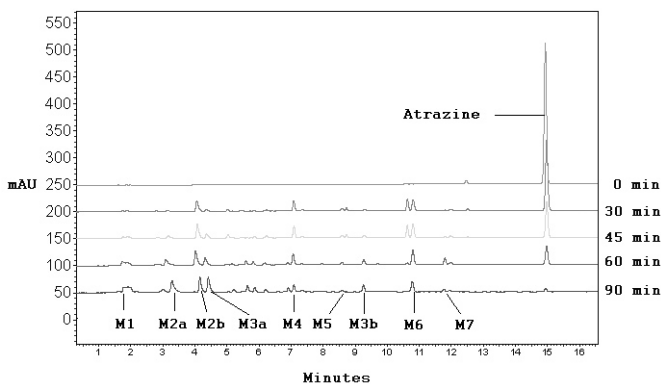**Figure 2.** *Atrazine conversion as a function of treatment time in the DBD reactor.*

Figure 3. *HPLC-UV chromatograms of the initial atrazine solution and of the treated solution for various plasma treatment durations, up to 90 min.*

The evolution of the CO_2 from the atrazine solution during discharge was confirmed by FT-IR analysis of the gas exiting the reactor. The FT-IR online analysis has been used to determine the amount of CO_2 released during plasma discharge. The reproducibility of the FT-IR was verified by passing commercial mixtures of CO_2 in air of known concentration (49.2, 249.8 and 498.5 ppm) as standards through the reactor and integrating corresponding signal due to CO_2 bond stretching (Marotta et al., 2011). The calibrated FT-IR response would help to determine the instantaneous concentration of the CO_2 in the air flowing out the DBD reactor during the degradation of atrazine.

Figure 4. shows the time profile for CO_2 in the air flowing over the solution released from atrazine processing for 300 min. When the discharge on, the CO_2 signal rapidly rises from zero to a maximum intensity which corresponds to a concentration of 0.09 mg L^{-1} and after a series of decrease and increase it finally reaches 0.1 mg L^{-1}. In a similar rapid manner the signal intensity drops to zero when the discharge is turned off. Control experiments have shown that some CO_2 is detected also upon application of the discharge in the case of pure water. However, this amount is much less than that released in the presence of the organic contaminant, from which can be easily subtracted thus confirming that CO_2 is formed mainly from the oxidation of atrazine. Fig. 4 also shows that the discharge induced production of CO_2 progresses well beyond 90 min, which is enough for the atrazine consumption. From these observations I confirmed the presence of some degradation by-products which are oxidized more slowly than atrazine. I have identified some of these by-products by means of HPLC analysis with UV-VIS and MS detectors.

Since a constant gas flow rate was used throughout these experiments (30 mL min^{-1}), integration of the concentration versus time curves reported in Fig. 4 yields the mass of CO_2 formed during the selected treatment time. It is thus found that after 90 min, a treatment time sufficient to decompose completely atrazine, only 0.77 mg of CO_2 was produced corresponding to a process selectivity of about 10%. After 5 h of treatment the mineralization yield increased to 54%, which means that 46% of the total organic carbon originally present is still in solution in form of by-products. The profile shows three main maxima which could correspond to the formation and further degradation of three or more by-products.
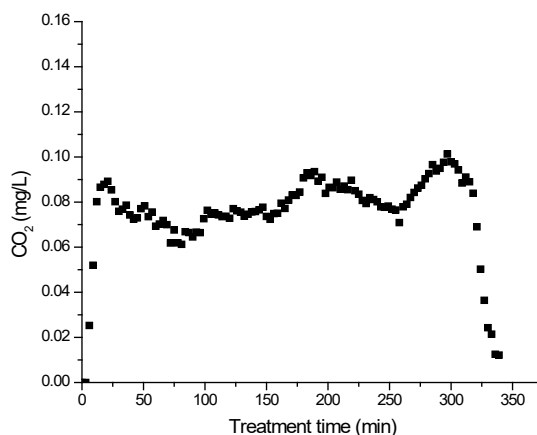

Figure 4. *Time profile for CO_2 concentration in the air flowing out of the DBD reactor during atrazine processing (initial concentration 5 × 10^{-5} M).*

MS analysis and identification of degradation by-products

The total ion current chromatograms (TICs) of the DBD treated samples shows a main peak with a retention time of t_R = 15.5 min under the conditions at which atrazine also elutes. The mass spectrum corresponding to this peak was also identical to that of atrazine including a peak at m/z 216, which is the mass of the protonated molecular ion. The peak in the extracted ion chromatogram (EIC) at m/z 174 (Fig. 5b) was corresponding to fragment ion of atrazine. LC/MS data of atrazine and DBD treated atrazine solutions are shown in Table 1. Fragmentation pattern of atrazine and its transformation products are shown in Fig. 6.
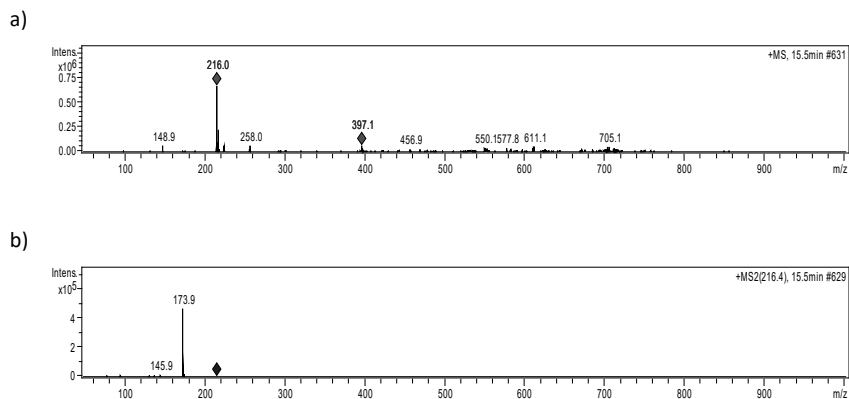
a)

b)

Figure 5. *a) Mass spectrum of atrazine, b) MS/MS spectrum of atrazine.*

Table 1. *LC/MS^n data of atrazine and plasma treated atrazine solution.*

Compound	t_R/min	MS, [M+H]$^+$	MS fragment ions (m/z)
Atrazine	15.5	216	174
M1	1.7	170	128
M2a	3.5	212	170, 128
M2b	4.3	212	170, 128
M3a	4.6	188	146
M4	7.4	174	–
M5	9	216	–
M3b	9.6	188	146
M6	11.3	230	188, 146
M7	12.3	214	172, 105
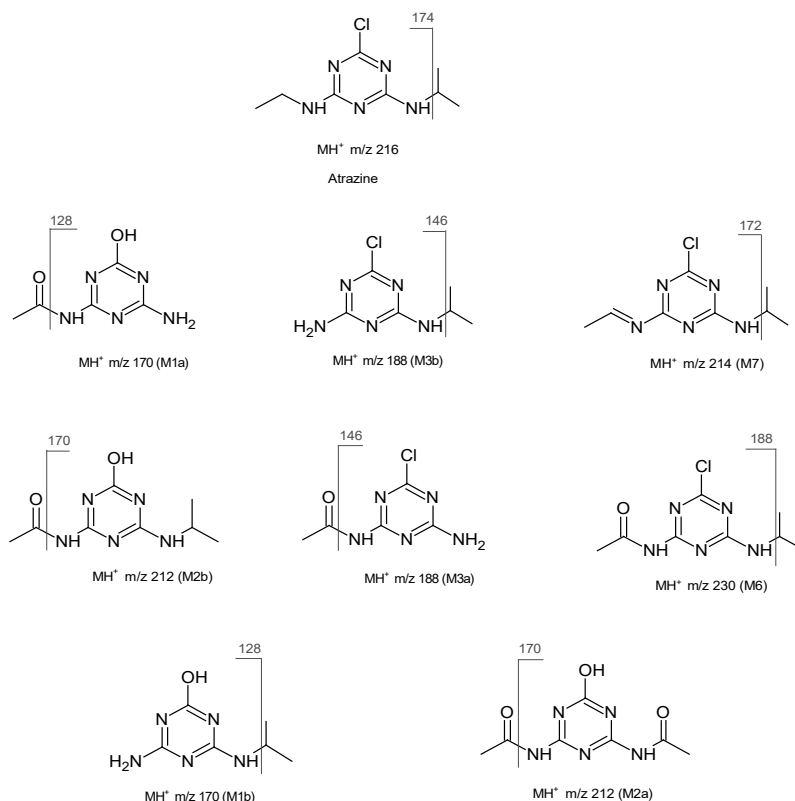
Figure 6. *Fragmentation pattern of atrazine and its transformation products.*

Degradation mechanism

The atrazine transformation products, resulting from the degradation of 5×10^{-5} M aqueous solution of atrazine under dielectric barrier discharge at reaction time 60 and 90 min, were identified by HPLC-MS analysis. Structures of the transformation products were confirmed by the analysis of the corresponding mass spectrum. The proposed reaction pathways of atrazine decay are presented in Fig. 7. Identification of the by-products revealed that the oxidation of atrazine involves chemical processes, such as dealkylation, dehalogenation and alkyl chain oxidation of the s-triazine ring. Nine atrazine transformation products at detectable levels, which are probably corresponding to the new intermediates, can be observed concurrent with the disappearance of the protonated atrazine (m/z 216).

The peak at m/z 170 with retention time 1.7 min in the mass spectra of DBD treated atrazine solution corresponds to the product M1. By using our MS and MS/MS spectra we could not confirm the structure of the product M1. But it must be either M1a or M1b. If the product was formed by the dehalogenation of M3b, the product would be M1b and if it was formed by the dealkylation of M2b, the product would be M1a.

The peak at m/z 212 with retention time 3.5 min in the MS spectra implies the existence of M2a and the same mass peak with retention time 4.3 min implies the existence of the isomer M2b. The product M2b is formed by the dehalogenation of M6 and the product M2a is formed by the alkyl chain oxidation of M2b. Similarly, the products M3a and M3b are isomers and shows mass peak at m/z 188 with retention times 4.6 and 9.6 min respectively. The product

M3a is formed by the dealkylation of M6. The products M3b and M4 (m/z = 174) are formed by the partial dealkylation of atrazine aminoalkyl groups. The products M5 (m/z = 216) and M6 (m/z = 230) are formed by the oxidation of the atrazine aminoalkyl groups. The peak at m/z 214 reveals the presence of atrazine imine (M7), which is formed by the dehydrogenation of atrazine.
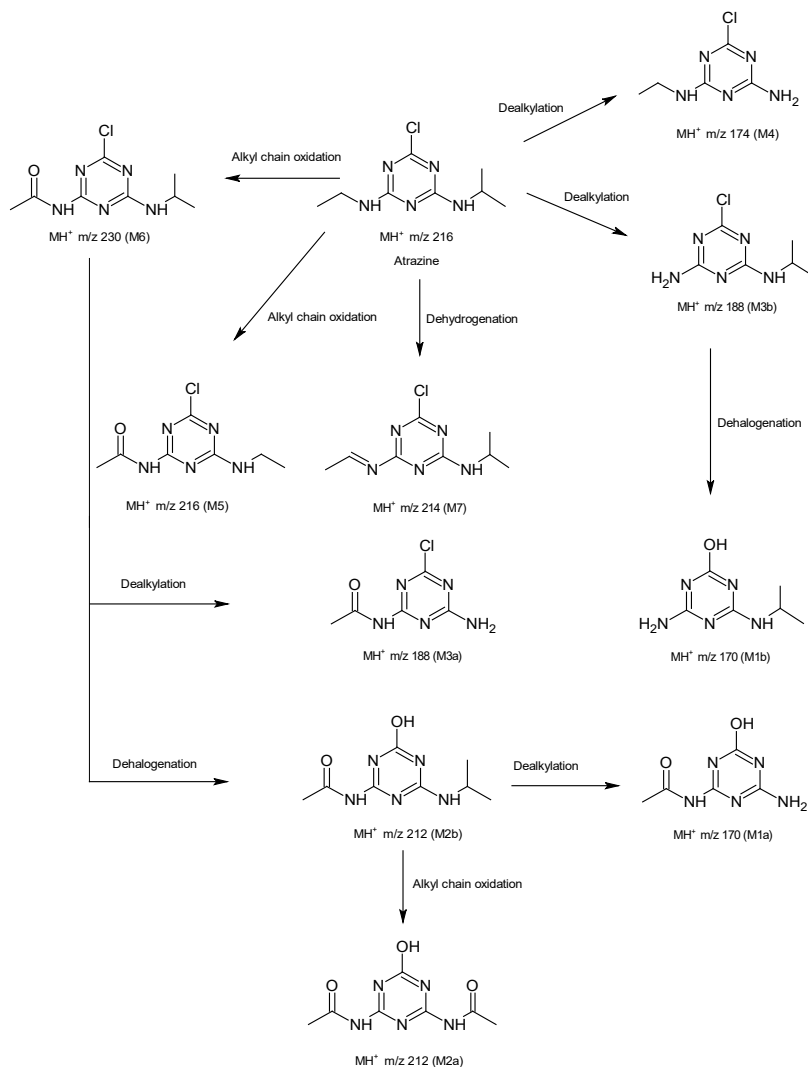

Figure 7. *Proposed degradation pathways of atrazine under plasma treatment.*

Hydrocortisone degradation

Degradation kinetics and mineralization yield

The degradation of hydrocortisone in milliQ water by non-thermal plasma treatment in the DBD reactor was studied at an initial concentration of 5×10^{-5} M (Fig. 5). The decay profile of hydrocortisone is shown in Fig. 8, where 99% of hydrocortisone was removed within 90 min. A pseudo-first order kinetics was observed for the plasma based degradation of

hydrocortisone at rate constant 0.050 min^{-1} and the corresponding half-life time was 14 min. Fig. 9 shows the chromatograms corresponding to the pure hydrocortisone initial solution and the hydrocortisone solutions treated in DBD reactor for durations of 30, 45, 60 and 90 min. The chromatograms recorded for the solutions exposed to discharge showed three chromatographic peaks, which corresponds to hydrocortisone and its transformation products M1 and M2 (not visible in the chromatogram).
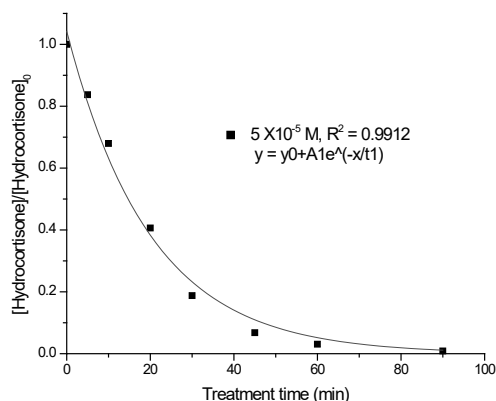

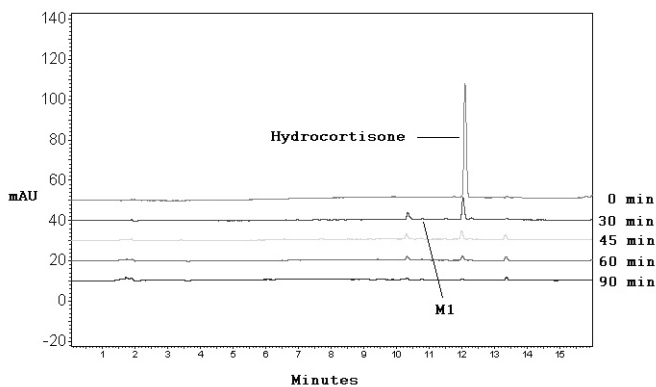**Figure 8.** *Hydrocortisone conversion as a function of treatment time in the DBD reactor.*

Figure 9. *HPLC-UV Chromatograms of samples taken at various time intervals during DBD degradation of Hydrocortisone.*
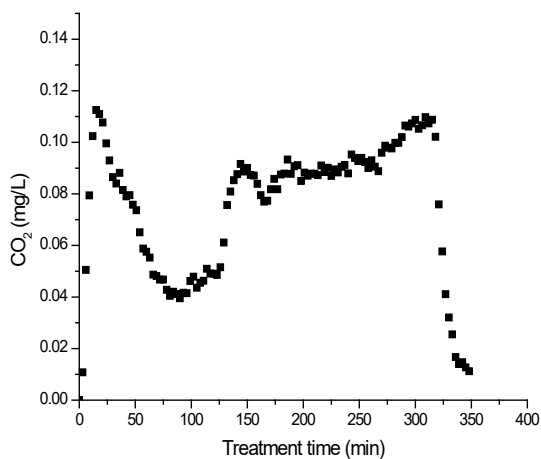
Figure 10. *Time profile for CO_2 concentration in the air flowing out of the DBD reactor during hydrocortisone processing (initial concentration 5×10^{-5} M).*

The time profile for the CO_2 produced in the process of degradation of hydrocortisone is represented in Fig. 10. Integration of the area under the curve reveals that after five hours of treatment 21% of the pollutant has been converted to CO_2. The profile shows three maxima which could correspond to the formation and further degradation of two or more by-products.

MS analysis and identification of degradation by-products

The total ion current chromatograms (TICs) of the DBD treated samples shows a main peak with a retention time of t_R = 12.5 min under the conditions at which hydrocortisone also elutes. The mass spectrum corresponding to this peak was also identical to that of hydrocortisone including a peak at m/z 363.1, which is the mass of the protonated molecular ion. The peaks in the extracted ion chromatogram (EIC) at m/z 345, 327 and 309 (Fig. 11b) were corresponding to fragment ions of hydrocortisone. LC/MS data of hydrocortisone and DBD treated hydrocortisone solutions are shown in Table 2. A possible fragmentation route of hydrocortisone is shown in Fig. 12.
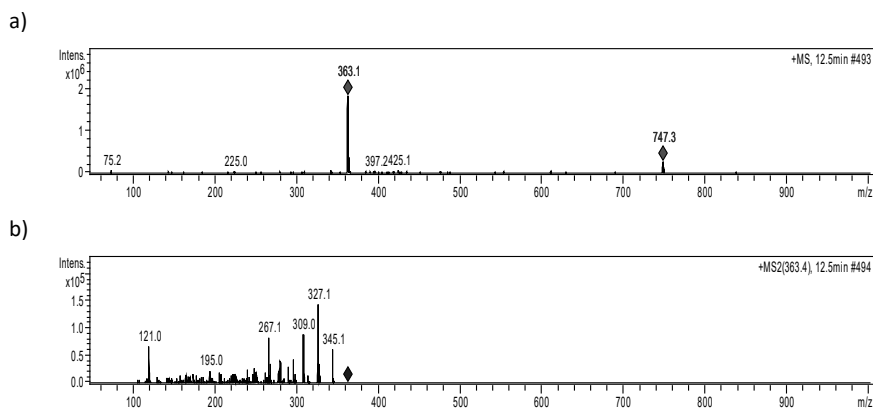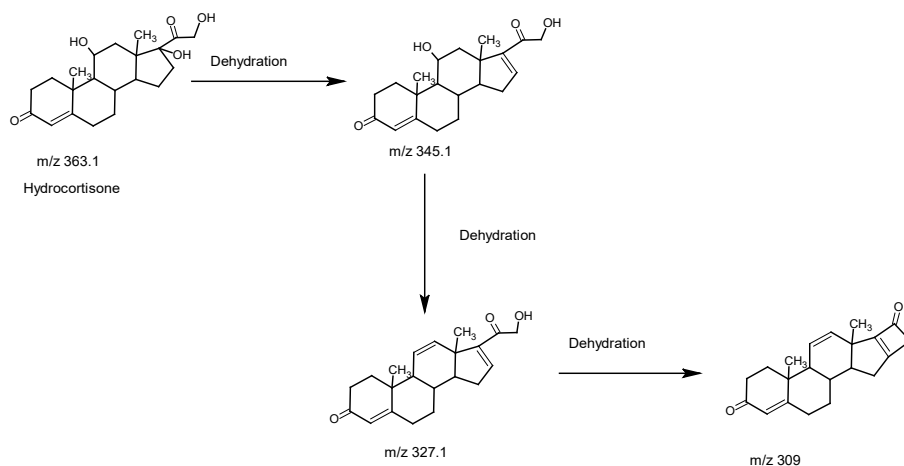

Figure 11. *a) Mass spectrum of hydrocortisone, b) MS/MS spectrum of hydrocortisone.*

Table 2. *LC/MS^n data of hydrocortisone and plasma treated hydrocortisone solution.*

Compound	t_R/min	MS [M+H]$^+$	MS fragment ions (m/z)
Hydrocortisone	12.5	363.1	345, 327,309, 267, 195,121
M1	10.9	377.1	359, 341, 323, 285, 255, 227, 173, 121
M2	12.8	361.1	343, 265, 237, 163, 121, 208

Figure 12. *Fragmentation route of hydrocortisone.*

Degradation mechanism

The hydrocortisone transformation products, resulting from the degradation of 5×10^{-5} M aqueous solution of hydrocortisone under dielectric barrier discharge at reaction time 30 min were identified by HPLC-MS analysis. Structures of the transformation products were confirmed by the analysis of the corresponding mass spectrum. The proposed structures of degradation by-products of hydrocortisone decay are presented in Fig. 13. Two hydrocortisone degradation by-products at detectable levels, which are probably corresponding to the new intermediates, can be observed concurrent with the disappearance of the protonated hydrocortisone (m/z 363.1). The mechanism of formation of degradation by-products M1 and M2a or M2b are not known yet. Though the product M1 looks like an oxidation product of hydrocortisone and product M2a or M2b looks like dehydrogenated products of hydrocortisone, the actual mechanism might be complex due to the interaction between hydrocortisone molecules and reactive species in plasma discharge.
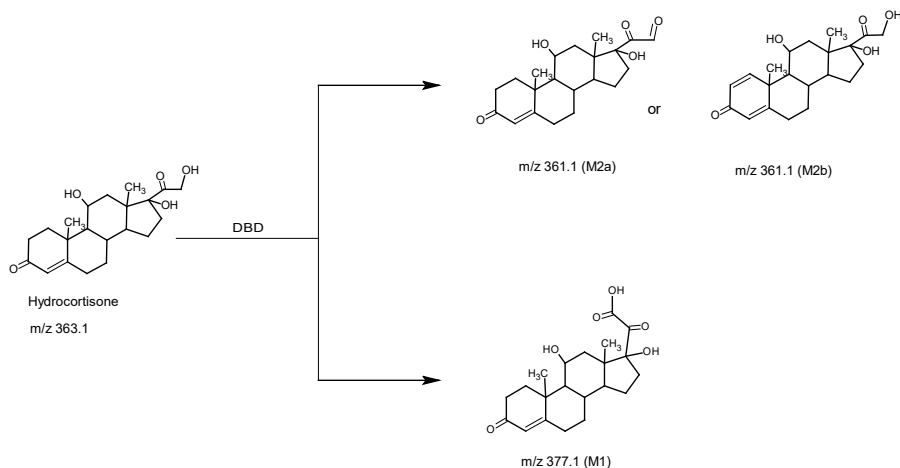
Figure 13. *Proposed degradation by-products of hydrocortisone under plasma treatment.*

Conclusion

The efficiency of dielectric barrier discharge on the degradation of atrazine and hydrocortisone was investigated. Atrazine was almost completely degraded after 90 min DBD treatment. The rate constant of this process was 0.029 min^{-1} and the corresponding half-life time was 24 min. After five hours of treatment, 54% of the atrazine has been converted to CO_2. Hydrocortisone was also completely degraded after 90 min DBD treatment. The rate constant of this process was 0.050 min^{-1} and the corresponding half-life time was 14 min. After five hours of treatment 21% of the hydrocortisone has been converted into CO_2.

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CHAPTER 3

PRODUCTS AND MECHANISM OF VERAPAMIL REMOVAL IN WATER BY DIELECTRIC BARRIER DISCHARGE TREATMENT

Krishna, S., Ceriani, E., Marotta, E., Giardina, A., Spatenka, P., Paradisi, C., 2016. Products and mechanism of verapamil removal in water by air non-thermal plasma treatment. Chem. Eng. J. 292, 35–41.

My share on this work was about 50%.

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Chemical Engineering Journal

Products and mechanism of verapamil removal in water by air non-thermal plasma treatment

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HIGHLIGHTS

- This is the first report of verapamil removal from water by air non-thermal plasma.
- Intermediates of verapamil oxidation in plasma reactor were identified by LC/ESI-MS.
- Non-thermal plasma induces efficient conversion and mineralization rate of verapamil.

GRAPHICAL ABSTRACT
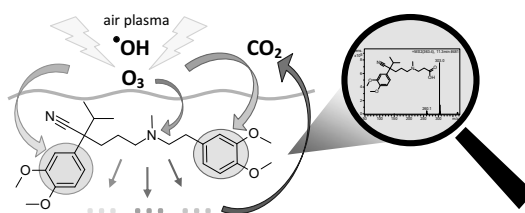
ARTICLE INFO

ABSTRACT

Verapamil, a drug widely used to treat cardiovascular disorders and an important water pollutant, has been subjected for the first time to advanced oxidation by air non-thermal plasma (NTP) in a previously described DBD reactor. Product analysis was performed to assess the extent of mineralization to CO_2, quantified by FT-IR analysis, and to detect and identify oxidation intermediates by LC/ESI-MS/MS. Many intermediates form and their time profile was monitored during the treatment. Thorough mass spectrometric analysis and comparison with literature data on the oxidation of the functional groups of verapamil by the reactive species present in the air plasma allowed us to identify most of the intermediates formed by non-thermal plasma activation. The majority of the identified compounds can be attributed to reactions of verapamil with ozone, one of the major oxidizing species in our DBD reactor. A few intermediates, though, appear to form following direct attack by hydroxyl radicals, whereas there is no evidence of any byproduct attributable to reaction with reactive nitrogen species. When treated at low initial concentration verapamil is almost completely mineralized (98%), as determined by total carbon analysis.

1. Introduction

The presence of pharmaceuticals and personal care products (PPCPs) in the aquatic environment is raising concern because of their adverse effects on human health and eco systems. Water pollution by pharmaceuticals can be attributed to several sources, such as emissions from production sites due to insufficient treatment of manufacturing effluents and direct disposal of unused medicine and drug containing wastes from human and animal medical care. Most of the pharmaceuticals used in medicine are excreted by patients in an intact or only partially metabolized form

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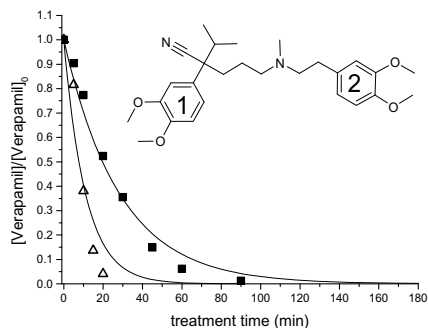 E-mail address: ester.marotta@unipd.it (E. Marotta).

Fig. 1. Verapamil conversion as a function of treatment time in the DBD reactor (initial concentration ($\triangle$) $1 \cdot 10^{-5}$ M and ($\blacksquare$) $5 \cdot 10^{-5}$ M).
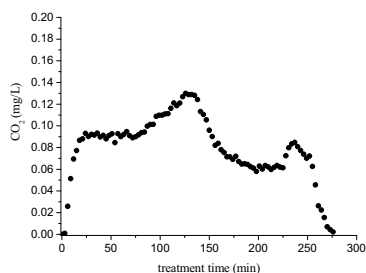

Fig. 2. Time profile for CO_2 concentration in the air flowing out of the DBD reactor during verapamil processing (initial concentration $5 \cdot 10^{-5}$ M).

and end up as such in surface waters, ground water and drinking water [1,2]. Certain pharmaceuticals and many organic compounds are harmful even in very low concentrations [3]. Owing to their physical and chemical properties they can pass easily through the sewage treatment plants (STPs) [4]. Therefore it is necessary to develop efficient treatment processes for limiting the presence of pharmaceutical contaminants in aquatic environments.

Conventional processes such as coagulation, flocculation, sedimentation, microfiltration or ultrafiltration are ineffective in the removal of trace persistent organic compounds whereas advanced oxidation processes (AOPs) can achieve significant removal or transformation [5,6]. AOPs such as ozonation and treatments with H_2O_2/UV, TiO_2/UV and photo-Fenton are important alternatives to conventional procedures and have recently received considerable attention for the degradation of pharmaceutical compounds in water [7–12]. In AOPs highly reactive hydroxyl radicals ($^\cdot$OH) form and can be exploited for the destruction of organic pollutants present in wastewater.

Non-thermal plasma (NTP) based processes are being developed as a viable alternative to more traditional AOPs. At comparable energy requirements for contaminant degradation, NTP offers the advantage of generating oxidants without the need for chemicals or UV lamps [13–15]. The major oxidant species in non-thermal plasma generated by electrical discharges in the air over liquid water are OH radicals, O_3, and H_2O_2. These species can react with the pollutants on the surface of the aqueous solution or dissolve and react in the bulk phase.

Thus, NTPs generated by dielectric barrier discharges (DBD), corona discharges and glow discharges are important potential alternatives for the degradation of organic compounds. Recently, the degradation of several different pharmaceutical compounds using NTP has been reported [16–20]. To the best of our knowledge, the compounds tested so far do not include verapamil hydrochloride ($C_{27}H_{38}N_2O_4HCl$), a phenylalkylamine calcium-channel blocker widely used since several decades for the treatment of various cardiovascular disorders such as angina pectoris, cardiac arrhythmias, hypertension and hypertrophic cardiomyopathy. On the contrary the study of the removal kinetics and of the degradation pathways of verapamil in contaminated water is of very actual interest as proven by few very recent publications dealing with the removal of this drug by ozonation and UV irradiation techniques [21,22]. The aim of the present work was to investigate the efficiency of verapamil degradation induced by air NTP in a DBD reactor developed previously in our laboratory [23,24]. Thorough product analysis allowed us to identify intermediates formed in the early steps of the long oxidation chain leading to verapamil mineralization and to propose possible degradation mechanisms and the reactive species involved.

2. Materials and methods

2.1. Chemicals and reagents

Verapamil hydrochloride (Sigma–Aldrich, 99% purity) solutions were prepared in MilliQ water, obtained by filtration of deionized water with a Millipore system. Pure air used in the experiments was a synthetic mixture (80% nitrogen and 20% oxygen) from Air Liquide with specified impurities of H_2O (<3 ppm), of C_nH_m (<0.5 ppm), of CO_2 (<1 ppm) and of CO (<1 ppm).

2.2. Plasma reactor and experimental set-up

The apparatus was described in detail in a previous paper [23]. The reactor is composed of a glass vessel ($95 \times 75 \times 60$ mm) and a Teflon cover. A 70 mL volume of the aqueous solution to be treated is placed in the vessel and a flow (30 mL $\times$ min^{-1}) of a humidified mixture of 80% N_2 and 20% O_2 ("pure air") is established above the liquid surface through openings of the reactor cover. Discharge is produced in the gas above the water surface by an AC high voltage of 18 kV and 50 Hz applied to two parallel stainless steel wires fixed upon the tips of four electrodes passing through the cover. A silver film on the outside surface of the reactor base works as the ground electrode. In the reactor, the height of the liquid was 10 mm and its distance from the wires was 10 mm.

2.3. Analytical procedures

The decomposition of verapamil $1 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ M was monitored by measuring its conversion as a function of treatment time at constant applied voltage. At desired times the discharge was briefly interrupted and a 0.5 mL aliquot of the treated solution was sampled. The samples were thus analyzed by HPLC (Thermo Scientific Products instrument with P2000 pump and UV6000LP Diode array detector) at 280 nm, using a Phenomenex column Kinetex 5 µm C18 100 Å 150×4.6 mm. The eluents were 0.1% formic acid in water (eluent A) and 0.1% formic acid in acetonitrile (eluent B). The gradient for B was as follows: 5% for 1 min, 50% in 15 min, 100% in 5 min, 100% for 2 min.

The fraction of residual verapamil, [verapamil]/[verapamil]$_0$ (where [verapamil]$_0$ and [verapamil] are the concentrations at time zero and t, respectively), was plotted against treatment time
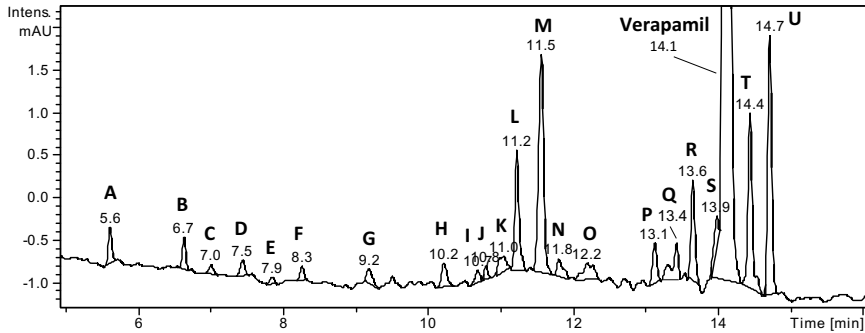
Fig. 3. HPLC chromatogram acquired at 280 nm of a solution of verapamil $5 \cdot 10^{-5}$ M in MilliQ water after 30 min of treatment in the DBD reactor.
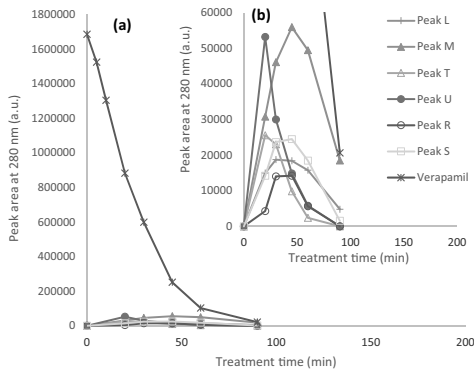

Fig. 4. (a) Time profile of verapamil and of its main intermediates (chromatographic peaks L, M, T, U, R and S) in the plasma treatment of verapamil $5 \cdot 10^{-5}$ M; (b) enlargement of the same graph.

and the data were fitted to Eq. (1) to obtain the process pseudo-first order rate constant, k:

$$[\text{verapamil}]/[\text{verapamil}]_0 = e^{-k \cdot t} \qquad (1)$$

For the identification of the intermediates, selected samples were analyzed using the same eluents, column and gradient but a different HPLC system (Agilent Technologies 1100 series) connected to a diode array and a mass spectrometer detector (MSD Trap SL model G2245D). The ionization was performed within the electrospray (ESI) source in positive polarity with the following parameters: nebulizer 50 psi, dry gas flow rate 11 L min^{-1}, dry gas temperature 350 °C, capillary voltage 3.5 kV, capillary exit 143.5 V, and skimmer 40 V.

The gas exiting the reactor was analyzed by FT-IR on a Nicolet 5700 spectrometer using a 10 cm long flow cell and a range from 4000 to 1100 cm^{-1}. From IR spectra elaboration the final oxidation product released by the process, carbon dioxide, was monitored and quantified. The calibration and quantification procedure was described in a previous paper [25]. Briefly, for the whole time of the experiment, a spectrum was collected every 3 min. In each spectrum the area of the CO$_2$ band at 2350 cm^{-1} was integrated and converted to a concentration value in mg/L units. All the concentration data were reported in a graph as a function of the gas volume flown through the reactor. Finally the area under the curve was integrated to obtain the mass of CO$_2$ released by the decomposition process. The CO$_2$ quantification experiments were repeated twice with a reproducibility of 5%.

The final solution was analyzed by total carbon analysis using a Shimadzu TOC-V$_{CSN}$ instrument, equipped with an autosampler and an automatic diluter. The instrument was calibrated using solutions of standard potassium hydrogen phthalate automatically diluted in the range of interest. The operative range of the instrument is 50 µg/L–25 g/L.

3. Results and discussion

3.1. Verapamil degradation kinetics and mineralization yield

The degradation of verapamil in MilliQ water by plasma treatment in the DBD reactor was studied at two different initial concentrations, $1 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ M (Fig. 1). The observed kinetic constants obtained by the interpolation of the data with Eq. (1) are equal to 0.097 and 0.035 min^{-1}, for initial concentrations of $1 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ M, respectively. The higher process efficiency observed in the more dilute solution is a known feature of non-thermal plasma treatments and can be attributed to the higher ratio between the concentration of the reactive species and that of the reacting organic compounds [25].

The time profile of the CO$_2$ produced in the process of degradation of verapamil at $5 \cdot 10^{-5}$ M initial concentration is reported in Fig. 2. Integration of the area under the curve reveals that after 4 h of treatment 14% of the pollutant has been converted to CO$_2$. The profile shows two maxima which could correspond to the formation and further degradation of two or more intermediates.

No other significant signals relative to other gaseous products, apart from water, were detected by FT-IR analysis.

The mineralization degree was much better for treatment of the more dilute verapamil solution ($1 \cdot 10^{-5}$ M initial concentration), 98% after 5 h treatment, as determined by total carbon analysis.

3.2. Degradation products and intermediates

HPLC/UV-Vis and LC/ESI-MS analyses of samples withdrawn at different treatment times show the formation of many intermediates of NTP verapamil oxidation. Fig. 3 shows an expansion of the UV chromatogram acquired at 280 nm after 30 min of treatment of
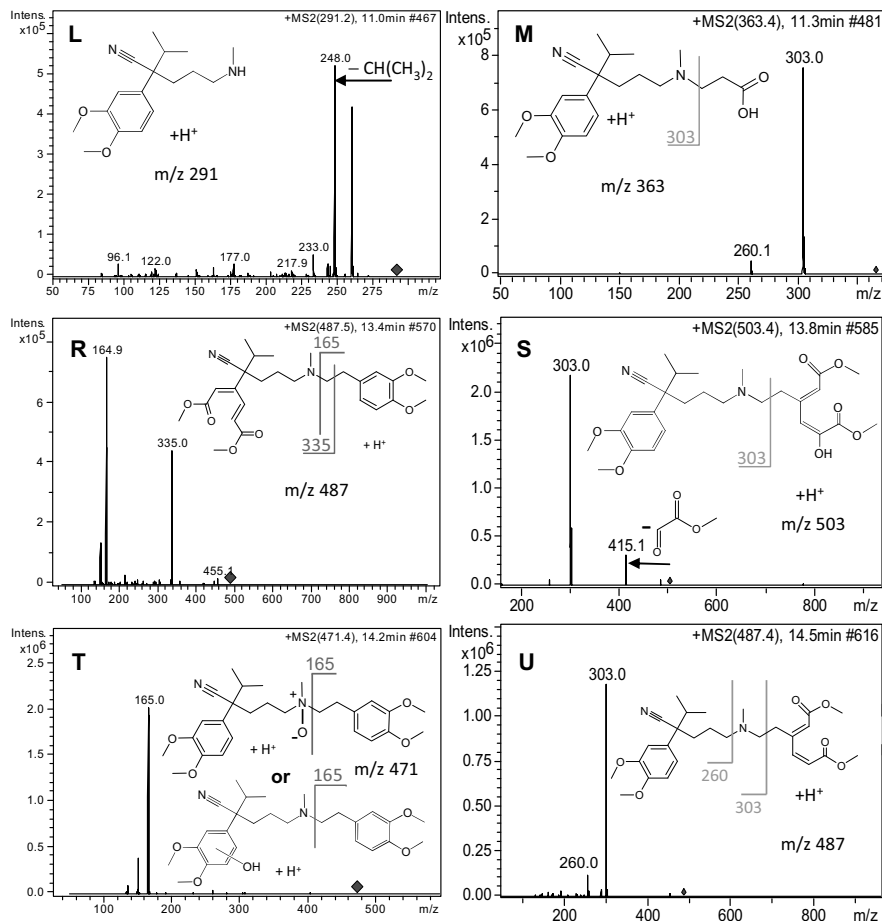
Fig. 5. MS/MS spectra of the products corresponding to the UV chromatographic peaks **L**, **M**, **R**, **S**, **T**, **U**.

verapamil $5 \cdot 10^{-5}$ M. The peak out of scale at 14.1 min is due to verapamil, the others, of much lower intensities, are due to numerous reaction intermediates (**A–U**). The concentration of these intermediates increases to a maximum and then decays as they in turn undergo oxidation, as shown in Fig. 4, which reports the time profile of the major peaks (**L**, **M**, **R**, **S**, **T**, **U**).

Inspection of the chromatograms recorded over the whole range of wavelengths of our diode array detector revealed no significant additional peaks with respect to those detected at 280 nm and described above.

MS and MS/MS spectra acquired by analyzing selected samples by HPLC/ESI-MS allowed us to assign structures to each of them, as reported in Fig. 5. This was done by searching in the MS/MS spectra characteristic signals indicating which functional group of verapamil has been modified during plasma treatment. For example, the presence of a fragment at m/z 303 indicates that the [(4-(3,4-dimethoxyphenyl)-4-nitryl-5-methyl)hexyl]methylamino moiety

of the molecule has not been modified and suggests that oxidation must have taken place on the remaining part of the molecule. This is the case of compounds corresponding to peaks **M**, **S** and **U**. Similarly, the presence of a fragment at m/z 165 suggests that the (3,4-dimethoxyphenyl)ethyl moiety is still intact in the reaction intermediate (peaks **R** and **T**). Thus, the MS/MS spectra are adequately informative to distinguish isomeric structures, as is the case for peaks **R** and **U**, which are both detected at m/z 487, a mass which corresponds to that of verapamil plus two oxygen atoms. Thus, it is proposed that the isomeric intermediates **R** and **U** are formed by oxidative opening of one of verapamil benzene rings and specifically of ring 1 in the case of **R** and of ring 2 in the case of **U**. The proposed products are typical for the attack of ozone on aromatic compounds and are due to the addition of ozone, the formation of an ozonide and its following breakdown [26]. The presence of the methoxy substituents, which have an electron-donating effect, activates the benzene ring towards electrophilic attack [27].
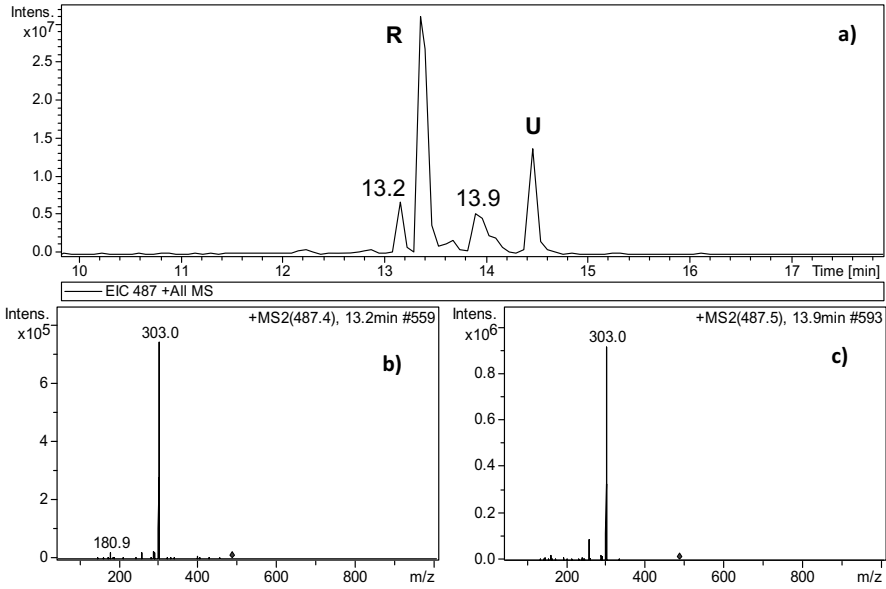
Fig. 6. (a) Extracted ion chromatogram of *m/z* 487; (b) MS/MS spectrum of *m/z* 487 eluting at 13.2 min; (c) MS/MS spectrum of *m/z* 487 eluting at 13.9 min.
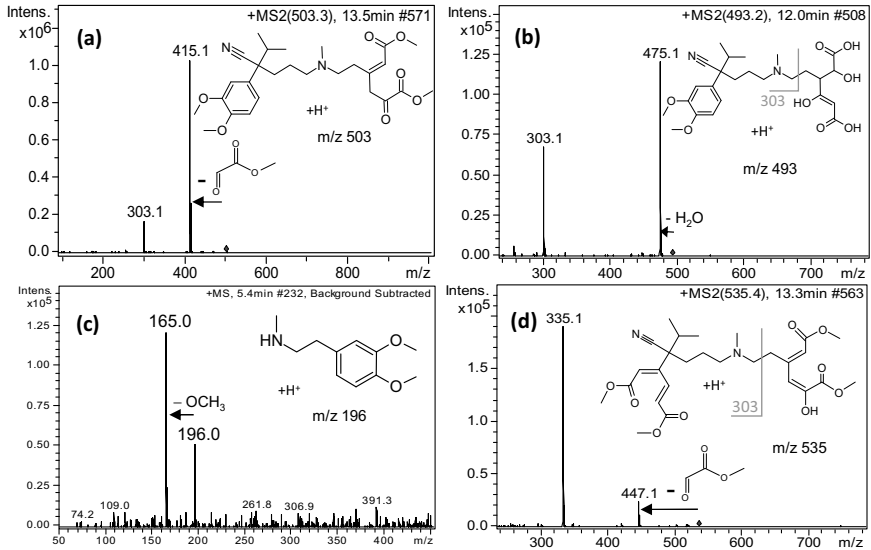
Fig. 7. (a) MS/MS spectrum of *m/z* 503 eluting at 13.5 min; (b) MS/MS spectrum of *m/z* 493 eluting at 12.0 min; (c) MS spectrum of peak **A**; (d) MS/MS spectrum of *m/z* 535.

The structures proposed for compounds **R** and **U**, due to attack of ozone on the benzene ring carbons substituted with the methoxy groups, are based on the known reactions of ozone with 1,2-dimethoxybenzene [26,27]. However, inspection of the extracted ion chromatogram (EIC) of *m/z* 487 (Fig. 6a) reveals the presence of additional peaks due to other minor isomeric products. These

are much less abundant and are not so well separated from the other products, so that it was not possible to identify their corresponding peaks in the UV chromatogram. The MS/MS spectra of the ions at m/z 487 eluting at 13.2 and 13.9 min are reported in Fig. 6b and c, respectively. These are very similar to that of peak **U** and can thus be attributed to attack by ozone to a different position on ring 2.

All the isomeric products detected at m/z 487 deriving from ozone attack on one of the aromatic rings are expected to undergo further oxidation during NTP treatment. From the time profiles reported in Fig. 4 and considering the structures compatible with the MS/MS spectra of Fig. 5, it can be proposed that products **S** ([M+H]$^+$, m/z 503) and **M** ([M+H]$^+$, m/z 363) are formed from **U** via addition of a water molecule followed by further oxidation. Many isomeric structures can be drawn corresponding to m/z 503 and indeed, as already found for m/z 487, many isomers are detected if the EIC of the ions at m/z 503 is analyzed. The structure attributed to **S** accounts for the loss of a neutral with a mass of 88 u, corresponding to glyoxylic acid methyl ester, to give the fragment ion at m/z 415. The alternative structure shown in Fig. 7a, which is the keto tautomer of **S** (Fig. 5), has been attributed to the isomer at m/z 503 eluting at 13.5 min, the MS/MS spectrum of which shows the same peaks detected in the spectrum of **S** but with different relative abundances. In particular the fragment at m/z 415 is of higher abundance suggesting that it is formed by a more facile rearrangement than is required in the case of **S** to lose the same neutral.

Further reaction of intermediate **S** involves hydrolysis of the two ester moieties to acid functions (m/z 475, low abundance, spectrum not shown) which can also be subjected to water addition (m/z 493, Fig. 7b).

As for the structure attributed to **M** (Fig. 5), this constitutes the last step of the benzene ring oxidation before the formation of CO_2. This is comparable to the formation of formic acid from phenol reported in previous publications [28].

A different reaction path with respect to the addition of ozone on the aromatic rings can justify the formation of the products corresponding to peaks **L** and **T** (Fig. 5). Verapamil contains indeed another functional group sensitive to ozone attack, which is the tertiary amino function. O_3 adds to the lone pair of nitrogen forming an adduct (CH_2R'')R'RN$^+$-O-O-O$^-$ which can lose O_2 giving the first structure proposed for **T** or dissociate into (CH_2R'')R'RN$^{+\bullet}$ and $O_3^{-\bullet}$. The reaction of (CH_2R'')R'RN$^{+\bullet}$ in aqueous solution, described in the literature [26], produces the secondary amine R'RNH and the aldehyde O=CHR''. The structure attributed to **L** (Fig. 5) thus corresponds to the secondary amine formed through this mechanism. The secondary amine with R corresponding to 3,4-(dimethoxyphenyl)ethyl- was also identified (Fig. 7c). The peak relative to this product in the UV chromatogram of Fig. 3 is peak **A**.

On the other hand, m/z 471 can also be attributed to a product in which a hydrogen of ring 1 has been substituted by an OH group due to the attack of a hydroxyl radical (Fig. 5). An isomer of m/z 471 was detected at 14.2 min, which suggests that both $\bullet$OH reactions occur.

Another interesting product, detected at m/z 535, is assigned the structure shown in Fig. 7d. It is easily seen that this product arises by ozonation of both aromatic rings of verapamil. It can therefore be viewed as the common product formed by ozonation of either intermediate **R** and **U**, the structures of which are shown in Fig. 5.

4. Conclusions

The successful application of air non-thermal plasma (NTP) to achieve verapamil removal from water is reported here for the first time. In the reactor used for this application, NTP is generated by a DBD discharge in the air above the surface of the contaminated water. It was shown that in this novel advanced oxidation process mineralization of verapamil to CO_2 is achieved in high yield (98%) through a complex mechanism involving parallel and consecutive reactions and many intermediates. These were detected and characterized by means of a thorough investigation based on high performance chromatographic and mass spectrometric analyses and on the comparison with literature studies pertaining to the oxidation of the functional groups of verapamil by the reactive species present in the air plasma. In particular it is proposed that many intermediates of NTP induced oxidation in our plasma reactor are formed by attack of ozone onto the aromatic rings and the amino group of verapamil and that a few others are instead due to attack by hydroxyl radicals. Failure to detect any nitrated and/or nitrosated byproducts of verapamil degradation suggests that the contribution of reactive nitrogen species (RNS) is marginal in the process induced by the electrode configuration adopted for our reactor. This is an important result relevant to issues dealing with the feasibility of an NTP-treatment stage in water remediation plants – nitrated and nitrosated organic byproducts are usually more toxic and persistent than their precursor pollutants – and with the detection and characterization of RNS in discharges with liquids and their effects, which is presently a hot area in NTP research [29,30].

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CHAPTER 4

DEGRADATION OF VERAPAMIL HYDROCHLORIDE IN WATER BY GLIDING ARC DISCHARGE

Krishna, S., Maslani, A., Izdebski, T., Horakova, M., Klementova, S., Spatenka, P., 2016. Degradation of verapamil hydrochloride in water by gliding arc discharge. Chemosphere 152, 47–54.

My share on this work was about 50%.

Degradation of Verapamil hydrochloride in water by gliding arc discharge

CrossMark

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HIGHLIGHTS

- This is the first report of the degradation mechanism of Verapamil in water by gliding arc discharge.
- The presence of hydroxyl radicals in the gliding arc discharge was confirmed by optical emission spectroscopy.
- The degradation kinetics of Verapamil under gliding arc discharge was investigated.

ARTICLE INFO

ABSTRACT

This study investigated the influence of gliding arc plasma discharge on the degradation of Verapamil hydrochloride in water. The plasma discharge was characterized by means of optical emission spectroscopy. Spectra of various atomic and molecular species were observed. Aqueous solution of Verapamil hydrochloride was exposed to gliding arc discharge operated in continuous discharge at atmospheric pressure and room temperature. The identification of Verapamil, the degradation mechanisms of Verapamil and its transformation products were performed using liquid chromatography — mass spectrometry (HPLC-MS). Experimental results indicate that the atmospheric pressure gliding arc plasma treatment has noticeable effects on Verapamil with satisfactory degradation efficiency. Plausible mechanisms of the degradation were discussed.

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1. Introduction

The presence of pharmaceutical compounds has been detected in the aquatic environment (Espulgas et al., 2007; Trovo et al., 2008). Although the amount of these substances in the surface water is low, its continuous input may constitute in the long-term a potential risk for aquatic and terrestrial organisms. Therefore, over the past few years they are considered as emerging pollutants in water bodies and their removal may be necessary for water use or reuse applications.

Advanced oxidation processes (AOPs) such as direct ozonation, Fenton's reaction, electrochemical methods, photocatalysis and direct photolysis have been applied to degrade organic pollutants in water (Pekarek, 2003; Brillas et al., 2005; Aranami and Readman, 2007; Yang et al., 2008; Deng and Ezyske, 2011). In AOP the formation of highly reactive hydroxyl radicals ($\cdot$OH), can be utilized in the destruction of organic pollutants present in the wastewater (Locke et al., 2006). The widely investigated AOPs in wastewater treatment including UV/H_2O_2 and O_3/H_2O_2 require substantial chemical addition and residual H_2O_2 quenching, which represents a

significant portion of their operational costs (Pekarek, 2003; Locke et al., 2006). But, emerging technologies based on plasmas can provide viable alternatives.

Plasmas are broadly classified into two categories, namely, thermal (or equilibrium) and non-thermal (or non-equilibrium). Thermal plasmas include arc discharges, plasma torches and radio frequency inductively coupled plasmas. Non-equilibrium plasmas have been traditionally generated in low pressures, such as direct current glow, corona, radio frequency, microwave and nanosecond high-voltage discharges. Unlike thermal plasmas they have high chemical selectivity and are capable of homogeneous activation. In non-thermal plasma, electrons can reach temperatures of 10,000—100,000 K while molecules can remain at ambient temperature (Petipas et al., 2007). For several years, non-thermal plasmas (NTPs) have been widely used for the degradation of organic compounds in water (Gao et al., 2003; Magureanu et al., 2008, 2010; Krause et al., 2009). The degradation of pharmaceutical compounds using NTP has also been reported (Magureanu et al., 2011; Drobin et al., 2013; Horakova et al., 2014).

The gliding arc or glidarc is a unique non-thermal plasma that has a relatively high plasma density, power and operating pressure in comparison with other non-equilibrium discharges, a high electron temperature (>1 eV), relatively low gas temperatures (<3000 K), and good chemical selectivity in comparison with thermal discharges. High temperature electrons are more efficient at producing ions, radicals and excited and dissociated molecules than those in equilibrium plasma (<1 eV), and the gas temperatures are still high enough to accelerate the interaction between neutral species. As compressed air contains variety of molecular species (N_2, O_2 and H_2O), $\cdot OH$ and $NO\cdot$, the main radicals in the non-thermal phase, are formed after the decomposition of those molecules under the electric field. The oxygen radical, ozone and UV radiations are formed in the gas-phase discharge, while $\cdot OH$ and H_2O_2 can be formed in the liquid-phase discharge (Du and Yan, 2007; Abdelmalek et al., 2008). Moreover, the gliding arc plasma device is well known for its simplicity of design and applicability. Recently, gliding arc discharge has been applied in the degradation of organic pollutants in water because of its low cost equipment and satisfactory decontamination (Horakova et al., 2014; Lesage et al., 2013; Ghezzar et al., 2013; Hentit et al., 2014).

The compound targeted in this study is Verapamil hydrochloride ($C_{27}H_{38}N_2O_4HCl$), a phenylalkylamine calcium-channel blocker, has been broadly used as anti-arrhythmic drugs to manage supraventricular tachyarrhythmias. Due to its vasodilating and negative inotropic properties, it has been indicated for the treatment of hypertension, ischemic heart disease, and hypertrophic cardiomyopathy (Singh et al., 1978). As a result of the extensive use in past decades, the presence of this compound has been detected in the surface waters of Czech Republic (Grabicova et al., 2015). The aim of the present work is to investigate the efficiency of the gliding arc discharge on the degradation of Verapamil in water and to propose the plausible degradation mechanisms by identifying the structure of the generated intermediates.

2. Materials and methods

2.1. Chemicals and instrumentation

Verapamil hydrochloride (CAS number: 152-11-4) was obtained from Sigma—Aldrich Corporation (USA). LC-MS grade acetonitrile and formic acid were purchased from VWR international.

The HPLC-MS analyses were performed using chromatograph by Shimadzu 8040 comprised of LC system (LC-30AD), a diode array detector (SPD-M30A), and a triple quadrupole MS system. Nebulising gas flow was 3 L/min, DL temperature was 250 °C, heat block temperature was 400 °C, drying gas flow was 15 L/min, and eluent flow was 0.3 mL/min. Positive full scan method from 50 to 500 m/z was used to find fragments preliminary. Single ion monitoring method was used to verify the target compound presence and plotting degradation curves. Multiple reaction monitoring and product ion scan methods were used to find and identify the fragment ions and byproducts. The column used was Acquity UPLC HSS T3 1.8 μm, 2.1 × 100 mm. The eluents used were 0.1% formic acid in water and 0.1% formic acid in acetonitrile. The gradient started with 0% acetonitrile, then increased to 95% within 9 min.

2.2. Experimental setup

Gliding arc discharge (GAD) was studied by means of emission spectra. Schematic view of the experiment is shown in Fig. 1. The image of visible part of the plasma flow was projected through the lens with focal distance 500 mm onto the entrance of the optical cable, which transfers signal to the spectrometer Jobin Yvon — Spex Triax 550. The output spectrum was detected by the intensified CCD (Charge-Coupled Device) detector with 1024 × 256 pixels connected to the CCD 3000 controller and to the PC. Two optical gratings with 300 and 1200 grooves/mm giving spectral resolutions 0.16 nm/pixel and 0.036 nm/pixel respectively were used. All spectra were integrated in time scales about 3 s, which was optimal with respect to signal intensity. However, any phenomena with shorter effective time were then averaged.

In addition, spectra were averaged in two spatial dimensions, which were perpendicular to the axis z of the gliding arc (Fig. 1 bottom): integration of radiation was because of positioning of the entrance slit of the optical cable. In other words, we collected all radiations at the given distance z. Therefore, we can analyse differences in spectra only along z axis, as the entrance slit together with lens is moved along it. Photo of the plasma flow in Fig. 1 also includes approximate positions of three distances (1 mm, 4 mm and 10 mm from the electrodes), in which spectra were measured.

The experimental apparatus used for water treatment by GAD is fully described in Horakova et al. (2014) and Kriz et al. (2012). Briefly, the GAD was generated by plasma source 750 W between two diverging copper electrodes of half-circle shape with minimal gap of 5 mm. The device cover exceeds 5 mm over the edge of electrodes. The power source was operated at frequency of 50 Hz. Compressed air was used as carrier working gas. The overpressure of the air was maintained at approximately 600 kPa, the air flow was kept constant at 0.86 $m^3 h^{-1}$ and the distance between the plasma device and the surface of the Verapamil solution was fixed at 10 cm as it was optimized by Kriz et al. (2012). The measured temperature at a distance 10 cm from the electrodes was 40 °C. The cooling system with water as cooling medium was used during plasma treatment process to avoid the heating of the tested solution.

2.3. Verapamil treatment experiments

A 25 mL of 5 × 10^{-5} M aqueous solution of the Verapamil was transferred into the reaction chamber. The gliding arc discharge was then applied on the surface of the solution to investigate the influence and efficiency of AOP on the degradation of Verapamil. During these experiments Verapamil solutions were treated separately by GAD for various treatment times of 5, 10, 20, 40 and 80 min. Each experiment was triplicated and standard deviation was calculated. The experiment was then repeated with another concentration (5 × 10^{-4} M) to find out its influence on the degradation. The fraction of residual Verapamil, [Verapamil]/[Verapamil]$_0$ was plotted against treatment time and the data were fitted by Equation (1) to obtain k, the rate constant of the decomposition
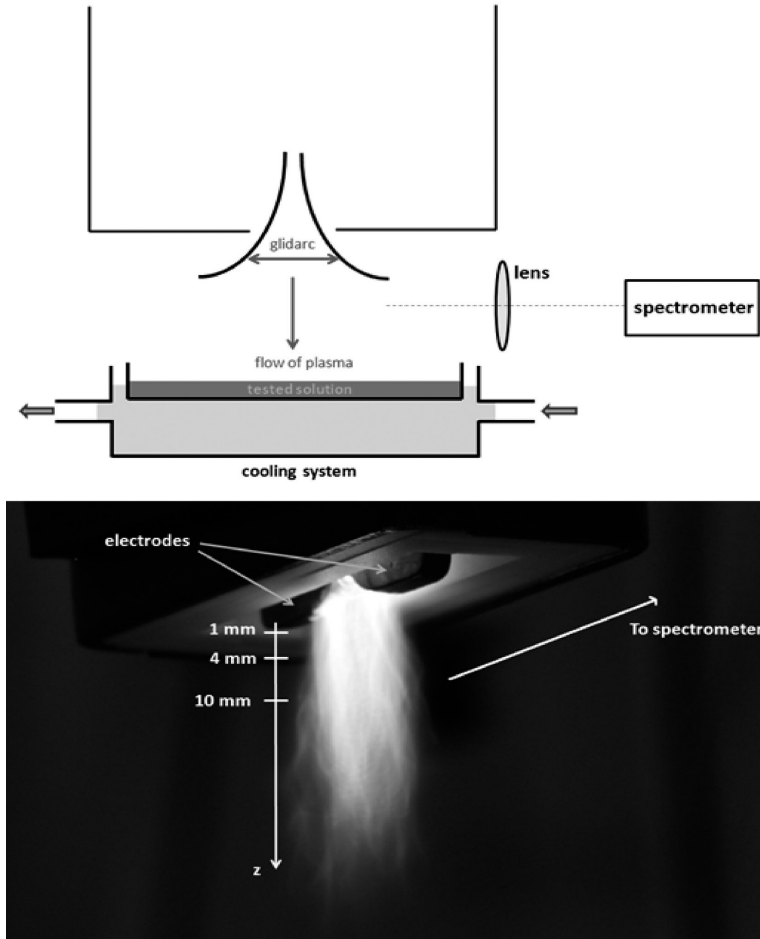
Fig. 1. Simplified scheme of emission spectroscopy experiment and water treatment using GAD (top) and photograph of GAD in operation with approximate positions of measurement along z axis (bottom).

process.

$$\frac{[Verapamil]}{[Verapamil]_0} = e^{-kt} \tag{1}$$

where $[Verapamil]_0$ and $[Verapamil]$ are the concentrations at time zero and t, respectively.

The half-life time of Verapamil was thus calculated by Equation (2)

$$t_{1/2} = 0.693/k \tag{2}$$

where k is the rate constant of degradation reaction.

The conversion of Verapamil is calculated by Equation (3)

$$R(\%) = \left[\frac{\left(C_i - d \times C_f \right)}{C_i} \right] \times 100 \tag{3}$$

where C_i is initial concentration of Verapamil and C_f is final concentration after the treatment, d is evaporation coefficient, it is defined by $V_f\,(mL)/V_i\,(mL)$ where V_i is initial volume of the solution and V_f is final volume of the solution after the treatment. The efficiency of pollutant degradation is better illustrated by the yield, defined as the amount of Verapamil decomposed per unit energy consumed in the process. i.e.

$$Y(g/kWh) = \frac{C_0(g/L) \times V(L) \times R(\%) \times 0.01}{P(kW) \times t(h)} \qquad (4)$$

where C_0 is initial mass concentration of the pollutant in grams per liter, V_i is volume of the solution in liter, t is time of treatment in hours, P is power of the discharge in kilowatts and R is conversion of the pollutant in percent.

3. Results and discussion

3.1. Characterization of GAD using emission spectroscopy

Firstly, low resolution overview spectra from UV through visible light to infrared spectral region were measured using grating with 300 grooves/mm. Most important parts of these spectra for $z = 1$ mm are shown in Fig. 2a and b. In the UV region mainly emission spectra of diatomic molecules N_2, N_2^+ and •OH, partly overlapping with each other, were observed. These emissions are typical for air plasmas; also OH radicals, which are considered as an evidence of water presence, are often registered due to air humidity. We could also see two strong lines of neutral copper, as

a)

b)

Fig. 2. (a,b). Emission spectrum of gliding arc at distance $z = 1$ mm; low resolution a) UV spectral range, b) visible/IR spectral range.

atoms of copper enrich the plasma because of erosion of electrodes. Fig. 2b shows the spectral region between 500 nm and 850 nm, in which various atomic emissions were detected. Apart from copper lines we have here also lines of nitrogen and oxygen coming from air; moreover we can see well known doublet of sodium at 589 nm, which is probably result of some small impurities.

At a distance of one mm we observed mainly the discharge region, in which dissociation and excitation of individual species takes place. Going downstream the flow, on the other hand, recombination and de-excitation processes become more important. This is demonstrated in Fig. 3a—c, in which high resolution spectra were taken using grating with 1200 grooves/mm which are shown for distances 1 mm, 4 mm and 10 mm respectively. We chose here UV region of spectrum between 300 nm and 360 nm, where two strong copper lines as well as various molecules were measured. It is obvious from Fig. 3(b, c) that the intensity of copper lines substantially decreases at 4 mm and at 10 mm these lines almost disappear. As for other atomic species shown in Fig. 2b, their emissions are not available even at 4 mm. Probably, the discharge does not spread down to 4 mm anymore and in the free flow of plasma fast recombination occurs; only weak emission of copper still persists. On the other hand, molecular emissions are still observable at 4 mm as well as at 10 mm and only their intensity slowly decreases. It means that the conditions in these regions are suitable for excitation of air components (N_2, O_2), and formation of molecules N_2^+ and OH together with their excitation is still possible.

High resolution spectra of three copper lines at 510.6 nm, 515.3 nm and 521.8 nm were used for estimation of excitation temperature, which is obtained by well-known method of the so called Boltzmann plot (Griem, 1997; Kunze, 2009). As it was mentioned already, these lines are available only for $z = 1$ mm. Obtained value of temperature is 5800 K. Interpretation of this temperature is however complicated, in spite of excitation temperature is often assumed to be corresponding to electron temperature. Our measurement has several limitations, which does not allow making unambiguous conclusion: As was mentioned already, spectra are integrated in time and space therefore we can speak about an average temperature at the distance $z = 1$ mm. Another problem is that we could use only three copper lines, which is not enough for reliable statistics. Relevant Boltzmann plots usually contain higher number of measured transitions. Finally, it was shown by other authors that in non-thermal plasmas Boltzmann plots of spectral lines of various metallic species, including copper, are complicated and obtained temperatures should be critically analyzed (Zhao and Horlick, 2006; Zhang et al., 2011). Excitation processes can be, depending on the energy of the excited level, thermal, non-thermal or their mixture and thus resulting temperature can have in each case different meaning. We can suppose that in our case the temperature 5800 K is somewhere between temperatures of heavy particles and electrons. Excitation temperature from copper lines is a simple example of temperature determination in non-thermal plasmas from emission spectra. Similarly, rotational and vibrational temperatures from molecular spectra can be estimated. However, we would face comparable or even bigger problems with their interpretation as summarized in Bruggeman et al. (2014).

3.2. Reaction kinetics

The degradation of Verapamil in water by GAD was studied at two different initial concentrations 5×10^{-4} M and 5×10^{-5} M. The Verapamil degradation by atmospheric pressure GAD at room temperature is shown in Fig. 4, where 37% and 97% of Verapamil were removed within 80 min, for initial concentrations of 5×10^{-4} M and 5×10^{-5} M respectively. A first order kinetics was
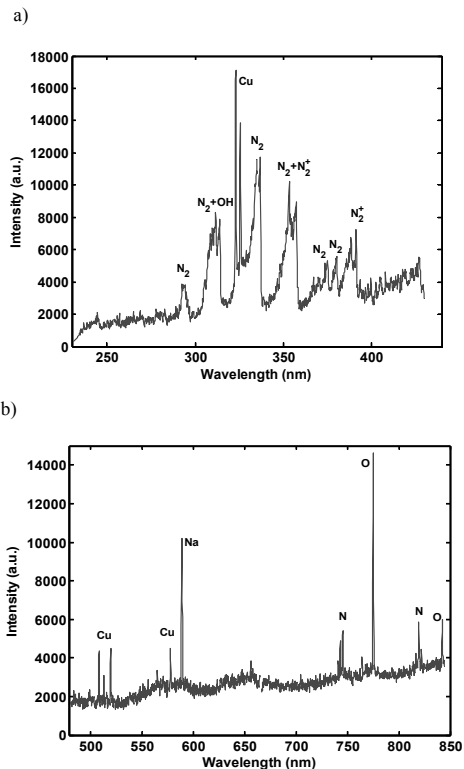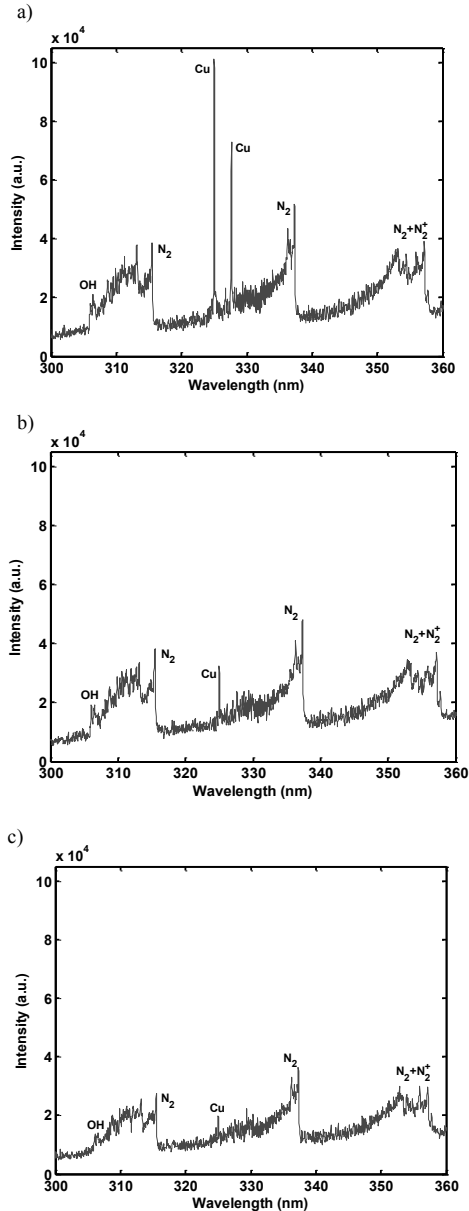
a)

b)

c)

Fig. 3. (a,b,c). Emission spectrum of gliding arc in UV spectral range; high resolution; a) z = 1 mm, b) z = 4 mm, c) z = 10 mm.
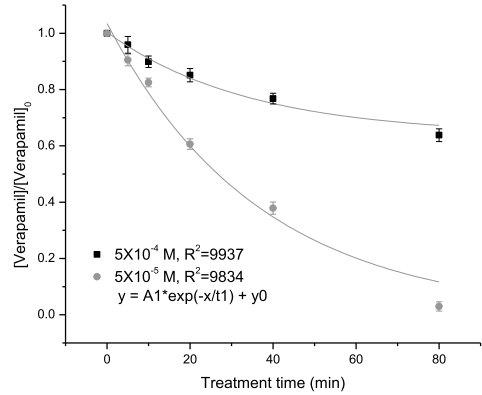

Fig. 4. Decay profile of Verapamil under atmospheric pressure GAD at room temperature.

observed for the plasma based degradation of Verapamil at rate constants 0.01 min^{-1} and 0.026 min^{-1} for initial concentrations of 5×10^{-4} M and 5×10^{-5} M respectively. The corresponding half-life times were 69 min and 27 min. The increase in rate constant with decrease in concentration is a known feature of non-thermal plasma treatment and can be attributed to the higher ratio between the concentration of the reactive species and that of the target compounds (Marotta et al., 2011). The obtained degradation is due to the synergistic effect of active particles, radicals, ozone and UV radiation present in the GAD. The power introduced in the discharge was very high (750 W), leading to low energy yields, $Y = 4 \times 10^{-3}$ g/kWh and $Y = 6 \times 10^{-4}$ g/kWh for initial concentrations of 5×10^{-4} M and 5×10^{-5} M respectively.

3.3. MS analysis and identification of transformation products

The total ion current chromatograms of the GAD treated samples showed a main peak with a retention time of $t_R = 6.1$ min, under the conditions at which Verapamil also elutes. The mass spectrum corresponding to this peak was also identical to that of Verapamil including a peak at $m/z = 455$, which is the mass of the protonated molecular ion. The peaks in product ion scan chromatograms at $m/z = 303$, 165 and 150 were corresponding to fragment ions of Verapamil, which were useful for identification of transformation products. LC/MS data of Verapamil and GAD treated Verapamil solutions are shown in Table 1. Fragmentation pattern of Verapamil and its transformation products are shown in Fig. 5.

Table 1
LC/MS data of Verapamil and plasma treated Verapamil solution.

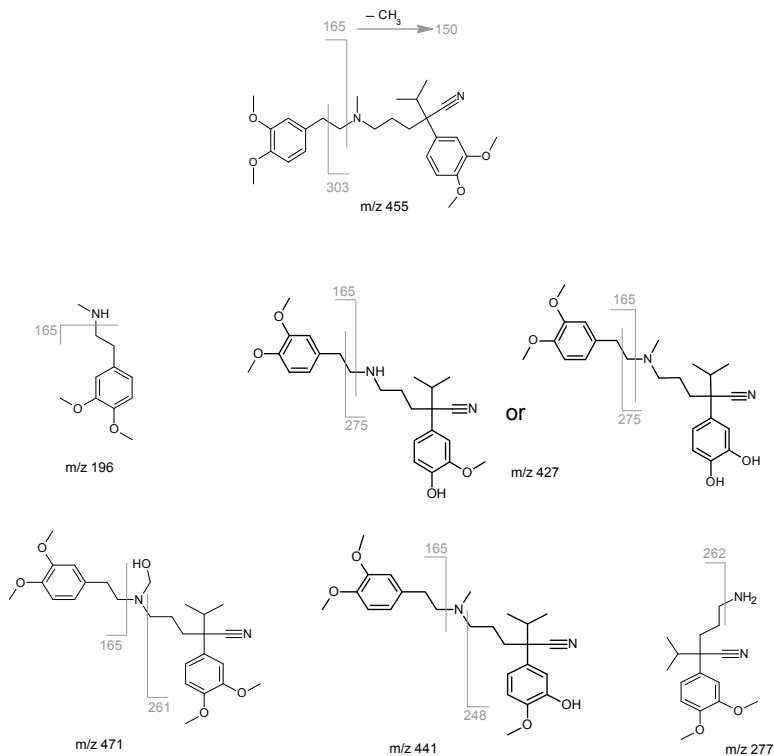| Compound	t_R/min	MS [M+H]$^+$	MS fragment ions (m/z)
Verapamil	6.1	455	303, 165, 150
M1	3.4	196	165
M2	5.3	427	275, 165
M3	5.1	471	261, 165, 150
M4	5.7	441	303, 165, 150
M5	7.4	277	262, 171, 101

Fig. 5. Fragmentation pattern of Verapamil and its transformation products.

3.4. Degradation mechanism

The Verapamil transformation products or degradation byproducts, resulting from the degradation of its aqueous solution under GAD were identified by HPLC-MS analysis. The structural identification of the degradation byproducts was based on the analysis of the corresponding mass spectrum. HPLC-MS analyses indicate that the plasma degradation of Verapamil yield five transformation products (M1–M5). The proposed degradation pathways of Verapamil and structures of the Verapamil transformation products are presented in Fig. 6.

For decomposition products at detectable levels, which are probably corresponding to the new intermediates can be observed concurrent with the disappearance of protonated Verapamil ($m/z = 455$). The product M1 showed pseudo-molecular ion $[M+H]^+$ at $m/z = 196$, which was 259 u lower than that of Verapamil and was formed by oxidative dealkylation. Here, the highly substituted phenylbutyl moiety was removed during dealkylation. The presence of the fragment ion at m/z 165 in the MS/MS spectrum of product M1 suggested that the phenylethyl moiety was still intact after plasma treatment and hence confirms the proposed structure. The product M2 showed pseudo-molecular ion $[M+H]^+$ at $m/z = 427$, which was 28 u lower than that of parent drug suggesting the loss of two methyl groups from Verapamil. The presence of the

fragment ion at m/z 165 in the MS/MS spectrum of product M2 suggested that the phenylethyl moiety was unaltered. In other words, the demethylation must have occurred at the phenylbutyl moiety. If the O-demethylation of verapamil occurred twice, the product M2a and if one O-demethylation followed by N-demethylation occurred, the product M2b would be formed.

The product M3 showed pseudo-molecular ion $[M+H]^+$ at $m/z = 471$, which was 16 u higher than the parent drug and it might be formed by direct hydroxylation initiated by GAD. The presence of fragment ions at m/z 261 and 165 in the MS/MS spectrum of product M3 suggested that the phenylbutyl moiety and phenylethyl moiety were unaltered. Therefore, hydroxylation must have occurred at the methyl group bound to nitrogen. The product M4 showed pseudo-molecular ion $[M+H]^+$ at $m/z = 441$, which was 14 u lower than that of the parent drug, suggesting the loss of a methyl group from Verapamil. The presence of the prominent ion at m/z 165 in the MS/MS spectrum of product M4 suggested that the phenylethyl moiety was unaltered. The presence of fragment ion at m/z 248 indicated that the demethylation was carried out on the highly substituted phenylbutyl moiety. The product M5 showed pseudo-molecular ion $[M+H]^+$ at $m/z = 277$, which was 178 u lower than that of the parent drug, formed by oxidative dealkylation followed by N-demethylation. Here, phenylethyl moiety was removed from Verapamil during dealkylation. The presence of the
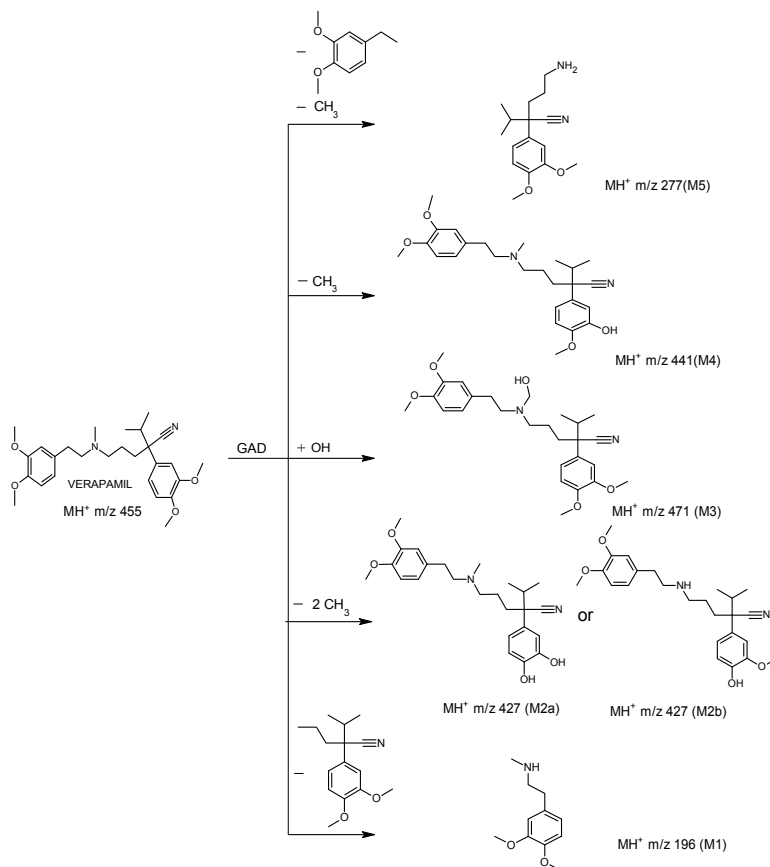
Fig. 6. Proposed degradation pathways of Verapamil during GAD.

fragment ion at *m/z* 262 in the MS/MS spectrum of product M5 confirms the proposed structure (Walles et al., 2003; Trautwein et al., 2008).

4. Conclusion

The gliding arc plasma discharge was characterized by optical emission spectroscopy. The emission spectra of atoms (O, N, Cu, Na) were observed mainly in the discharge region of the gliding arc. Going down with the flow at a distance of 10 mm only the molecular emissions (OH, N_2, N_2^+) were detected. Farther than 10 mm from electrodes emission spectra more or less disappears. Thus the influence of individual species in the distance 10 cm, where Verapamil degradation takes place, could not be directly assessed. It is just evident that the discharge produces relevant active species like O or OH radicals, which may play key role in degradation reaction.

It was first time that the determination of degradation efficiency and investigation of degradation mechanisms of Verapamil during GAD treatment were conducted successfully. Having got half-lives of 69 min and 27 min, for initial concentrations of 5×10^{-4} M and 5×10^{-5} M respectively, the reactive species in plasma were able to degrade Verapamil. The rate constants of the degradation processes were 0.01 min^{-1} and 0.026 min^{-1}. The plasma degradation mechanisms of Verapamil were dominated by high energy electrons, ozone and hydroxyl free radicals. The structure of the intermediates or transformation products of Verapamil during the degradation process was confirmed by MS analysis. Plausible mechanisms for the formation of the intermediates were also proposed.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.02.083.

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CHAPTER 5

DEGRADATION OF ORGANIC POLLUTANTS IN WATER BY ELECTROHYDRAULIC SPARK DISCHARGE

Krishna, S., Izdebski, T., Spatenka, P., 2016. Degradation of organic pollutants in water by advanced oxidation processes (Manuscript).

My share on this work was about 60%.

DEGRADATION OF ORGANIC POLLUTANTS IN WATER BY ELECTROHYDRAULIC SPARK DISCHARGE

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ABSTRACT

Studies have shown that recalcitrant pollutants remain in water even after conventional treatment systems. Advanced oxidation processes (AOPs) are continuously in progress in order to improve treatment efficiency of pollutants in water. Non-thermal plasmas (NTPs) have been investigated in recent years as an innovative physicochemical technique for wastewater treatment at atmospheric pressure and ambient temperature. This study investigated the influence of different AOPs on the degradation of organic pollutants in water. Our processes were mainly based on plasmas (Glidarc and Electrohydraulic spark discharge), and ozonation. Experimental results indicate that AOPs have noticeable effects on target pollutants with satisfactory degradation efficiency. The kinetics of the pollutant removal has also been investigated.

Keywords: glidarc, spark discharge, ozonation, organic pollutants, half-life

INTRODUCTION

The contamination of water by organic compounds has been reported worldwide and constitutes an issue of great concern at regional, national and global levels (Neamtu et al., 2003; Andreozzi et al., 2003; Guo et al., 2006; Maloschik et al., 2007; Luo et al., 2014). Water pollution with organic compounds can be attributed to several sources, such as emission from the production sites due to insufficient treatment of manufacturing effluents, direct disposal of unused pharmaceuticals and personal care products (PPCPs), accidental discharges of farm wastes from silage manufacture and from intensive livestock rearing, which contain very high concentrations of organic contaminants. Also, strong organic pesticides in agricultural runoff and accidental spillage of pesticides can lead to its high concentrations in the water and the effects on aquatic vertebrates will be associated with acute toxicity. Some of these compounds are harmful even at low concentrations. Most of these organic pollutants are not completely eradicated in wastewater treatment plants (WWTPs), and therefore remain in effluents and contaminate surface and ground waters. Although the amount of some of these contaminants in the surface water is low, its continuous input may constitute in the long-term a potential risk for aquatic and terrestrial organisms (Halling-Sorensen et al., 1998;

Ternes, 1998). Therefore, it is necessary to treat the effluents containing these contaminants adequately before discharging them.

Advanced oxidation processes (AOPs) are very effective on the degradation of numerous organic pollutants in water (Brillas et al., 2005; Aranami and Readman, 2007; Yang et al., 2008; Deng and Ezyske, 2011). These processes are based on the *in situ* generation of highly reactive transitory species, such as $OH\bullet$, $O_2\bullet$-, O_3, H_2O_2, which plays key role in the degradation of organic pollutants in wastewater (Espulgas et al., 2002; Pera-Titus et al., 2004). The most widely investigated AOPs in wastewater treatment including UV/H_2O_2 and O_3/H_2O_2 require substantial chemical addition and residual H_2O_2 quenching, which represents a significant portion of their operational costs (Pekarek, 2003; Locke et al., 2006). Hence, emerging technologies providing viable alternatives are required.

Non-thermal plasma (NTP) may be a viable alternative to more common AOPs due to its comparable energy requirements for contaminant degradation and its ability to generate oxidants without the addition of chemicals or UV lamps (Gerrity et al., 2010). NTP can be regarded as highly efficient because there is no energy loss in heating the surrounding liquid, which allows the energy to be focused on the excitation of electrons (Pekarek, 2003). In NTP, electrons can reach temperatures of 10,000–100,000 K while molecule remains at ambient temperature (Petipas et al., 2007). The major products of non-thermal plasma generated in electrical discharge in gaseous phase over liquid surface are O_3, OH radicals and H_2O_2, whereas the amount of OH radicals is promoted by increased humidity (Hayashi et al., 2000). In the liquid phase the dominant discharge products are OH radicals and H_2O_2 (Sun et al., 1998). The degradation of organic compounds in water using ozone has been widely studied (Ternesa et al., 2003). The influence of plasma discharge on the decomposition of organic pollutants in water has also been reported (Sun et al., 1999; Gao et al., 2003; Grymonpre et al., 2004; Magureanu et al., 2008, 2010 and 2011; Krause et al., 2009; Horakova et al., 2014).

This study assesses and compares the removal of atrazine and verapamil from aqueous solutions by means of a non-thermal plasma discharge (Glidarc), electrohydraulic spark discharge and ozonation. Verapamil, a phenylalkylamine calcium-channel blocker, has broadly been used in the treatment of various cardiovascular disorders such as angina pectoris, cardiac arrhythmias, hypertension and hypertrophic cardiomyopathy. As a result of the extensive use in past decades, presence of this compound has been detected in the surface waters of Czech Republic (Grabicova et al., 2015). Atrazine, a herbicide considered as an endocrine disrupting compound (EDC), has been banned in the European Union due to the widespread contamination of drinking water supplies (Mackul'ak et al., 2011).

EXPERIMENTAL

Chemicals and Instrumentation

Verapamil hydrochloride (CAS number: 152–11–4) was obtained from Sigma-Aldrich Corporation (USA). Pesticide: Atrazine (99%) was purchased from Labor Dr Ehrenstorfer. Test solutions were prepared in ultrapure water. LC-MS grade acetonitrile and formic acid were purchased from VWR international. All chemicals were used as received without further purification.
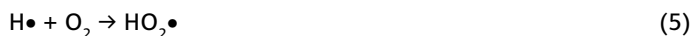
The HPLC-MS analyses were performed using chromatograph by Shimadzu 8040 comprised of LC system (LC-30AD), a diode array detector (SPD-M30A), and a triple quadrupole MS system. Nebulising gas flow was 3 L min^{-1}, DL temperature was 250 °C, heat block temperature was 400 °C, drying gas flow was 15 L min^{-1}, and eluent flow was 0.3 mL min^{-1}. Positive full

scan method from 50–500 m/z was used to find fragments preliminary. Single ion monitoring method was used to verify target compound presence and plotting degradation curves. Multiple reaction monitoring and product ion scan methods were used to find and identify fragment ions and by-products. The column used was Acquity UPLC HSS T3 1.8 μm, 2.1 ×100 mm. The eluents used were 0.1% formic acid in water and 0.1% formic acid in acetonitrile. The gradient started with 0% acetonitrile, and then increased to 95% within 9 min.

Experimental setup

Gliding Arc Discharge

The gliding arc discharge (GAD) used for this study is shown in chapter 4 Fig. 1. The discharge is generated by high voltage transformer (10 kV/160 mA) between two diverging copper electrodes of half-circle shape with minimal gap of 5 mm. The device cover exceeds 5 mm over the edge of electrodes. The power source is operated at frequency of 50 Hz. Compressed air was used as carrier working gas. The overpressure of the air was maintained at approximately 600 kPa. The air flow was kept constant as 0.86 m^3 h^{-1} controlled by an air flowmeter. In this study, the NTP discharge is used to produce active species in compressed air. The efficiency of the gliding arc discharge is due to the reactive chemical species such as •OH, NO•, HO_2•, H_2O_2 and O formed by the following reactions.

$$H_2O + e- \rightarrow H• + •OH + e- \tag{1}$$

$$O_2 + e- \rightarrow O(^3P) + O(^1D) + e- \tag{2}$$

$$N_2 + e- \rightarrow N(^4S) + N(^2D) + e- \tag{3}$$

$$N(^2D)+ O_2 \rightarrow •NO + O \tag{4}$$

$$H• + O_2 \rightarrow HO_2• \tag{5}$$

$$HO_2• + HO_2• \rightarrow H_2O_2 + O_2 \tag{6}$$

$$HO_2• + NO• \rightarrow NO_2 + •OH \tag{7}$$

$$•OH + •OH \rightarrow H_2O_2 \tag{8}$$

$$NO_2 + •HO \rightarrow H^+ + NO_3^- \tag{9}$$

$$NO• + •HO \rightarrow HNO_2 \tag{10}$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \tag{11}$$

The main advantage of this process is that it can produce active species without chemical addition or the use of UV lamps. The species formed in the plasma depend on the nature of the feeding gas. Humid air contains nitrogen, oxygen and water. The presence of highly reactive OH and NO radicals in the humid air plasma were identified by emission spectroscopy and quantified. The plasma in humid air was characterized by a high predominance of OH radicals over NO radicals when measuring their respective densities. The NO• spectrum was characterized by a double-headed band at 237 nm and the •OH spectrum was characterized by a transition band located at 306 nm (Benstaali et al., 2002).

A 5 × 10⁻⁵ M aqueous solution of the target pollutant (25 mL) was transferred into the reaction chamber. The gliding arc discharge was then applied on the surface of the solution to investigate the influence and efficiency of AOP on the degradation of model pollutant. During

these experiments, test solutions were treated separately by GAD at various time intervals of 5, 10, 20, 40 and 80 min. Samples were analyzed by means of HPLC-MS.

Electrohydraulic Spark Discharge

The experimental apparatus used for water treatment by electrohydraulic spark discharge (ESD) is presented in Fig. 2. Briefly, the reactor was a PTFE cylinder having inner diameter 25 mm and height 60 mm. The high voltage electrode was a stainless steel hypodermic needle having an inner diameter of 1.6 mm and an outer diameter of 2 mm. The ground electrode was a stainless steel rod having diameter of 5 mm. The gap between the electrodes was 3 mm.

Figure 2. *Spark discharge reactor.*

An overall scheme of the experimental set-up including reactor placement, electrical connections and power supply is presented in Fig. 3. A 100 mL of test solution was flowing through the reactor during the discharge in a closed loop at a flow rate of 30 mL min^{-1}. Voltage pulses of 17–20 kV were applied to the needle electrode with a repetition rate of 50 Hz. Single pulse energy was in the range of 1.2–1.4 J (Izdebski et al., 2011). Samples were collected at various time intervals after treatment and analyzed by means of HPLC-MS.
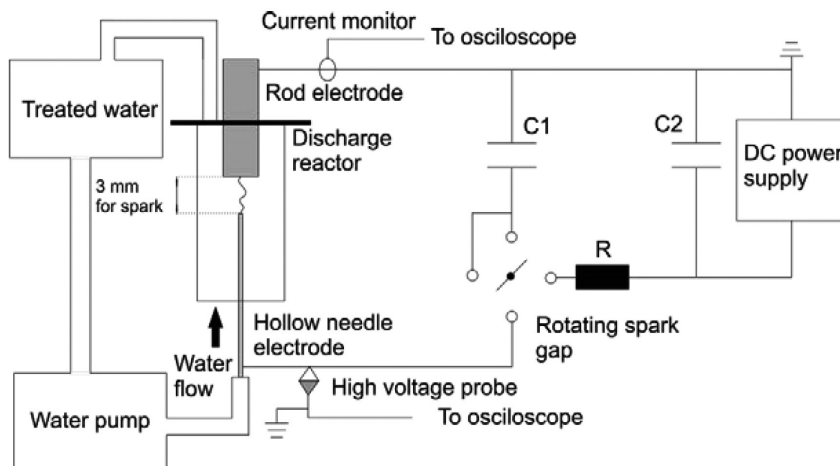

Figure 3. *Experimental set-up scheme of spark discharge reactor and power supply. C1 = 2 nF, C2 = 22 nF, R = 10 kΩ.*

Ozonation

For ozonation we used a commercially available ozonizer made by Dora Co., Poland, with frequency of 1.6 kHz. To generate ozone, a 25 cm long cylindrical DBD tube is used. The ozonizer power was set to 20 W which resulted in constant ozone concentration of 20 g m^{-3}. The ozone was made from oxygen (99.9%) flowing through the ozonizer with a flow rate of 1 L min^{-1}. Ozonation was performed using the gas mixture composed of oxygen and ozone was introduced into a gas washing bottle filled with 200 mL of the test solution. The solution was treated with the gas mixture for 5 min. Samples were collected at various time intervals and analyzed by means of HPLC-MS.

The fraction of residual compound, $[C]/[C]_0$ was plotted against treatment time and the data were fitted by equation (1) to obtain k, the rate constant of the decomposition process.

$$\frac{[C]}{[C]_o} = e^{-kt} \tag{1}$$

Where $[C]_0$ and $[C]$ are the concentrations at time zero and t, respectively.

The half-life time of compound was thus calculated by Eq. (2):

$$t_{1/2} = 0.693/k \tag{2}$$

Where k is the rate constant of degradation reaction.

The conversion of compound is calculated by Eq. (3):

$$\text{Conversion:} \quad R(\%) = \left[\frac{(C_i - d \times C_f)}{C_i} \right] \times 100 \tag{3}$$

Here C_i is the initial concentration of compound and C_f the final concentration after the treatment, d is the evaporation coefficient, it is defined by V_f (mL)/V_i (mL) where Vi is the initial volume of the solution and V_f is final volume of the solution after the treatment. The efficiency of pollutant degradation is better illustrated by the yield, defined as the amount of target compound decomposed per unit energy consumed in the process. ie;

$$Y(g/kWh) = \frac{C_0(g/L) \times V(L) \times R(\%) \times 0.01}{P(kW) \times t(h)} \tag{4}$$

Where C_0 is the initial mass concentration of the pollutant in grams per liter, V is the volume of the solution in liter, t is the time of treatment in hours, P is the power of discharge in kilowatts and R is the conversion of the pollutant in percent.

RESULTS AND DISCUSSION

Reaction Kinetics and degradation mechanism

The degradation of verapamil and atrazine by atmospheric pressure GAD at room temperature is shown in Fig. 4, where 97% of verapamil and 72% of atrazine was removed within 80 min. A pseudo-first order kinetics was observed for the plasma based degradation of verapamil and atrazine at rate constants $k = 0.026$ min^{-1} and $k = 0.025$ min^{-1} respectively. The half-life times of verapamil and atrazine with GAD were 27 min and 28 min respectively. The power introduced in the discharge was very high (750 W), leading to low energy yields ($Y = 6 \times 10^{-4}$ g/kWh) and ($Y = 2.4 \times 10^{-4}$ g/kWh) for verapamil and atrazine respectively. Degradation by-products of verapamil during GAD have been reported in chapter 4. The obtained degradation is due to the synergistic effect of active particles, radicals, ozone and UV radiation present in the GAD. I could not detect any degradation by-products of atrazine during GAD.
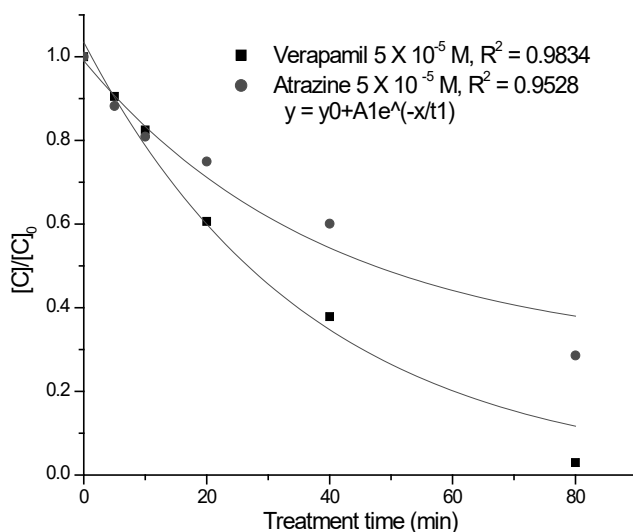
Figure 4. *Decay profile of verapamil and atrazine during GAD.*

The decay profile of verapamil and atrazine by spark discharge is shown in Fig. 5, where 87% of verapamil and 83% of atrazine was degraded within 40 min. A pseudo-first order kinetics was observed at rate constants $k = 0.065$ min^{-1} and $k = 0.094$ min^{-1} for verapamil and atrazine respectively. The half-life times of verapamil and atrazine with spark discharge were 10.7 min and 7.35 min, respectively. The power introduced in the discharge was (60 W), leading to energy yields ($Y = 5.1 \times 10^{-2}$ g/kWh) and ($Y = 2.3 \times 10^{-2}$ g/kWh) for verapamil and atrazine respectively.

Figure 5. *Decay profile of verapamil and atrazine during spark discharge.*

The degradation intermediates of verapamil during spark discharge was identified by HPLC-MS analyses. LC/MS data of verapamil and spark discharge treated verapamil solutions are shown in Table 1. I could not detect any degradation by-products of atrazine during spark discharge.
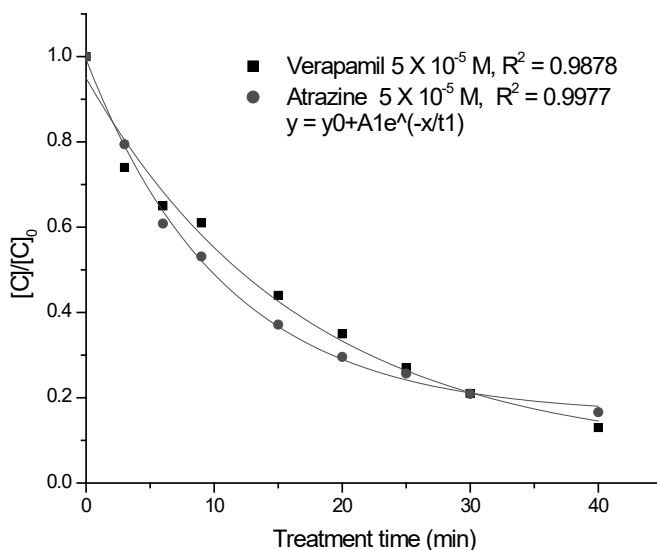
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Compound	t_R/min	MS [M+H]$^+$	MS fragment ions (m/z)
Verapamil	6.1	455	303, 165, 150
M1	3.4	196	165
M2	5.1	471	261, 165, 150
M3	5.7	441	248, 165, 150

The proposed degradation pathways of verapamil during spark discharge are presented in Fig. 6. The product M1 (m/z = 196), corresponding to the loss of 259 mass units to the parent drug and was formed by oxidative dealkylation. The presence of the fragment at m/z 165 in the MS/MS spectrum of product M1 suggested that the phenylethyl moiety was still intact after plasma treatment and hence confirms the proposed structure. The product M2 (m/z = 471), corresponding to the addition of 16 mass units to the parent molecule and might be formed by direct hydroxylation initiated by spark discharge. The presence of fragment ions at m/z 261 and 165 in the MS/MS spectrum of product M2 suggested that the phenylbutyl moiety and phenylethyl moiety were unaltered. Therefore, hydroxylation must have occurred at the methyl group bound to nitrogen. The product M3 (m/z = 441), which was 14 u lower than that of the parent drug, suggesting the loss of a methyl group from verapamil. The presence of the prominent ion at m/z 165 in the MS/MS spectrum of product M3 suggested that the phenylethyl moiety was unaltered. The presence of fragment ion at m/z 248 indicated that the demethylation was carried out on the highly substituted phenylbutyl moiety (Walles et al., 2003; Trautwein et al., 2008).
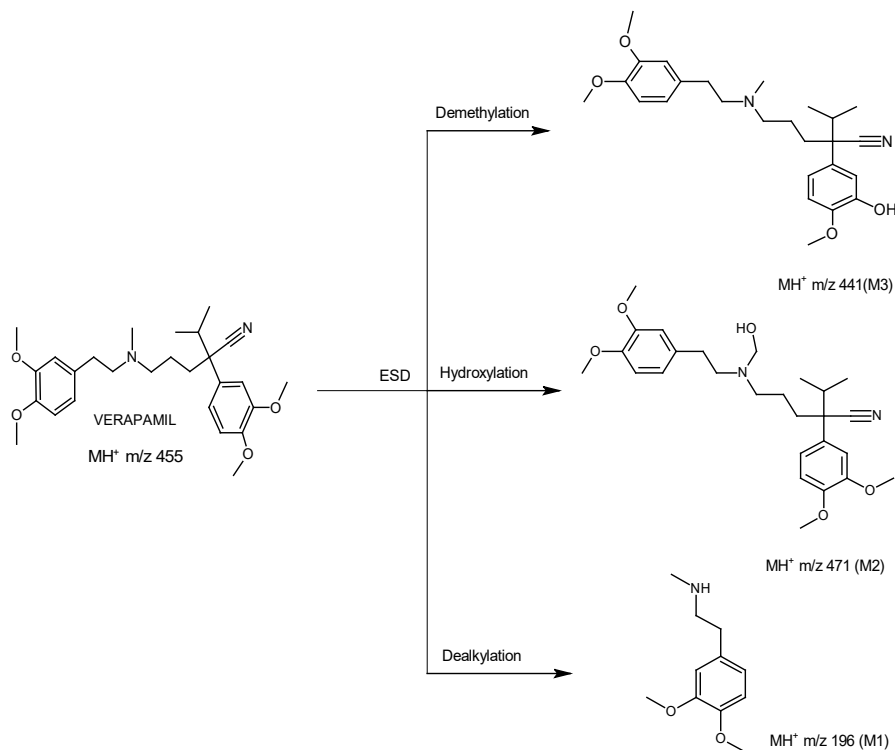
Figure 6. *Proposed degradation pathways of verapamil under electrohydraulic spark discharge.*

The degradation of verapamil and atrazine by ozonation is shown in Fig. 7, where 100% of verapamil was removed within 1.5 min, while atrazine was almost completely (99.8%) removed within 4 min. A pseudo-first order kinetics was observed for verapamil and atrazine at rate constants k = 2.56 min^{-1} and k = 0.769 min^{-1} respectively. The half-life times of verapamil and atrazine with ozone were 0.27 min and 0.9 min respectively. The power applied was (20 W), leading to energy yields (Y = 9.4 g/kWh) and (Y = 1.6 g/kWh) for verapamil and atrazine respectively.
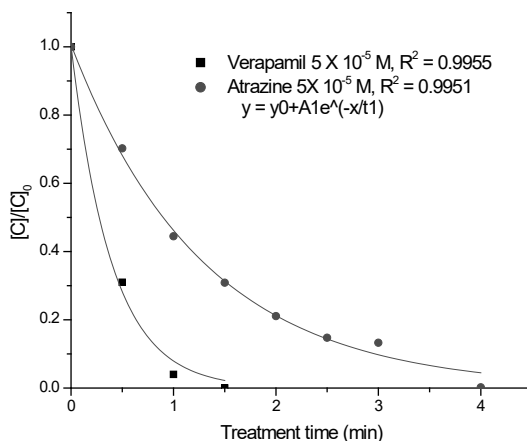
Figure 7. *Decay profile of verapamil and atrazine during ozonation.*

The degradation intermediates of verapamil during ozonation was identified by HPLC-MS analyses. LC/MS data of verapamil and ozonized verapamil solutions are shown in Table 1. I could not detect any degradation by-products of atrazine during ozonation.

Table 2. *LC/MS data of verapamil and ozonated verapamil solution.*

Compound	t_R/min	MS [M+H]$^+$	MS fragment ions (m/z)
Verapamil	6.1	455	303, 165, 150
M1	3.4	196	165
M2	5.1	471	261, 165, 150
M3	7.4	277	262, 171, 101

The proposed degradation pathways of verapamil and structures of the verapamil transformation products are presented in Fig. 8. The product M1 (m/z = 196), corresponding to the loss of 259 mass units to the parent drug and was formed by oxidative dealkylation. The presence of the fragment at m/z 165 in the MS/MS spectrum of product M1 suggested that the phenylethyl moiety was still intact after plasma treatment and hence confirms the proposed structure. The product M2 (m/z = 471), corresponding to the addition of 16 mass units to the parent molecule and might be formed by hydroxylation of verapamil during ozonation. The presence of fragment ions at m/z 261 and 165 in the MS/MS spectrum of product M2 suggested that the phenylbutyl moiety and phenylethyl moiety were unaltered. Therefore, hydroxylation must have occurred at the methyl group bound to nitrogen.

The product M3 (m/z = 277), which was 178 u lower than that of the parent drug, formed by oxidative dealkylation followed by N-demethylation. Here, phenylethyl moiety was removed from verapamil during dealkylation. The presence of the fragment ion at m/z 262 in the MS/MS spectrum of product M3 confirms the proposed structure (Walles et al., 2003; Trautwein et al., 2008).
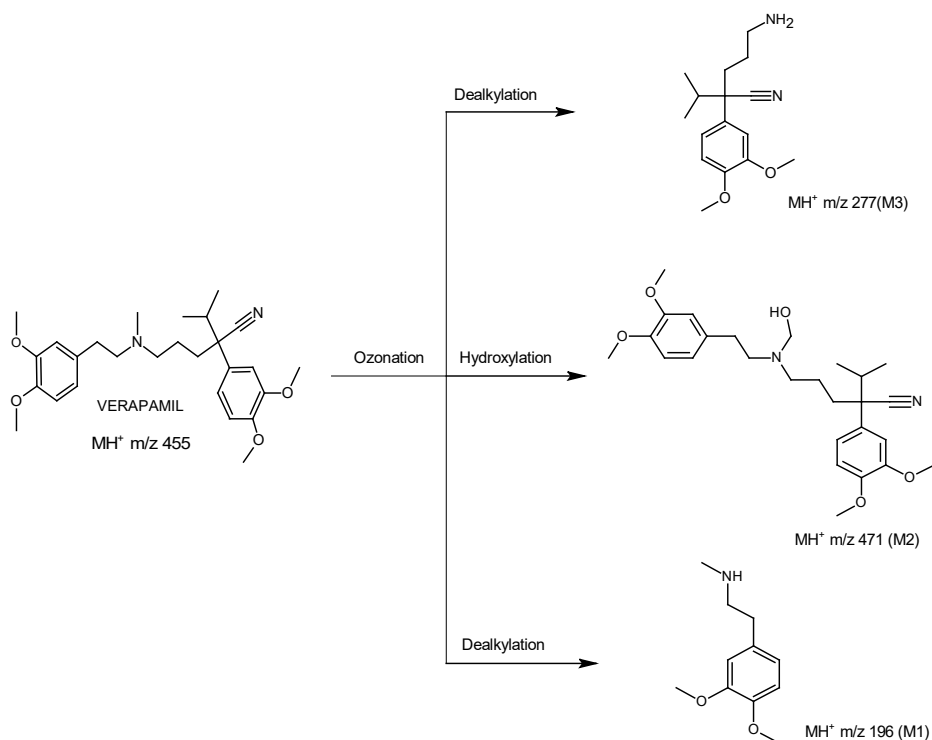
Figure 8. *Proposed degradation pathways of verapamil during ozonation.*

The decomposition of verapamil and atrazine in terms of half-life during different AOPs is represented in Fig. 9. During GAD treatment verapamil showed a half-life of 27 min while atrazine showed 28 min. Dielectric barrier discharge was more efficient than GAD in the decomposition of verapamil and atrazine with observed half-lives of 19.80 min and 24 min respectively. But the rate of decomposition is considerably increased with spark discharge and the half-lives of verapamil and atrazine were decreased to 10.70 min and 7.35 min respectively. The increased rate of decomposition during spark discharge may be due to the reactivity of the generated oxidative radicals inside the water. Ozonation was the best method to degrade verapamil and atrazine. During ozonation, verapamil and atrazine showed half-lives of 0.27 min and 0.9 min respectively.

Figure 9. *Comparison of half-lives of verapamil and atrazine at initial concentration of 5×10^{-5} M in water during different advanced oxidation processes.*
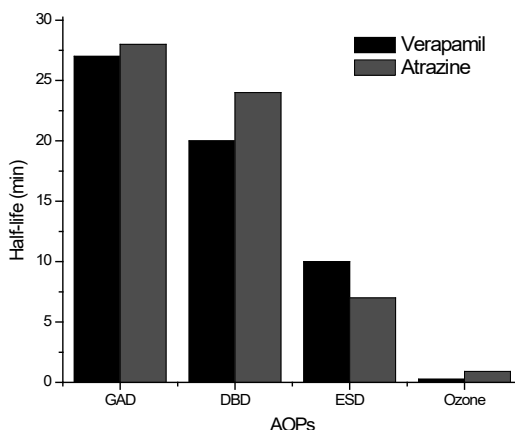
CONCLUSION

The efficiency of our GAD, DBD (chapter 2 & 3), ESD and Ozonation on the degradation of verapamil and atrazine in water was investigated. Verapamil, 97% and atrazine, 72% were degraded under GAD within 80 min at rate constants 0.026 min^{-1} and 0.025 min^{-1} respectively. The efficiency of the high power GAD in terms of the yield was 6×10^{-4} g/kWh and 2.4×10^{-4} g/kWh for verapamil and atrazine respectively. In the low power spark discharge reactor 87% of verapamil and 83% of atrazine was degraded within 40 min at rate constants 0.065 min^{-1} and 0.094 min^{-1} respectively. The corresponding energy yields were 5.1×10^{-2} g/kWh and 2.3×10^{-2} g/kWh for verapamil and atrazine respectively. Our ozonizer was very much efficient compared to our plasma devices due to its low input power. During ozonation, 100% of verapamil was removed within 1.5 min, while 99.8% of atrazine was removed within 4 min with rate constants 2.56 min^{-1} and 0.769 min^{-1} respectively. The efficiency in terms of energy yields were 9.4 g/kWh and 1.6 g/kWh for verapamil and atrazine respectively.

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CHAPTER 6

GENERAL DISCUSSION
ENGLISH SUMMARY
CZECH SUMMARY
ACKNOWLEDGMENTS
LIST OF PUBLICATIONS
TRAINING AND SUPERVISION PLAN DURING THE STUDY
CURRICULUM VITAE

GENERAL DISCUSSION

Degradation of organic pollutants in water by non-thermal plasma based advanced oxidation processes

In this work, I investigated the influence of non-thermal plasma based AOPs on the degradation of organic pollutants in water. Model organic pollutants used in this study included verapamil, atrazine and hydrocortisone. I concentrated my study on the degradation of verapamil and atrazine in water by three different types of non-thermal plasmas (dielectric barrier discharge, gliding arc discharge, and electrohydraulic spark discharge), and by ozonation.

The degradation of atrazine in water was successfully conducted in the DBD reactor. After 90 min of the DBD treatment 98% atrazine was removed from the aqueous solution of atrazine (5×10^{-5} M initial concentration). The rate constant of the degradation process was 0.029 min^{-1} and the corresponding half-life was 24 min. After 5 hours of treatment 54% of the atrazine was converted to CO_2. Similarly, the degradation of 5×10^{-5} M aqueous solution of hydrocortisone in the DBD reactor gives removal of 99% of hydrocortisone after 90 min treatment, which corresponds to the rate constant of 0.050 min^{-1} and half-life time 14 min. After five hours of DBD treatment 21% of the hydrocortisone was converted to CO_2.

The degradation rate constants of verapamil in the DBD reactor were equal to 0.097 min^{-1} and 0.035 min^{-1}, for initial concentrations of 1×10^{-5} M and 5×10^{-5} M, respectively. After four hours of treatment only 14% of the verapamil (5×10^{-5} M) was converted to CO_2. But, when the concentration is decreased to 1×10^{-5} M, the mineralization yield was increased to 98%. The higher process efficiency observed in the more dilute solution is a known feature of non-thermal plasma treatments and can be attributed to the higher ratio between the concentration of the reactive species and that of the reacting organic compounds (Marotta et al., 2011). So, I think our DBD reactor will be more efficient in degrading trace amount of biorefractory organic compounds in water.

During the degradation of verapamil in the DBD reactor, the majority of the identified compounds can be attributed to reactions of verapamil with ozone. Ozone is one of the major oxidizing species in our DBD reactor. A few intermediates are formed by the reaction of verapamil with OH radicals. Failure to detect any nitrated or nitrosated by-products of verapamil degradation suggest that the contribution of reactive nitrogen species (RNS) is marginal in the process induced by electrical discharge generated in our reactor. This is an important result relevant to issues dealing with the feasibility of an NTP-treatment stage in water remediation plants. Nitrated and nitrosated organic by-products are usually more toxic and persistent than their precursor pollutants. Detection and characterization of RNS in gas discharge plasmas and their effects on liquids is presently a hot area in NTP research (Brisset and Hnatiuc, 2012; Lukes et al., 2014).

Decomposition of verapamil using gliding arc was also studied. The gliding arc plasma discharge was also characterized by means of optical emission spectroscopy. In the UV region mainly emission spectra of diatomic species such as N_2, N_2^+ and •OH were observed. These are the characteristics of air plasmas and hydroxyl radicals are considered as an evidence of the water molecules present in the feeding gas (compressed air). These hydroxyl radicals played the key role in the decomposition of target pollutants. During water treatment experiments, the distance between the electrodes and test solution was fixed at 10 cm. The degradation of the target pollutants in the test solution is an evidence of the presence of hydroxyl radicals at this distance. It is further confirmed by the presence of hydroxylated by-product in the GAD treated verapamil solution. Benstaali et al. (2002) have demonstrated the presence of •OH and NO• in a gliding arc discharge by emission spectroscopy. These authors have also showed

that plasma in humid air was characterized by a high predominance of OH radicals over NO radicals when measuring their respective densities. I used a concentration of 5×10^{-5} M solutions of the target pollutants for the comparison of different plasma based AOPs. The rate constant of the degradation process of the verapamil solution at this concentration during GAD is 0.026 min^{-1} and the corresponding half-life time is 27 min. So I think this type of non-thermal plasma discharge is suitable to degrade biorefractory organic pollutants present in the textile, pharmaceuticals and pesticide industrial effluents.

The degradation of verapamil and atrazine by two different types of plasmas was compared with ozonation. A 5×10^{-5} M solution of verapamil and atrazine was degraded by atmospheric pressure GAD at room temperature, where 97% of verapamil and 72% of atrazine were removed within 80 min of treatment. The kinetic constants of the degradation processes of verapamil and atrazine were 0.026 min^{-1} and 0.025 min^{-1} respectively, and the corresponding half-life time were 27 min and 28 min. The power introduced in the GAD was 750 W. The energy yields of the processes were 6×10^{-4} g/kWh and 2.4×10^{-4} g/kWh for verapamil and atrazine respectively.

During spark discharge, 87% of verapamil and 83% of atrazine were degraded within 40 min. The rate constants of the degradation processes were 0.065 min^{-1} and 0.094 min^{-1} for verapamil and atrazine respectively. The power introduced in the discharge was 60 W and is very low compared to the power of GAD. As a result, relatively high energy yields 5.1×10^{-2} g/kWh and 2.3×10^{-2} g/kWh were achieved for verapamil and atrazine respectively.

Verapamil was completely removed by ozonation within 1.5 min, while atrazine was almost completely removed within 4 min. The rate constants of the degradation processes were 2.56 min^{-1} and 0.769 min^{-1} for verapamil and atrazine respectively, and the corresponding half-lives were 0.27 min and 0.9 min. The power applied during ozonation was very low (20 W) compared to plasma discharges, leading to high energy yields 9.4 g/kWh and 1.6 g/kWh for verapamil and atrazine respectively. Ozone is a strong oxidant. It can decompose in water to form OH radicals which are stronger oxidants than ozone and can immediately attack the target pollutant (Mantzavinos and Psillakis, 2004; Dantas et al., 2007; Ikehata and El-Din, 2004). I confirmed the presence of hydroxylated by-product in the ozonized verapamil solution by HPLC-MS analysis.

During DBD degradation of verapamil, isomeric intermediates were formed by oxidative opening of one of the verapamil benzene rings. The proposed products are typical for the attack of ozone on the aromatic compounds and are due to the addition of ozone, the formation of an ozonide and its following breakdown. During GAD and spark discharge treatments of verapamil, degradation by-products were obtained as a result of hydroxylation, demethylation and dealkylation reactions. Verapamil degradation by ozonation produced two dealkylated products and one hydroxylated product.

Taking into account the half-life time data between different AOPs (GAD, DBD, ESD and Ozonation) studied for the degradation of verapamil and atrazine, having observed lowest half-lives, it can be concluded that direct ozonation appears to be the suitable method for the treatment of aqueous solutions containing biorefractory organic compounds.

Conclusion and future perspectives

Widely applied AOPs, including UV/H_2O_2 and O_3/H_2O_2, require significant chemical addition and residual H_2O_2 quenching, which represent a significant portion of their operational costs. The primary benefit of the NTP based AOP is the ability to generate UV light, ozone and highly reactive hydroxyl radicals without chemical addition or the use of UV lamps. Though the true capital costs of large-scale NTP reactors for water and wastewater treatment are still

relatively unclear, our studies indicate that NTP may be a viable alternative to more common AOPs due to its chemical-free operation and high degradation efficiency. AOPs can improve the biodegradability and reduce the toxicity of organic compounds (Comninellis et al., 2008). The results of the three plasma discharges and ozonizer used in this study suggest that ozonizer is more efficient than the plasma discharges. In this context, for the degradation of biorefractory organic compounds, I suggest ozonation as a pre-treatment method to enhance biodegradability and reduce toxicity of the industrial effluents, followed by biological treatments.

In future, study will be extended to investigate the influence of ozonation on the degradation of biorefractory organic compounds in water in presence of UV light and a suitable photocatalyst. I think it will be more efficient than the ozonation alone due to the synergistic effect of ozonation, photolysis and photocatalysis. To make our plasma discharges more competitive to ozonation, further studies will be done by changing the plasma reactor geometry or by changing electrode materials and configurations. Furthermore, the influence of plasma-induced photocatalysis on the degradation of biorefractory organic compounds in water will be investigated.

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ENGLISH SUMMARY

Degradation of organic pollutants in water by non-thermal plasma based advanced oxidation processes

Water pollution by organic contaminants and other anthropogenic substances is one of the major global problems nowadays. The aquatic contaminants include pesticides, pharmaceuticals and personal care products (PPCPs), steroid hormones and synthetic dyes. The presence of these compounds in water can have potential health effects on humans, through drinking water or consumption of food irrigated by polluted water, and may also affect aquatic organisms or ecosystems. Major organic pollutants arise from chemical and pharmaceutical industries, food technologies, petrochemical plants, oil refineries, dye and textile production units, agro-industrial activities and others. Organic contaminants and their metabolites have been detected in drinking water and food, clearly showing that some of these compounds cannot be eliminated during wastewater treatment. Therefore, it is necessary to treat the effluents containing these compounds adequately before discharging them. Traditional processes such as UV irradiation at disinfection doses, coagulation, flocculation, precipitation, microfiltration and ultrafiltration are ineffective for the complete removal of organic contaminants in water, whereas the so called advanced oxidation processes (AOPs) are very effective in the oxidation of numerous organic compounds. The most widely used AOPs include heterogeneous photocatalysis based on near UV or solar visible irradiation, electrolysis, the Fenton's reaction, ozonation, ultrasound and wet air oxidation. AOPs are based on the generation of highly reactive hydroxyl radicals ($\bullet$OH), which will attack the organic pollutants. However, the lifetimes of these radicals are so short to utilize them effectively. Therefore, the direct radical generations by plasmas are widely researched.

Therefore, the main goal of my thesis was to investigate the influence of non-thermal plasma on the degradation of organic contaminants (verapamil, atrazine and hydrocortisone) in water. Three different types of plasma discharges (dielectric barrier discharge, gliding arc discharge and electrohydraulic spark discharge) were applied to investigate the degradation kinetics of the target pollutants in water. Firstly, the degradation of atrazine, verapamil and hydrocortisone were conducted successfully in the DBD reactor. After 90 min DBD treatment all the target pollutants were almost completely removed. Presence of the intermediates was confirmed by HPLC/UV analysis. The efficiency of dielectric barrier discharge on the degradation of atrazine, verapamil and hydrocortisone was investigated. Atrazine was almost completely degraded after 90 min DBD treatment. The rate constant of this process was 0.029 min^{-1} and the corresponding half-life time was 24 min. After five hours treatment time 54% of the atrazine was converted to CO_2. Hydrocortisone was also completely degraded after 90 min DBD treatment. The rate constant of this process was 0.050 min^{-1} and the corresponding half-life time was 14 min. After five hours of treatment 21% of the hydrocortisone was converted to CO_2. The degradation rate constants of verapamil in the DBD reactor were equal to 0.097 min^{-1} and 0.035 min^{-1}, for initial concentrations of 1×10^{-5} M and 5×10^{-5} M, respectively. Structure of the intermediates was identified by HPLC/MS analysis. Plausible mechanisms for the degradation of target pollutants were also proposed.

In the second part of my experiments, I characterized the gliding arc plasma discharge by means of optical emission spectroscopy. The presence of highly reactive hydroxyl radicals in the gliding arc discharge was confirmed. These hydroxyl radicals played the key role in the decomposition of the target pollutants. It is further confirmed by the presence of hydroxylated product in the GAD treated verapamil solution. Degradation kinetics and degradation mechanism of verapamil in water under GAD was investigated. The kinetic constants of the

degradation processes of verapamil and atrazine were 0.026 min^{-1} and 0.025 min^{-1} respectively. So I think this type of non-thermal plasma discharge is suitable to degrade organic pollutants present in the textile, pharmaceuticals and pesticide industrial effluents.

In the final part, the degradation kinetics of verapamil and atrazine by using electrohydraulic spark discharge and ozonation was investigated. During spark discharge, 87% of verapamil and 83% of atrazine were degraded within 40 min. The rate constants of the degradation processes were 0.065 min^{-1} and 0.094 min^{-1} for verapamil and atrazine respectively. The power introduced in the discharge was 60 W and is very low compared to the power of GAD. As a result, relatively high energy yields 5.1×10^{-2} g/kWh and 2.3×10^{-2} g/kWh were achieved for verapamil and atrazine respectively. Verapamil was completely removed by ozonation within 1.5 min, while atrazine was almost completely removed within 4 min. The rate constants of the degradation processes were 2.56 min^{-1} and 0.769 min^{-1} for verapamil and atrazine respectively. The power applied during ozonation was very low (20 W), compared to plasma discharges, leading to high energy yields 9.4 g/kWh and 1.6 g/kWh for verapamil and atrazine respectively. The degradation kinetics of verapamil and atrazine in water under DBD, GAD, ESD and ozonation has been compared. The shortest half-lives of verapamil and atrazine were observed during ozonation. So, I can say that among our AOP systems, ozonation is the most efficient in degrading verapamil and atrazine in water.

CZECH SUMMARY

Degradace organických znečišťujících látek ve vodě nízkoteplotním plazmatem na bázi pokročilých oxidačních procesů

Znečištění vody organickými kontaminanty a dalšími antropogenními látkami je jedním z hlavních globálních problémů současnosti. Vodní kontaminanty zahrnují pesticidy, farmaceutika a prostředky osobní péče (FPOP), steroidní hormony a syntetická barviva. Přítomnost těchto sloučenin ve vodě může mít potenciální dopad na zdraví lidí, a to pitím pitné vody nebo spotřebou potravin zavlažovaných znečištěnou vodou. Tyto sloučeniny mohou také ovlivnit vodní organizmy nebo ekosystémy. Hlavní organické znečišťující látky vznikají z chemického a farmaceutického průmyslu, potravinářských technologií, petrochemických závodů, ropných rafinerií, výroby barviv a textilií, zemědělsko-průmyslových aktivit a dalších. Organické kontaminanty a jejich metabolity, které byly detekovány v pitné vodě a potravinách, jasně ukazují, že některé z těchto sloučenin nemohou být vyloučeny během čištění odpadních vod. Z tohoto důvodu je nutné adekvátně ošetřit odpadní vody obsahující tyto sloučeniny v dostatečné míře před jejich vypouštěním. Tradiční postupy, jako je UV ozařování v dezinfekčních dávkách, koagulace, flokulace, srážení, mikrofiltrace a ultrafiltrace, jsou pro úplné odstranění organických znečišťujících látek ve vodě neúčinné, zatímco tzv. pokročilé oxidační procesy (POP), jsou velmi účinné při oxidaci velkého množství organických sloučenin. Mezi nejrozšířenější POP řadíme heterogenní fotokatalýzu na bázi UV, nebo viditelného slunečního záření, elektrolýzu, Fentonovu reakci, ozonizaci, ultrazvuk a oxidaci vzduchem za mokra. POP jsou založeny na bázi generování vysoce reaktivních hydroxylových radikálů (•OH), které napadají organické znečišťující látky. Nicméně, životnost těchto radikálů je pro jejich efektivní využití velmi krátká. Z tohoto důvodu jsou radikály generované plazmatem podstoupeny širokému výzkumu.

Hlavním cílem naší práce tedy bylo prozkoumat vliv nízkoteplotního plazmatu na degradaci organických polutantů (verapamil, vitrazine a hydrokortizon) ve vodě. Tři různé typy plazmatu (dielektrický bariérový výboj, klouzavý výboj a elektrohydraulický jiskrový výboj) byly použity ke sledování degradační kinetiky cílových znečišťujících látek ve vodě. Nejdříve byla úspěšně provedena degradace atrazinu, verapamilu a hydrokortizonu v reaktoru DBV. Po 90 minutách zpracování DBV byly všechny cílové znečišťující látky téměř zcela odstraněny. Přítomnost meziproduktů byla potvrzena HPLC /UV analýzou. Také byla zkoumána účinnost dielektrického bariérového výboje na degradaci atrazinu, verapamilu a hydrokortizonu. Atrazin byl téměř úplně degradován po 90 minutách ošetření DBV. Rychlostní konstanta tohoto procesu byla 0,029 min^{-1} a odpovídající poločas rozpadu byl 24 min. Po 5 hodinách ošetření bylo 54 % atrazinu přeměněno na CO_2. Hydrokortizon byl také zcela degradován po 90 minutách ošetření DBV. Rychlostní konstanta tohoto procesu byla 0,050 min^{-1} a odpovídající poločas rozpadu 14 min. Po pěti hodinách ošetření bylo 21% hydrokortizonu přeměněno na CO_2. Rychlostní konstanty verapamilu po ošetření DBV byly 0,097 min^{-1} a 0,035 min^{-1} a počáteční koncentrace byly 1×10^{-5} mol.L^{-1} a 5×10^{-5} mol.L^{-1}. Struktura meziproduktů byla identifikována pomocí analýzy HPLC/MS. Dále byly navrženy věrohodné mechanizmy pro degradaci cílových znečišťujících látek.

V druhé části experimentů byl charakterizován klouzavý výboj pomocí optické emisní spektroskopie. Přítomnost vysoce reaktivních hydroxylových radikálů v klouzavém výboji byla potvrzena. Tyto hydroxylové radikály hrají klíčovou roli v rozkladu našich cílových znečišťujících látek. To navíc potvrzuje přítomnost hydroxylovaného produktu ve zpracovaném roztoku verapamilu pomocí klouzavého výboje. Byly zkoumány degradační kinetika a degradační mechanizmus verapamilu ve vodě po ošetření KV. Rychlostní konstanta degradačního procesu

verapamilu a atrazine byla 0,026 min^{-1} a 0,025 min^{-1}. Tudíž se domníváme, že tento typ výboje nízkoteplotního plazmatu je vhodný pro využití k degradaci organických znečišťujících látek přítomných v textilních, farmaceutických látkách a v pesticidech průmyslových odpadních vod.

V závěrečné části byla zkoumána a porovnána degradace verapamilu a atrazinu pomocí dvou různých typů plazmatu a ozonizace. Při ošetření jiskrovým výbojem bylo 87 % verapamilu a 83 % atrazinu degradováno během 40 min. Rychlostní konstanta degradačních procesů byla 0,065 min^{-1} pro verapamil a 0,094 min^{-1} pro atrazin. Uvedený výkon výboje byl 60 W a je velmi nízký ve srovnání s výkonem KV. Výsledkem je, že byly dosaženy relativně vysoké energetické výtěžky 5,1 × 10^{-2} g.kWh^{-1} pro verapamil a 2,3 × 10^{-2} g.kWh^{-1} pro atrazin. Verapamil byl zcela odstraněn ozonizací během 1,5 min., zatímco atrazin byl téměř kompletně odstraněn během 4 min. Rychlostní konstanty degradačních procesů byly 2,56 min^{-1} v případě verapamilu a 0,769 min^{-1} pro atrazin. Výkon použitý během ozonizace byl velmi nízký (20 W), ve srovnání s plazmatem, což vede k vysokým výtěžkům energie 9,4 g.kWh^{-1} pro verapamil a 1,6 g.kWh^{-1} pro atrazin. Ozonizace se tudíž jeví jako nejúčinější metoda pro AOP rozklad verapamilu a atrazinu ve vodě.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my supervisor Prof. Petr Spatenka for his support, encouraging and personal guidance, patience, wide knowledge, constructive criticism, understanding, and prompt feedback. Prof. Spatenka gave me a lot of academic freedom during my study, for this, I am very grateful to him. It has been an honor for me being his student. I would like to express my deepest and sincere gratitude to my advisor, Dr. Ester Marotta (University of Padova), for the continuous support of my research and for her patience, motivation, and immense knowledge.

I gratefully acknowledge Prof. Cristina Paradisi (University of Padova), who paid attention to successful progression of all phases of my research. My warm appreciation is extended to my colleagues Dr. Pavel Kriz, Dr. Petr Bartos, Dr. Marta Horakova, Dr. Girish Kumar, Dr. Sarka Klementova, Dr. Roman Grabic, Dr. Oksana Golovko, Dr. Elisa Ceriani, Agata Giardina, Dana Spatenkova, Mohammad Abdul Momin Siddique, Pavel Osln and Pavel Cerny for their helpful suggestions and inspiration during my Ph.D. research. I would like to thank Lucie Kacerova for her academic supports and all of my colleagues from the Faculty of Fisheries and Protection of Waters in Vodnany, who helped me with my experiments and laboratory works.

I would also like to thank Dr. Alan Maslani, Dr Oldrich Zivny (Institute of Plasma Physics, Prague, Czech republic), and Tomasz Izdebski (Polish Academy of Sciences) for their guidance, encouragement and continuous support during my Ph.D. research.

It makes me very happy to mention my wife, Syama Syam, for her support and patience during thesis writing.

I dedicate this Ph.D. thesis to my parents.

This Ph.D. thesis was financially supported by -

LIST OF PUBLICATIONS

PEER – REVIEWED JOURNALS WITH IF

Krishna, S., Ceriani, E., Marotta, E., Giardina, A., Spatenka, P., Paradisi, C., 2016. Products and mechanism of verapamil removal in water by air non-thermal plasma treatment. Chem. Eng. J. 292, 35–41. (IF 2015 = 5.310)

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Krishna, S., Izdebski, T., Klementova, S., Spatenka, P., 2016. Degradation of verapamil in water using advanced oxidation processes. In: 27th Symposium on Plasma Physics and Technology, Prague, Czech Republic, 20–23 June 2016. (Poster Presentation)

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Krishna, S., Horakova, M., Klementova, S., Kriz, P., Spatenka, P., Golovko, O., Hajkova, P., Exnar, P., 2013, The synergistic effect of advanced oxidation processes to eliminate resistant chemical compounds. In: The 5th Central European Symposium on Plasma Chemistry, Balatonalmadi, Hungary, 25–29 August, 2013. (Poster Presentation)

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