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Electrochemical oxidation of humic acid and sanitary landfill leachate: Influence of anode material, chloride concentration and current density

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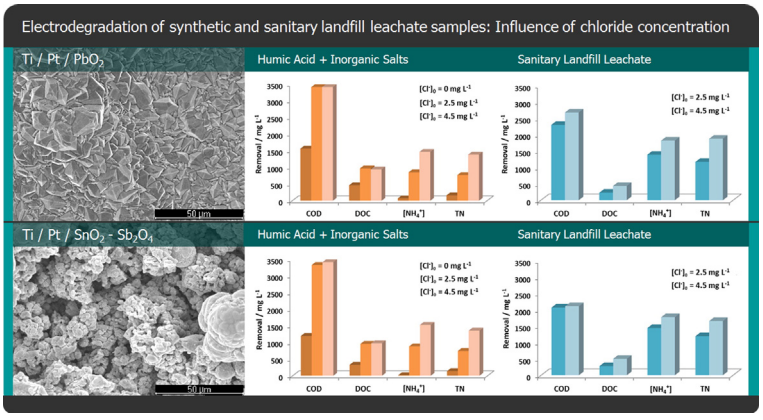
HIGHLIGHTS

- Ti/Pt/PbO_2 and Ti/Pt/SnO_2–Sb_2O_4 anodes have similar performance to that of BDD.
- Ti/Pt/PbO_2 presents better performance than Ti/Pt/SnO_2–Sb_2O_4 for pollutants removal.
- Ti/Pt/PbO_2 promotes the lowest nitrate formation and the highest TN elimination rate.
- Optimum COD/[Cl^-] for maximum chloride indirect oxidation performance
- COD and TN removals increase with current density and in the presence of Cl^-.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of applied current density and chloride ion concentration on the ability of Ti/Pt/PbO_2 and Ti/Pt/SnO_2–Sb_2O_4 anodes for the electrochemical oxidation of humic acid and sanitary landfill leachate samples was assessed and compared with that of BDD anode. For the experimental conditions used, results show that both organic load and nitrogen removal rates increase with the applied current density and chloride ion concentration, although there is an optimum COD/$[Cl^-]_0$ ratio below which there is no further increase in COD removal. Metal oxide anodes present a similar performance to that of BDD, being the results obtained for Ti/Pt/PbO_2 slightly better than for Ti/Pt/SnO_2–Sb_2O_4. Contrary to BDD, Ti/Pt/PbO_2 promotes lower nitrate formation and is the most suitable material for total nitrogen elimination. The importance of the optimum ratio of Cl^-/COD/NH_4^+ initial concentrations is discussed.

1. Introduction

Electrochemical oxidation (EO) is the most popular electrochemical procedure for removing organic pollutants from wastewaters (Brillas and Martínez-Huitle, 2015) and its application in the treatment of complex effluents, such as sanitary landfill leachates, has been reported by

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numerous authors with promising results (Anglada et al., 2011, 2010a, 2010b, 2009a; Fernandes et al., 2015, 2014a, 2014b, 2012,; Panizza and Martinez-Huitle, 2013; Panizza et al., 2010; Pérez et al., 2012; Turro et al., 2011; Urtiaga et al., 2012). Since the anode material strongly influences the selectivity and the efficiency of the EO process (Brillas and Martínez-Huitle, 2015), different anode materials have been investigated, being the highest organic oxidation rates and the highest current efficiencies attained with boron-doped diamond (BDD) electrodes (Anglada et al., 2009b; Fernandes et al., 2015). This is due to the chemical, physical and electrochemical outstanding properties of this anode material, when compared with other conventional electrode materials (Fryda et al., 1999; Panizza and Cerisola, 2005). Removals of 100% in chemical oxygen demand (COD) and ammonium nitrogen (AN) contents have been achieved for the EO of sanitary landfill leachates using BDD anodes (Anglada et al., 2010b; Cabeza et al., 2007a, 2007b). However, despite the BDD electrodes exceptional properties and the good results obtained when this electrode is used, the most common BDD electrodes are Si-supported, which present difficulties related to their industrial transposition, due to the fragility and the relatively low conductivity of the Si substrate (Brillas and Martínez-Huitle, 2015). BDD films synthesized on Nb, Ta and W have also shown promising results, but their large-scale utilization is impossible due to the unacceptably high costs of these metal substrates (Brillas and Martínez-Huitle, 2015). Therefore, it is necessary to study the application of new electrode materials that can successfully remove the pollutants with lower capital and operational costs. Among the different electrode materials studied for the EO process, metal oxides have shown promising results, even when used to treat complex effluents such as sanitary landfill leachates (Chiang et al., 1995; Cossu et al., 1998; Feki et al., 2009; Fernandes et al., 2014b; Panizza and Martinez-Huitle, 2013; Panizza et al., 2010). A study comparing BDD and two different metallic oxides anodes, Ti/Pt/PbO_2 and Ti/Pt/SnO_2–Sb_2O_4, in the EO of a sanitary landfill leachate showed that metal oxides anodes promoted COD removals similar to that of BDD and lower energy consumptions, although the difference between the COD and dissolved organic carbon (DOC) removals for BDD was less pronounced than for the other anodes, suggesting that BDD promotes more easily the complete combustion of the organic matter (Fernandes et al., 2014b). Also, regarding nitrogen removal, metal oxide anodes were found to be more effective in the ammonium removal, whereas BDD was more efficient in the organic nitrogen removal (Fernandes et al., 2014b). In a similar study, Panizza and Martinez-Huitle (2013) compared the performance of BDD, PbO_2 and $TiRuSnO_2$ and different results were achieved, since BDD yielded complete COD, color and AN removal, whereas with PbO_2 a residual COD remained and, when $TiRuSnO_2$ was used, the organic pollutants were only partially oxidized. Also, faster oxidation rate, higher current efficiency and lower specific energy consumption were achieved using the BDD anode, resulting, consequently, in lower treatment costs (Panizza and Martinez-Huitle, 2013). Although the results presented by Fernandes et al. (2014b) and Panizza and Martinez-Huitle (2013) were different, it must be noticed that whereas the leachate samples used by the first authors presented COD/AN/chloride concentrations of 6200/480/4700 mg L^{-1}, the leachate samples used by the second authors only had 780/266/1800 mg L^{-1}. Also, the lead and stannous electrodes used by Fernandes et al. (2014b) had a Pt layer between the titanium foil and the metallic oxide, which was not the case of the electrode used in the other study.

Besides the anode material, applied current density and chloride ion concentration also have shown to play an important role in the EO performance. Several authors reported an increase in COD and AN removals by increasing the applied current density or the chloride ion concentration (Anglada et al., 2011, 2009a; Bashir et al., 2009; Cabeza et al., 2007a, 2007b; Chiang et al., 1995; Cossu et al., 1998; Feki et al., 2009; Moraes and Bertazzoli, 2005; Pérez et al., 2012; Turro et al., 2011; Zhang et al., 2011, 2010). In a study performed by Anglada et al. (2009a), it was observed that an increase in the current density from 300 to 450 A m^{-2} scarcely affected the removal rate of the organic matter, but at higher current densities the oxidation levels increased with current density, which suggested a change in the oxidation mechanism of the organic matter, since at high current densities mediated electrochemical oxidation processes, such as indirect oxidation by hydroxyl radicals and by other electrogenerated oxidants, had a strong influence. Also, the influence of the applied current density was much more significant in the ammonium oxidation than in the COD removal, even if ammonium removal occurred at a slower rate than that of COD. Different results were achieved by Zhang et al. (2011, 2010) that reported an increase in the COD removal with increasing current density, but only up to a certain value of current density, from which a further increase would lead to a decrease in the COD removal rate. This behavior was explained by the authors taken into account that, at lower current densities, organic matter anodic oxidation with hydroxyl radicals was favored against chlorine evolution at the anode, and thus the increase in current density would lead to the increase in COD removal rate. However, a further increase in the current density would enhance chlorine generation and hence the anodic oxidation with hydroxyl radicals would be depressed. In the meantime, the AN removal would be dominant in the competition between AN and COD removal by the indirect oxidation, via active chlorine, and, consequently, COD removal rate would decrease with current density (Zhang et al., 2011, 2010). The effect of the indirect oxidation through chlorine/hypochlorite species in the EO treatment of landfill leachates had already been studied by Chiang et al. (1995) that provided additional chloride ions to the leachate as supporting electrolyte during the electrolysis. The experimental results showed that when 2.5 g L^{-1} chloride was added, both COD and AN removal rates increased, being the AN removal rate much higher than that of COD.

Pérez et al. (2012) identified nitrogen and nitrate as the main ammonium oxidation products obtained in the EO of a landfill leachate with a BDD anode: for high chloride concentration, nitrogen gas was the main product, having the percentage of ammonium transformed into nitrogen gas increased from 74 to 85%, after 4 h, when the chloride content was increased from 5 to 20 g L^{-1}, while the percentage of ammonium converted into nitrate varied from 26% to 15%. Also, the formation of chloramines, chlorate and perchlorate was hindered by increasing the initial concentration of chloride ions.

Since the difficulties in treating complex effluents such as landfill leachates is associated to the presence of persistent organic pollutants, the oxidation of synthetic wastewaters with different test substances has been investigated. The electrochemical oxidation of synthetic solutions, containing glucose and humic acid using BDD anodes was performed by Woisetschläger et al. (2013) and the results showed that the degradation process was increasingly inhibited by the increase in the amount of humic acid. According to these authors, during the electrochemical oxidation, hydroxyl radicals primarily react with organic substances to form partially oxidized intermediate products and carbon dioxide. Retardation and inhibition of these reactions due to mass transport limitations or because of the low reactivity of constituents will preferably lead to the decomposition of hydroxyl radicals as gaseous oxygen. As a consequence, the dissolved oxygen content increases, being the current efficiency and COD removal low.

Since Ti/Pt/PbO_2 and Ti/Pt/SnO_2–Sb_2O_4 have already shown to be promising electrode materials for the EO of sanitary landfill leachates (Fernandes et al., 2014b), in the present work it was decided to study the influence of the applied current density and of the chloride ion concentration on the oxidation ability of these two metal oxide anodes and compare the obtained results with those achieved with a BDD anode. In that previous study (Fernandes et al., 2014b), it was also performed the electrodegradation of simulated samples with nitrogen content analogous to that of the leachate, but without organic matter. To better understand the influence of the experimental conditions on the elimination of organic matter and nitrogen in the presence of