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

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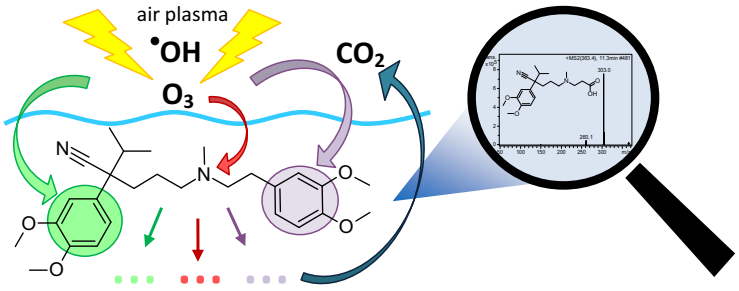
HIGHLIGHTS

- 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



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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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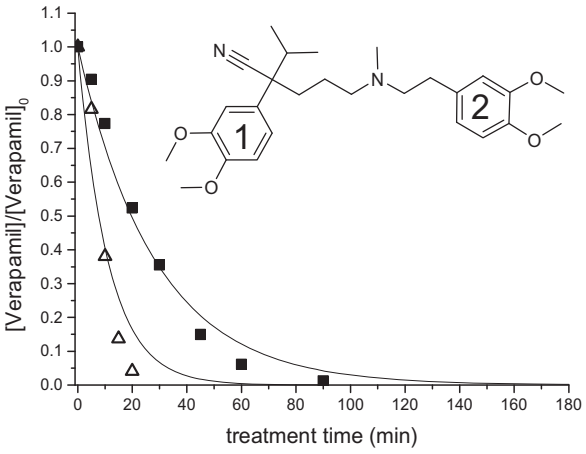

Fig. 1. Verapamil conversion as a function of treatment time in the DBD reactor (initial concentration (△) $1 \cdot 10^{-5}$ M and (■) $5 \cdot 10^{-5}$ M).

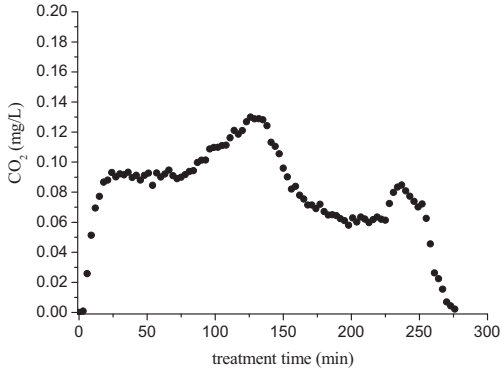

Fig. 2. Time profile for CO_2 concentration in the air flowing out of the DBD reactor during verapamil processing (initial concentration $5 \cdot 10^{-5}$ M).

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 (·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 × 75 × 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 × 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