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Review

Degradation of pharmaceutical compounds in water by non-thermal plasma treatment

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ABSTRACT

Pharmaceutical compounds became an important class of water pollutants due to their increasing consumption over the last years, as well as due to their persistence in the environment. Since conventional waste water treatment plants are unable to remove certain non-biodegradable pharmaceuticals, advanced oxidation processes was extensively studied for this purpose. Among them, non-thermal plasma was also recently investigated and promising results were obtained. This work reviews the recent research on the oxidative degradation of pharmaceuticals using non-thermal plasma in contact with liquid. As target compounds, several drugs belonging to different therapeutic groups were selected: antibiotics, anticonvulsants, anxiolytics, lipid regulators, vasodilatators, contrast media, antihypertensives and analgesics. It was found that these compounds were removed from water relatively fast, partly degraded, and partly even mineralized. In order to ensure the effluent is environmentally safe it is important to identify the degradation intermediates and to follow their evolution during treatment, which requires complex chemical analysis of the solutions. Based on this analysis, degradation pathways of the investigated pharmaceuticals under plasma conditions were suggested. After sufficient plasma treatment the final organic by-products present in the solutions were mainly small molecules in an advanced oxidation state.

1. Introduction

Water pollution with pharmaceutical compounds started to be regarded as a serious environmental problem, despite their minute concentrations, due to detrimental effects on aquatic ecosystems and uncertainty regarding the effects on human health. Especially the influence of chronic exposure to complex mixtures of low concentrations of pharmaceuticals is unpredictable, since in combination the individual effects may be additive (Daughton and Ternes, 1999; Khetan and Collins, 2007).

The presence of pharmaceutical products in surface water and ground water is reported in numerous works. Some of these contaminants are persistent and accumulate in water, such as the antiepileptic carbamazepine, the antihypertensive valsartan, the antibiotic erythromycin etc. (Kasprzyk-Hordern et al., 2008). Some others are named "pseudo-persistent" – although they have short half-lives, their removal is balanced by the high continuous input, leading to a permanent background concentration in water, which is the case for the anti-inflammatory drug diclofenac (Khetan and Collins, 2007). Several pharmaceuticals can not be removed in drinking water treatment plants, as documented in various studies reporting these chemicals in drinking water (Homem and Santos, 2011; Khetan and Collins, 2007; Loraine and Pettigrove, 2006; Mompelat et al., 2009). The presence of certain pharmaceuticals in water (even in tap water) proves that conventional water treatment is unable to remove them, since they are often not designed to handle pharmaceuticals (Khetan and Collins, 2007; Mompelat et al., 2009). Therefore, alternative methods named advanced oxidation processes (AOPs) are considered for this purpose. The most frequently studied AOPs are photocatalysis, ozonation, Fenton and photo-Fenton oxidation and UV/H_2O_2 oxidation, while other emerging processes include ionizing radiation, non-thermal plasma and sonolysis (Homem and Santos, 2011; Klavarioti et al., 2009).

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Non-thermal plasma in liquid and gas-liquid environments generates in situ oxidizing species, such as hydroxyl radicals, ozone, hydrogen peroxide, peroxynitrites etc., which degrade the organic contaminants in water. The formation of ·OH radicals in water-containing plasmas is evidenced by optical techniques (Bruggeman et al., 2009; Kanazawa et al., 2011) and chemical probe measurements (Kanazawa et al., 2011; Marotta et al., 2011). The major reaction channels for the production of ·OH are discussed in detail in Bruggeman and Schram (2010). Ozone generation in discharges above water is reported in numerous studies (Lukes et al., 2004, 2005) and its transfer to the liquid is also suggested by several authors (Dobrin et al., 2013; Hoeben et al., 1999; Marotta et al., 2011). Experimental data on the formation of H_2O_2 in a wide variety of plasma–liquid systems are summarized in the review of Locke and Shih (2011). The generation of peroxynitrites in discharges in air–liquid environment is discussed in detail in Brisset et al. (2011), Brisset and Hnatiuc (2012) and Lukes et al. (2014). All these oxidizing species contribute in different proportions to the degradation of water contaminants by plasma, and their main reactions with organic compounds are addressed in Lukes et al. (2012).

Non-thermal plasma in contact with liquid recently started to be investigated for the degradation of pharmaceutical compounds in water (Gerrity et al., 2010; Krause et al., 2009; Magureanu et al., 2010, 2011). A recent review summarizes results published between 1996 and 2013 on water decontamination from organic compounds by plasma, and also includes a section on pharmaceuticals degradation, which is discussed in terms of removal efficiency and energy yield (Hijosa-Valsero et al., 2014).

The present work reviews results on the degradation of pharmaceutical compounds in water by non-thermal plasma (NTP). It includes a short presentation of the sources of pharmaceuticals in the environment and an overview of the most important classes of pharmaceuticals detected in water. The main part of the paper is dedicated to the results obtained on the degradation of various pharmaceutical compounds by non-thermal plasma in contact with liquid. The removal rate of the target compounds and the energy efficiency of the plasma removal process are comparatively discussed. Information on the mineralization degree (reflected by the removal of total organic carbon) as well as the biodegradability of the treated solutions is provided. The reaction products resulting from the degradation of the investigated compounds are also addressed and the degradation pathways of the pharmaceuticals under plasma conditions are discussed.

2. Sources of pharmaceutical compounds in water

The consumption of pharmaceutical compounds has been rising considerably in the last years, due to several reasons, such as the population growth and the inverting age structure, as well as the appearance of new target age groups, the discovery of new drugs or of new uses for existing ones (Khetan and Collins, 2007). Consequently, the risk of water contamination with these chemicals has increased. Pharmaceuticals and their metabolites can enter the environment via several routes, illustrated in Fig. 1.

Excretion is considered as one of the main sources of contamination of water resources. Excreted human pharmaceuticals pass through the sewage network and reach wastewater treatment plants (WWTP). Many are not completely eliminated during this treatment, since WWTP are often not designed to handle such chemicals (Khetan and Collins, 2007; Mompelat et al., 2009), and thus are transported to surface water. Excreted veterinary pharmaceuticals firstly contaminate soil mainly by manure spreading in the fields and then, by run-off and leaching, reach surface and ground water. The sludge from WWTP, which may contain undegraded pharmaceuticals, is also used as fertilizer, having the same fate as described above. Veterinary pharmaceuticals may also be directly discharged in water in case of their application in aquaculture. Improper disposal of unused medicines deposited in landfills may contribute to ground water contamination by leaching. Release of pharmaceutical waste from manufacturing facilities or accidental spills during manufacturing or distribution can also be regarded as a source of water contamination. Finally, contaminated surface and ground water may reach drinking water treatment plants (DWTP), but some pharmaceuticals can still escape this treatment, and thus reach tap water.

3. Pharmaceuticals frequently detected in water

The main therapeutic classes and specific pharmaceuticals significant from the point of view of water contamination are shown in Fig. 2. These compounds are detected in influents and effluents of WWTP, surface water, ground water and some of them even in drinking water.

The occurrence of antibiotic residues in the environment is often reported, in the higher μg/L range in hospital effluents, lower μg/L range in municipal wastewater and ng/L in surface, sea and groundwater (Evgenidou et al., 2015; Homem and Santos, 2011; López-Serna et al., 2012; Van Doorslaer et al., 2014; Watkinson et al., 2009), as well as in tap water (Loraine and Pettigrove, 2006; Yiruhan et al., 2010). The main concern is the emergence of antibiotic-resistant bacteria (Daughton and Ternes, 1999), followed by the persistence in the environment of some antibiotics, such as sulfonamides and fluoroquinolones, toxicity to aquatic organisms, and sometimes phytotoxicity (Homem and Santos, 2011; Khetan and Collins, 2007; Van Doorslaer et al., 2014).

Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) provide analgesic, antipyretic and anti-inflammatory effects. Due to very high consumption, they are ubiquitous in WWTP influents and effluents, in concentrations up to tens of μg/L (Evgenidou et al., 2015; Petrović et al., 2014) and in surface waters, in concentrations of tens to hundreds ng/L (Lolić et al., 2015; López-Serna et al., 2012; Luo et al., 2014; Petrović et al., 2014; Rabiet et al., 2006) and some, such as aspirin, acetaminophen, diclofenac, ibuprofen, naproxen, ketoprofen, are also reported in drinking water (Houtman et al., 2014; Petrović et al., 2014; Rabiet et al., 2006; Wen et al., 2014).

One of the most frequently reported pharmaceuticals in the environment is clofibric acid, which is the active metabolite of several widely used blood lipid regulators. It is detected in influents and effluents of wastewater treatment plants, in concentrations up to tens of μg/L (Evgenidou et al., 2015; Luo et al., 2014), surface water (López-Serna et al., 2012; Wen et al., 2014), ground water (Heberer and Stan, 1997; Heberer, 2002; Postigo and Barcelo, 2015) and even in tap water samples (Heberer and Stan, 1997; Houtman et al., 2014), suggesting the persistent behavior and high mobility of this chemical in the aquatic environment (Khetan and Collins, 2007). Besides clofibric acid, gemfibrozil and benzafibrate are also detected in surface water (López-Serna et al., 2012; Petrović et al., 2014; Vieno et al., 2005).

Among the various classes of antihypertensives, which lower blood pressure by different means, the most widely used are diuretics, ACE inhibitors, calcium channel blockers, beta blockers and angiotensin II receptor antagonists. Beta blockers such as metoprolol, atenolol and propranolol, are the most frequently reported in surface water, in concentrations up to tens of ng/L (López-Serna et al., 2012; Petrovic et al., 2014), ground water (Postigo and Barcelo, 2015), and sometimes drinking water (Petrovic et al., 2014), followed by the diuretic furosemide (López-Serna et al., 2012; Petrovic et al., 2014).