Degradation of Verapamil hydrochloride in water by gliding arc discharge

CrossMark

Syam Krishna [a, *], Alan Maslani [b], Tomasz Izdebski [c], Marta Horakova [d], Sarka Klementova [e], Petr Spatenka [d]

[a] University of South Bohemia in Ceske Budejovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zatisi 728/II, 389 25 Vodnany, Czech Republic
[b] Institute of Plasma Physics AS CR v.v.i., Za Slovankou 3, 18200 Prague, Czech Republic
[c] Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-952 Gdansk, Poland
[d] Czech Technical University in Prague, Department of Materials Engineering, Faculty of Mechanical Engineering, Karlovo nam. 13, 121 35 Prague, Czech Republic
[e] University of South Bohemia, Faculty of Science, Ceske Budejovice, Czech Republic

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.

© 2016 Elsevier Ltd. All rights reserved.

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 (•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

* Corresponding author.
  E-mail address: syambalakrishna@yahoo.com (S. Krishna).

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), •OH and NO•, 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 •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^3h^{-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