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Rapid degradation, mineralization and detoxification of pharmaceutically active compounds in aqueous solution during pulsed corona discharge treatment

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ABSTRACT

In the present study, plasma generated by pulsed corona discharge was used for the degradation of diclofenac, carbamazepine and ciprofloxacin. Pollutants in aqueous solution were plasma treated under two categories: single and mixed pollutant condition. Mixed pollutant condition showed an antagonistic behaviour and thus the degradation time was higher for mixed condition compared to the single condition. At different voltage and frequencies, degradation efficiency followed the trend, diclofenac>carbamazepine>ciprofloxacin. Acidic pH slightly favoured the degradation process whereas in presence of radical scavengers (HCO_3^-, CO_3^{2-} and humic acid) the degradation yield was significantly decreased. With an input power of 101.5 W, complete degradation was achieved within 4–16 min of plasma treatment for pharmaceutical's concentrations of 1–10 mg/L. As the pollutant concentration increased from 1 to 10 mg/L, the pseudo first order rate constant decreased, while yield increased. Complete degradation pathway of diclofenac, carbamazepine and ciprofloxacin in plasma treatment process are proposed by identifying the intermediates using LC-MS analysis. TOC analysis confirmed 80% mineralization within 10 min of plasma treatment for higher pharmaceutical's concentrations of 10 mg/L. The microalgae ecotoxicity study and disc diffusion test confirmed the complete detoxification of PACs that took place after 6 min of plasma treatment.

1. Introduction

The adverse effects of presence of emerging contaminants in water bodies such as pharmaceutically active compounds (PACs), pesticides and personal care products are well documented (Heberer, 2002; Jones et al., 2005; Stackelberg et al., 2004; Santos et al., 2010). Metabolised drugs excreted from humans, diagnostics compounds from laboratories and hospitals/household disposals are the prime source of PACs that contributes to the environmental contaminants (Santos et al., 2010). Worldwide, dozens of pharmaceuticals have been detected in surface water, conventional water treatment plants, wastewater treatment plant effluents, and sewage sludge (Heberer, 2002; Jones et al., 2005; Stackelberg et al., 2004). Continuous consumption of these PACs from water bodies even at sub–therapeutic concentrations have been reported to be detrimental to the humans and the aquatic organisms. Studies conducted on the aquatic organisms proved that these PACs are toxic, bio-accumulative, growth inhibitors, endocrine disrupters causing irreversible morphological and genetic abnormalities (Magdeburg et al., 2014; Santos et al., 2010). Present study used diclofenac (DCF), carbamazepine (CBZ) and ciprofloxacin (CPF) as representative PACs since they are one of the most commonly encountered contaminants in water bodies (Heberer, 2002; Santos et al., 2010). DCF is most commonly used analgesic worldwide, and its acute toxicity is very high (Santos et al., 2010). Its short-term acute toxicity was analyzed in algae and invertebrates (Thomaidi et al., 2015) and its lowest EC_{50} for phytoplankton and zooplankton was found to be 14.5 mg/L and 22.43 mg/L, respectively (Ferrari et al., 2004). CBZ is a commonly used neuroactive pharmaceutical compound. Its EC_{50} value was found to be 52.5 mg/L (5 min exposure) and 76.3 mg/L (96 h exposure) in *V. Fischeri* and *D. Magna* species, respectively (Kim et al., 2007). However, chronic toxicity of this compound is reported even at lower concentration (μg/L) on different aquatic species (Ferrari

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et al., 2003). CPF a commonly used antibiotic, was found to be at a concentration of 31000 μg/L in effluent from pharmaceutical industries (Larsson et al., 2007), which is almost 100 times higher than the LD_{50} values reported for bacteria (Larsson et al., 2007). Even if these compounds are present at very low concentrations, toxic level would increase due to continuous exposure during the lifecycle of the organism which would create adverse effects on future generations (Daughton and Ternes, 1999).

In this context, the application of advanced oxidation processes (AOPs) to reduce harmful effects of emerging contaminants has been increased for the treatment of water and wastewater. PACs degradation by ozonation (Naddeo et al., 2009), ultrasonication (Bel et al., 2009; Nie et al., 2014), advanced fenton (Karpinska et al., 2015; Sun et al., 2013), UV/H_2O_2 (Deng et al., 2013; Pérez-Estrada et al., 2005), advanced photo-catalytic oxidation (Bae et al., 2013; Doorslaer et al., 2011) and TiO_2 photo-catalytic ozonation (Márquez et al., 2014) are being studied. It is reported that some of the compounds were extremely reactive toward ozone and hydroxyl radicals. On the other hand, it was found that the halogenated pesticides and PACs were resistant to oxidative degradation (Mohamed et al., 2009; Senthilnathan and Philip, 2012). Though AOP is a promising technology, operating cost of such technologies are very high with a relatively large consumption of oxidants/catalyst (Klamerth et al., 2010). Also, degradation/treatment efficiency gets affected by the presence of certain water constituents like alkalinity and natural organic matter (Singh et al., 2016a).

Plasma processes for the treatment of micro-pollutants are gaining importance as they are one of the effective and clean technologies. Pulsed corona discharge near the water surface leads to the formation of hydroxyl radicals, hydrogen peroxides, aqueous electrons and other reactive species (Joshi et al., 1995; Locke et al., 2006). These reactive species are strong oxidants and have high capability to mineralize the complex and recalcitrant pollutants. Recently, some studies have reported the applicability of plasma for the PACs abatement from water. Magureanu et al., investigated the degradation of different PACs including antibiotics in a coaxial dielectric barrier discharge (DBD) reactor (Dobrin et al., 2013; Magureanu et al., 2011, 2010). Kim et al., investigated the degradation of nine veterinary antibiotics in DBD plasma reactor and reported different rates of degradation for different antibiotics (Kim et al., 2013). Degradation of carbamazepine, clofibric acid and iopromide in aqueous and landfill leachate solution using corona discharge over liquid surface was also investigated (Krause et al., 2011). Degradation and mineralization of diclofenac in water using pulsed corona discharge was investigated and by analyzing the intermediates, diclofenac degradation mechanism was proposed (Dobrin et al., 2013). Zeng et al. developed a novel wetted wall corona discharge reactor and shown a very good degradation yield for the treatment of ibuprofen (Zeng et al., 2015). Recently, seven pharmaceutical residues were treated by underwater corona discharge system and degradation yield ranged between 3 and 45 mg/kWh for the 90% pollutant degradation (Banaschik et al., 2015). Gerrity et al. investigated a pilot scale unit of a needle to plane geometry corona discharge reactor for the treatment of different pharmaceutical compounds (Gerrity et al., 2010). Panorel et al. used pulsed corona discharge reactor for the degradation of solution that were dispersed and showered as droplets or jets in the plasma channel (Panorel et al., 2013). The results of different plasma systems used for the degradation of PACs are summarized in Table 1.

Though different forms of plasma have been explored to treat micro-pollutant from water, there is not much information available about the effect of different environmental parameters on these treatment processes. Also, the fate of emerging pollutants during the treatment process is poorly understood. Nevertheless, it is very difficult to assess the toxicity when mixtures of emerging contaminants are present in water (Santos et al., 2010). Many times it has been reported that the intermediates formed during degradation remain toxic in spite of the parent compound degradation in treatment regime (Lu et al., 2011). Therefore, it is important to carry out ecotoxicity assays of the parent and intermediates compounds to ensure safety of treated water. To the best of author's knowledge, studies on the toxicity of the intermediate products formed in the plasma treatment process are very limited. Hence, this study aimed to evaluate the ability of corona discharge to remove PACs such as DCF, CBZ, and CPF from the water in single as well as mixed pollutant conditions. Characterization of the influencing parameters such as voltage magnitude, frequency, feed concentration, alkalinity, pH and natural organic matter on PACs removal process during treatment was systematically studied. The fate of pollutant degradation was evaluated using toxicity assay and the extent of mineralization was quantified.

2. Materials and methods

2.1. Materials

DCF, CBZ, and CPF analytical grades were procured from Sigma Aldrich, India. High purity analytical grade sodium bicarbonate (Rankem, India) and humic acid (Himedia, India) were used as radical scavengers. 0.1 M NaOH (Rankem, India) and 0.1 M HCl (Merck, India) solutions were used to change the pH of aqueous solutions. All solutions were prepared with Milli-Q water.

2.2. Experimental methods

The plasma reactor, a multiple needle-plane corona discharge system was described in our previous studies (Singh et al., 2016b, 2016c). In brief, multiple needles served as high voltage electrode, which was made up of tungsten. The high voltage electrodes were fixed at a height of 5 mm above the liquid surface. The ground electrode was made up of aluminium which fixed at the bottom part of the reactor as shown in Fig. 1. The cylindrical part of the reactor was made up of glass which served as container to acquire aqueous solution (50 mL) during the experiment. The depth of the water in the beaker was 2 cm. An iced water jacket was provided around the reactor to avoid a significant temperature rise during the experiments. A sampling port was provided at the top of the reactor. The square pulses were generated by charging a capacitor of 10 nF which was then discharged with a rotating spark gap (RSG) switch. The frequency was controlled by varying the speed of RSG. Plasma was generated in the ambient air. All the analyses were performed in aqueous solution; analyses for the off gases were not performed in this study. The recorded voltage and current waveforms are shown in Fig. S1 (supplementary material). The detailed description about the voltage-current characteristics can be found in our previous study (Singh et al., 2016d).

2.3. Analysis

An HPLC system (Dionex Ultimate 3000, USA) equipped with a C18 was used to analyse the concentration of PACs. The mobile phase consisting 80% acetonitrile and 20% water, was used for the analysis of DCF and CBZ, and for the CPF estimation 20% acetonitrile and 80% phosphate buffer (pH 4) was used. The mobile phase flow rate was kept at 1 mL/min, and injection volume of 20 μL was used. All the PACs were detected at 280 nm wavelength in UV/vis detector. The degradation efficiency of PACs was calculated from Eq. (1).