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Fenton chemistry promoted by sub-microsecond pulsed corona plasmas for organic micropollutant degradation in water

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ABSTRACT

Differences in the liquid chemistry due to different ground electrode materials (titanium, stainless steel) were compared for corona discharges in water. The plasma was generated by applying positive high voltage pulses that are characterized by short rise times of about 20 ns, a peak voltage of 80 kV and pulse lengths of about 150–160 ns (FWHM). Phenol was admixed to the water for quantification of the bulk reaction chemistry, such as phenol decomposition and H_2O_2-formation. Optical emission spectroscopy was conducted to relate chemistry to plasma processes. Possible electrode corrosion was determined by atomic absorption spectroscopy (AAS).

The post-discharge chemistry strongly depends on ground electrode material. With stainless steel electrodes, decomposition efficiency of phenol increased by about three quarters (74.9 %) when compared with titanium electrodes. This result can be explained by dissolved metal ions corroded from the ground electrode, which catalytically decomposed the H_2O_2 that had been formed into hydroxyl radicals again. Ground electrodes were corroded due to electrochemical processes. Corrosion rates and overall reaction chemistries cannot readily be described similar to conventional DC electrochemical processes at low voltages. The repetitive application of sub-microsecond high voltage pulses has to be taken into account explicitly. Altogether, electrode materials, ground electrode corrosion and associated catalytic processes are more important for plasma processes in aqueous solutions than was recognized so far. Therefore, the effects need to be taken into account in the analysis of laboratory results as well as the development of respective novel water treatment technologies.

1. Introduction

Plasmas provide different physical and chemical active processes, such as the formation of reactive species, UV-radiation, shock waves and strong electric fields. For water purification, these combined mechanisms can provide higher efficacy than traditional or more selective water treatment methods alone. Consequently, plasmas, such as pulsed corona discharges, have been successfully applied for the decomposition of organic pollutants and the killing of bacteria [1–6].

Decomposition of organic compounds is primarily mediated by the formation of transient species, e.g. hydroxyl radicals and peroxynitrites, but also due to long-lived chemical reaction products, such as ozone and hydrogen peroxide. If not consumed during oxidation processes, reactive species eventually recombine to pure water [7].

Fundamental principles of plasma generation in water include the application of nanosecond to millisecond high voltage pulses, preferably with positive polarity, in combination with high curvatures of the high voltage electrodes. For the application of short high voltage pulses is the voltage needed to instigate streamers considerably lower for positive polarity. Furthermore, streamers initiated with a positive high voltage are longer and more fractured in appearance than more bushy streamers that are obtained for negative voltages [8]. High curvatures (wire, needle tips) are hereby corresponding to higher electric fields close to the high voltage electrode, leading to plasma filaments propagating from the high voltage electrode to the ground electrode. The

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propagation of the plasma channel continues as long as the electric field is high enough to sustain an electron avalanche process from the liquid interface towards the anode. For positive voltages is a positive space charge at the streamer head promoting further ionization of water molecules [9]. Radical species, hydroxyl and hydrogen radicals, are formed along the discharge channel primarily by electron-impact dissociation and subsequent reactions of the species with each other and the surrounding liquid [10]. Production rates depend on ambient parameters, such as liquid conductivity and pH-value, as well as on operating parameters, foremost duration and amplitude of the applied high voltage pulses.

It is known that the high voltage electrode material does effect streamer propagation [11]. The lifetime of a discharge system is generally determined by the resilience of the high voltage electrode, which can suffer from erosive and corrosive processes when enveloped by plasma [12].

Consequently, high voltage electrode material can influence plasma chemical processes in water due to the release of metal ions and solid particles by its erosion in the discharge. Liquid catalytic reactions during and after the plasma treatment are promoted and contributing to the reaction chemistry [13–21].

Concerning the mechanism of the discharge-induced erosion of high voltage electrodes, the electrolytic anodic oxidation and plasma sputtering of metal are expected to play the main role in the release of electrode material into the liquid [22].

There are no apparent reasons for any influence of ground electrode materials, since these electrodes are not directly subjected to the plasma in corona discharges. Accordingly, research conducted so far has focused on high voltage electrode processes, while ground electrodes and ground electrode materials received little to no attention.

However, the post-discharge chemistry that was observed for the degradation of organic pollutants by corona plasma suggests that degradation rates strongly depend on the ground electrode material (Banaschik et al., 2015). Solutions containing phenol had to be quickly mixed with methanol to stop ongoing degradation chemistry after the plasma was switched off. Responsible for the ongoing process are presumably radicals that are still forming independently from the plasma. Methanol acts as a scavenger for these radicals. These findings could not yet been explained satisfactorily by high voltage electrode corrosion alone. In coaxial discharge geometries is the high voltage electrode usually surounded by a grounded metal electrode. Size and exposed surface of the ground electrode are generally orders of magnitude larger than for the high voltage electrode. Therefore, processes at the ground electrode interface, corrosion and release of material into the bulk liquid might conceivable affect overall bulk reaction chemistries after all and need to be evaluated in conjunction with plasma processes accordingly.

The objective of the research presented here was to determine the influence of different ground electrode materials (titanium, stainless steel) on the liquid chemistry associated with a coaxial large volume corona discharge plasma. Plasma chemistry was investigated using phenol as a chemical probe. Byproducts of phenol decomposition and quantification of formed hydrogen peroxide allow insight in reaction chemistries and reactive species that are formed during and following the plasma treatment. Studies on chemistry were complemented by optical emission spectroscopy (OES) of the discharges in pure water. With respect to ground electrode corrosion, content of submerged and dissolved titanium or iron was measured with atomic absorption spectroscopy (AAS).

2. Materials and Methods

2.1. Experimental Setup

The discharge chamber consisted of a glass tube with an inner diameter of 47 mm and length of 138 mm, holding a volume of 240 ml. A metal mesh, made of either titanium (Ti008710/11, Goodfellow, Huntingdon, England) or stainless steel (EN 1.4571/AISI 316Ti), was attached to the inner wall of the glass tube (Fig. 1) and served as ground electrode. Surface area covered with the mesh electrode was 170 cm^2 with openings in the mesh of 0.19 mm (titanium) and 0.4 mm (stainless steel). Wire thickness of the titanium mesh was 0.23 mm and 0.2 mm for the stainless-steel electrode.

Due to the possible relevance of ground electrode material, metal composition and purity of the mesh electrodes were investigated with a SPECTROMAXx metal analyzer (SPECTRO Analytical Instruments GmbH, Kleve, Germany). Mesh electrodes of the same batch as used in the experiments were melted in an arc furnace applying argon (4.8) as inert gas to prevent cross contamination. The metal nugget was then polished and its composition determined at least five times.

Material of the titanium mesh electrode was proven almost pure titanium (99.7%). Only small impurities with elements such as iron, copper, and chromium were observed (Table 1).

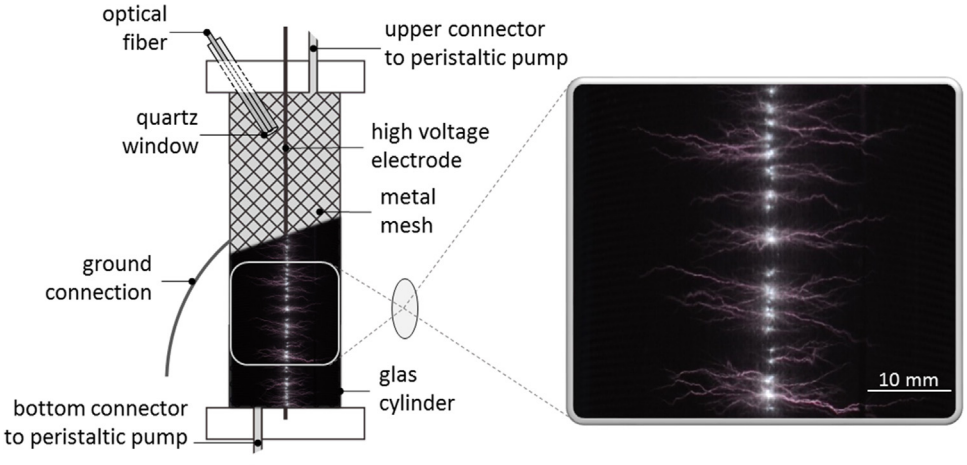

Fig. 1. Schematic of the experimental setup for pulsed corona discharges in liquids. A peristaltic pump with a pushing flow from the bottom to the top maintained a flow rate of 120 ml/min.