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An advanced oxidation process for wastewater treatment to reduce the ecological burden from pharmacotherapy and the agricultural use of pesticides

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ABSTRACT

The presence of pharmaceuticals and pesticides in the environment has been frequently confirmed and has been recognized as a potential threat to the environment. This paper describes an advanced wastewater treatment process based on the electrochemical oxidation of pollutants, and the development of a sensitive analytical method to monitor the analytes in wastewater samples comprised of solid phase extraction followed by LC–MS/MS analysis. The analytical method was successfully validated and achieved low limits of quantification (2.5–12.5 ng/L).

In our survey of some Slovenian wastewater samples, the occurrence of seven compounds from the list of ten monitored pollutants was confirmed and quantified. Bisoprolol, carbamazepine, ciprofloxacin, and metoprolol were determined in every assayed sample, while diclofenac reached the highest concentration (2 μg/L). Therefore, under laboratory conditions the degradation efficiency of investigated compounds by various electrode materials, including boron-doped diamond (BDD), mixed metal oxide (MMO), platinum electrode, and high voltage sparks (HVS) were tested. The applicability of methodologies was evaluated on a synthetic mixture comprised of eight frequently prescribed pharmaceuticals (bisoprolol, carbamazepine, ciprofloxacin, clofibric acid, diclofenac, fluoxetine, imatinib and metoprolol) and two pesticides (atrazine, simazine). The BDD and MMO electrodes showed >85% degradation in 60 min of treatment for the majority of the compounds, while the platinum electrode and HVS revealed low overall degradation efficiency. In addition, the BDD electrodes demonstrated an operational efficiency up to 70% also in a complex matrix of wastewater samples.

Based on our observations of the prototype electrolytic cell degradation efficiency of some pollutants commonly presents in wastewaters, one can assume that this new technology could be a viable and feasible option to upgrade existing wastewater treatment plants in order to achieve a significantly greater cleaning efficiency, and to lessen the ecological burden.

1. Introduction

The presence of pharmaceuticals and pesticides in the environment has been frequently confirmed, and has been recognized as a potential threat to the environment (Boix et al., 2015). The intensity of population ageing frequently dictates polypharmacy, and consequently an increased use of drugs. A significant part of the consumed xenobiotics can enter the environment either in unchanged form or as metabolites (Wooten, 2012). In addition, water sources in the environment are also under threat because of the tons of pesticides annually used in agriculture. A wide range of pharmaceuticals and their metabolites as well as pes-

Abbreviations: AOPs, advanced oxidation processes; BDD, a boron doped diamond; MMO, mixed metal oxide; HVS, high voltage spark; RH, retirement home; DE, degradation efficiency; WWTP, wastewater treatment plant.

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ticides have been found in wastewater treatment plant (WWTP) influents and effluents, consequently in surface water, and also in trace concentrations in drinking and tap water (Gracia-Lor et al., 2010; Huerta-Fontela et al., 2011; Kock-Schulmeyer et al., 2013; Richardson and Ternes, 2014; Roberts and Thomas, 2006; Zuccato et al., 2005). The pharmaceuticals are designed to be relatively stable in a biological environment. At the same time, they have an extremely high potency compared to all other pollutants, since they were designed to bind specifically and with a high affinity to biological receptors, exerting pharmacological actions in very low concentrations (ppb-ppt range). Therefore, it can be predicted that at least some compounds may pose a threat to ecosystem due to their high potency and persisting stability in ecosystems. Indeed, there were numerous studies regarding the harmful effects on living organisms caused by discharged pharmaceuticals in the environment (Castiglioni et al., 2005; Daughton and Ternes, 1999; Kolpin et al., 2002; Stackelberg et al., 2004). The growing use of these compounds in combination with low degradation efficiency by conventional methods in WWTPs has indeed resulted in new environmental problems (Castiglioni et al., 2005).

Wastewater treatment plants have not been primarily constructed to treat and remove these types of compounds, and consequently a large amount of them can enter the aquatic system (Hernando et al., 2006; Kolpin et al., 2002; Petrović et al., 2003, 2014). Thus, the elimination ability of pharmaceuticals and pesticides by WWTPs must be considered as an important issue in terms of controlling the ecological burden. Their potential possible activity against non-target organisms is a main reason for applying more advanced technology for degradation of pharmaceuticals in water. In recent years, the development of wastewater treatment processes has become extremely challenging. Physicochemical methods, such as absorption by coagulation and sedimentation (Westerhoff et al., 2005) and activated carbon (Bolong et al., 2009; Westerhoff et al., 2005), membrane filtration, as well as degradation by ozone (Ternes et al., 2003), UV irradiation and chlorine (Adams et al., 2002; Pinkston and Sedlak, 2004) have been applied so far as conventional tertiary wastewater treatment steps. Since many of them are energy- and material-demanding, they cause the formation of waste and toxic substances or do not offer a complete pollutant degradation and removal, so various more efficient methods emphasizing hydroxyl radical production have been developed. They are called 'advanced oxidation processes' (AOPs) and represent processes combining the use of ozone in combination with UV, H_2O_2, TiO_2, ultrasound, or irradiation with an electron beam, etc. and not ozone-based processes like H_2O_2 in combination with UV, Fe salts (Fenton reagent), electron cavitation, ultrasound, photo catalysis (UV + TiO_2), etc. – and in recent years electro-catalytic oxidation as an environmentally-friendly process. For example, only UV irradiation was insufficient to be considered as a feasible removal option (Adams et al., 2002; Hansen and Andersen, 2012), but membrane filtration technology, especially reverse osmosis, achieved an almost complete removal. The main disadvantage was high energy consumption, which made it more unfavorable (Bartman et al., 2010). Since conventional wastewater treatment processes do not achieve a complete degradation of complex and persistent organic compounds in wastewater, and certain compounds even impede the treatment process (Bolong et al., 2009), advanced processes such as AOPs seem to be promising and their abilities for efficient oxidation have already been demonstrated (Feng et al., 2013).

The efficiency of AOPs depends on the generation of reactive free radicals, in most cases hydroxyl radicals (Feng et al., 2013; Pérez et al., 2010). Initially, anodic oxidation was one of electrochemical technologies which was successfully applied in the treatment of wastewater. In terms of anodic oxidation used for degradation of pharmaceuticals (Altun et al., 2009; Dogan et al., 2007; Faber et al., 2014; Feng et al., 2013; Klavarioti et al., 2009; Michael et al., 2013; Olvera-Vargas et al., 2014; Urtiaga et al., 2013) and pesticides (Ikehata and Gamal El-Din, 2005; Ikehata et al., 2008) various materials have been used for anodes: graphite, platinum, IrO_2, RuO_2, SnO_2, PbO_2, Ti coated with oxides of Ru, Ir, Ta, and others (Bhaskar Raju et al., 2009; Sopaj et al., 2015; Tan et al., 2011). Recently it was shown that an organic oxidation productively takes place either on a boron-doped diamond (BDD), mixed metal oxide (MMO), or platinum (Pt) electrodes (Feng et al., 2013; Simond et al., 1997; Sopaj et al., 2015). The oxidation of organic substances on BDD, MMO, or Pt electrodes is mediated by hydroxyl radicals generated directly from water as shown in (Eq. (1)). Hydroxyl radicals are either powerful, non-selective oxidizing agents capable of reacting with organic matter until their total mineralization, or mediators that generate other reactive oxygen species (O_3 and H_2O_2), which may react with organic matter as well.

$$\text{BDD} + H_2O \rightarrow \text{BDD}(^{\bullet}OH) + H^+ + e^- \quad (1)$$

Previous research studies discussed various anode materials, and have shown a great difference in terms of electrochemical oxidation efficiency, cost-effectiveness, and stability – and all performed mostly under laboratory conditions (Vona et al., 2015; Zhou et al., 2011). Therefore, the aim of our work was to investigate the electrode materials proposed for the anode in an AOP under laboratory conditions, to identify the optimal one, and to evaluate it in terms of degradation efficiency of the selected organic compounds from real wastewater samples. A list of 10 representative compounds from a wide range of therapeutic classes was compiled based on their frequency of use to evaluate their presence and removal from wastewater: antibiotic ciprofloxacin, beta blockers metoprolol and bisoprolol (both widely used among the elderly), nonsteroidal anti-inflammatory drug diclofenac (the 3rd most prescribed drug in Slovenia in 2013), antiepileptic carbamazepine (a long history of use and persistent), antidepressant fluoxetine, anti-cancer drug imatinb, clofibric acid (a metabolite of clofibrate), as well as atrazine and simazine as agricultural pollutants (Gu et al., 2010; Heberer and Stan, 1997; Huerta-Fontela et al., 2011). Furthermore, manifest of their aquatic ecotoxicity (growth retardation, embryo developmental abnormalities, bacterial resistance to antibiotics, etc.) has been already reported elsewhere (Fent et al., 2006; Santos et al., 2010; Verlicchi et al., 2012). The electrochemical treatments were carried out in an electrolytic cell using various electrode materials. The effectiveness of a treatment was monitored by a newly developed and validated sensitive LC–MS/MS method. The optimal treatment procedure was firstly applied to synthetic (spiked) water mixtures, as well as to wastewater samples obtained from WWTP effluent and from direct discharge from retirement homes.

2. Materials and methods

2.1. Chemicals and reagents

Selected standards for atrazine, carbamazepine, clofibric acid, diclofenac, fluoxetine, metoprolol, and simazine were obtained from Sigma-Aldrich (Germany), imatinib and bisoprolol fumarate from Sequoia Researcher products (UK), ciprofloxacin from AppliChem GmbH (Germany), and radiolabeled $^{13}C_6$ haloperidol as an internal standard (IS) from Alsachim (France). The reagents used for standard and sample preparation including methanol (MeOH), acetonitrile (ACN), acetic acid (98%), formic acid (98–100%), and potassium dihydrogen phosphate were purchased from Merck (Germany). Ultra-pure water was obtained from a Millipore Milli-Q water purification system A10 Advantage (Millipore Corporation, Bedford, MA, USA).