Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Electrochemical oxidation remediation of real wastewater effluents — A review

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ARTICLE INFO

Article history:
Received 11 July 2017
Received in revised form 19 September 2017
Accepted 20 September 2017
Available online 28 September 2017

Keywords:
Wastewater treatment
Boron-doped diamond
Dimensionally stable anodes
Disinfection processes
Persistent organic pollutants
Anodic oxidation

ABSTRACT

Fate and health risks associated with persistent organic pollutants present in water effluents are one of the major environmental challenges of this century. In this paper, the electrochemical advanced oxidation process electrochemical oxidation is reviewed for its performance over the treatment of actual industrial and urban effluents. The electrochemical treatment of industrial effluents resulting from textile dyeing, petrochemical, paper mill, tannery industry as well as the treatment of domestic and urban wastewaters are discussed. Furthermore, the combination of electrochemical oxidation with other water treatment technologies as pre-treatment, post-treatment, and integrated treatment is also examined.

Contents

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http://dx.doi.org/10.1016/j.psep.2017.09.014
0957-5820/

1. Introduction

The presence of persistent organic pollutants (POPs) in water has emerged as a great environmental concern since the last decade (UNESCO, 2012; United Nations, 2004; Rühmland et al., 2015). Although these pollutants are usually detected at trace concentration level (i.e., ng up to mg) in water bodies (Rühmland et al., 2015; Eljarrat and Barceló, 2003), their presence – even at low concentration – produces hazardous effects owing to their toxicity, carcinogenicity, and mutagenicity (Eljarrat and Barceló, 2003; Verlicchi and Zambello, 2015; Umbuzeuro et al., 2005; Shengquan et al., 2008; Subedi and Kannan, 2015). Unfortunately, these pollutants are usually highly recalcitrant and hardly removed by conventional wastewater treatment technologies (Subedi and Kannan, 2015; Brillas and Martínez-Huitle, 2015). Hence, alternative and efficient technologies for the removal of POPs to recover and reuse important water resources are required. In order to face this environmental challenge, electrochemical advanced oxidation processes (EAOPs) have been highlighted as a potential subclass of alternative water treatment technologies. EAOPs have attracted increasing interest because they could completely mineralise highly refractory organic pollutants, such as pharmaceuticals (Domínguez et al., 2012; Cavalcanti et al., 2013; Olvera-Vargas et al., 2014), pesticides (Martínez-Huitle et al., 2008; Samet et al., 2010; Oturan et al., 2015), azo dyes (Umbuzeuro et al., 2005; Florenza et al., 2014; Labiadh et al., 2015), and even carboxylic acids (Garcia-Segura and Brillas, 2011; Scialdone et al., 2011; Garcia-Segura et al., 2016). Apart from the efficient remediation of POPs, the EAOPs also present several characteristics of environmental significance, such as: (i) mild operation conditions under ambient temperature and pressure, (ii) compact reactors of smaller physical footprint that require lesser land space requirement, (iii) no additional requirement of auxiliary chemicals, which means that transportation and storage of these chemicals are not required, (iv) do not produce secondary waste streams that require further treatment, (v) could be easily combined with other conventional water treatment technologies, (vi) could be fully automatised and (vii) present affordable capital and operational costs (Grafias et al., 2010; Garcia-Segura and Brillas, 2014; Moreira et al., 2015; Rivera et al., 2015). All these important characteristics make EAOPs environmentally friendly technologies with a small carbon footprint.

Among the EAOPs, the anodic oxidation (AO) or electrochemical oxidation (EO) is the most studied electrochemical process due to its versatility and ease of scalability (Brillas and Martínez-Huitle, 2015; Panizza and Cerisola, 2009). In the literature, the vast majority of experimental studies on EO and other EAOPs deal with the oxidation of POPs in synthetic wastewaters, while only a few studies have been devoted to synthetic water matrices and real wastewater effluents. The present review paper aims to understand the potential application and constraints of EO processes for the remediation of synthetic water matrices and real wastewater effluents at laboratory and pilot plant scales. The fundamentals of EO technology are briefly discussed to better understand its operation and its possible implications, the basis for environmental remediation of POPs, as well as the potential combination with other water technologies that are used as either pre- or post-treatment.

2. Fundamentals

2.1. *Electrochemical oxidation*

Generally, an electrochemical process involves oxidation reaction at the anode and reduction reaction at the cathode. The fundamental idea of electrochemical processes is taking advantage of the redox reactions occurring at both anode (e.g. oxidation of pollutants) and cathode (e.g. reduction of heavy metals) to remove pollutants, which have been widely used as a heavy metal remediation solution (Coman et al., 2013; Nancharaiah et al., 2015). Meanwhile, the application of electrochemical processes in removing organic pollutants resides in the possibility of attaining partial degradation or complete mineralisation by the anodic oxidation reaction. Thus, the electrocatalytic properties of anodic materials, which are used, play an indisputable role in the organic removal efficiency of the EO technology. The oxidation of organic pollutants in an electrolytic cell occur *via* two different pathways (Brillas and Martínez-Huitle, 2015; Garcia-Segura and Brillas, 2011; Panizza and Cerisola, 2009), namely (i) direct anodic oxidation, and (ii) indirect oxidation.

The direct anodic oxidation or electrolysis occurs directly on the anode (M) and involves direct charge transfer reactions between the anode surface and the organic pollutants involved. The mechanism only involves the mediation of the electrons, which are capable in oxidising some organic pollutants at defined potentials more negative the oxygen evolution reaction (OER) potential (Garcia-Segura and Brillas, 2011; Panizza and Cerisola, 2009). The direct electrolysis usually requires prior adsorption of pollutants onto the anode surface (see scheme in Fig. 1), which is the rate-limiting process and does not lead to the overall combustion of organic pollutants. When the direct electrolysis is conducted at applied potentials lower than the potential of water oxidation reaction, the electrodes are susceptible to surface poisoning and further inhibiting the EO process (Rodgers et al., 1999; Rodrigo et al., 2001).

On the other hand, the indirect EO processes are mediated by the in situ electro-generation of highly oxidant species at the electrode surface. Different kinds of oxidant species can be generated by the EO process, but in this review we highlight the electro-generation of (i) reactive oxygen species and (ii) chlorine active species.

2.1.1. *Electro-generation of reactive oxygen species*

The indirect EO by reactive oxygen species is based on the electro-generation of adsorbed hydroxyl radical ($^{\bullet}OH$) ($E^{\circ} = 2.8$ V/SHE) onto the anode surface as an intermediate of