Electrochemical production and use of chlorinated oxidants for treatment of wastewater contaminated by organic pollutants and disinfection

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Abstract

In the last years, an increasing attention has been devoted to the utilization of electro-generated chlorinated oxidants for the treatment of wastewater polluted by recalcitrant organics and/or for the disinfection of water contaminated by pathogen microorganisms. In this review, the more recent and relevant findings were presented and critically discussed. The main advantages and disadvantages of this technique were commented, including the potential formation of toxic chlorinated organic specie and of chlorate and perchlorate or the difficult selection of proper operative parameters, as well as the key points that should be addressed to enhance the utilization on an applicative scale.

Keywords: electrochlorination, active chlorine species, wastewater treatment, disinfection, toxic chlorinated compounds.

Introduction

During the recent years, one of the relevant emerging topics is the development of new technologies to restore the quality of contaminated water due to the water scarcity which is one of the main concerns of this century. In this context, many kinds of waters, contaminated by organic pollutants resistant to conventional biological processes and/or by pathogen microorganisms, can be treated by chlorinated oxidants, such as chlorine or hypochlorous acid. In the past decades, a very large number of scientific studies have shown that these oxidants can be effectively produced by anodic oxidation of chlorides (electrochlorination) such as sodium chloride, which is a rather cheap reagent often

present in liquid effluents [1-6]. Furthermore, it has been demonstrated that the removal of organics and pathogen microorganisms is particularly effective when carried out in the same electrochemical cell where the oxidants are generated. However, these methods present some relevant disadvantages, such as a difficult selection of most suitable operative conditions and, in particular, of the nature of the anode and the formation of chlorinated toxic compounds, that should be still completely solved. In the last years, some interesting results were obtained in this frame, but additional efforts are necessary to enhance the applicative perspectives of this tool, as synthetically described in this review.

Anodic oxidation of chlorides

As above mentioned, reactive chlorides species, which actively participate in the oxidation of organics and of pathogens, can be electrochemically generated from chloride ions. The anodic oxidation of chlorides involves a multistep reaction that can be synthetically represented by eq. (1) [1-6]. As reported in eq. (2), dissolved chlorine may undergo a disproportionation reaction, depending on the proton and chloride concentrations, forming chlorides and hypochlorous acid, a weak acid (pKa 7.5), that is in equilibrium with ClO^- (eq. (3)).

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \quad (1)$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + H^+ + Cl^- \quad (2)$$

$$HClO \leftrightarrows H + ClO^- \quad (3)$$

The relative concentrations of Cl_2, HClO and ClO^- depend on the pH solution value, as shown in fig. 1. Furthermore, at low pH the formation of chlorine bubbles can occur. If wastewaters are treated in the same electrochemical cell where the chlorinated oxidants are generated, higher abatements of the pollutants [7-10] and more lethal impact on bacteria [9-12] are achieved with respect to that obtained

using chlorinated oxidants in separated reactors. Indeed, organics can be oxidized also at the anode surface by adsorbed chloro and oxychloro radicals, as shown in fig. 2, and various other reactive oxygen species (ROS), including •HO, H_2O_2 and $•O_2^-$, produced by water anodic oxidation, can contribute to both oxidation of organics and disinfection [13-14].

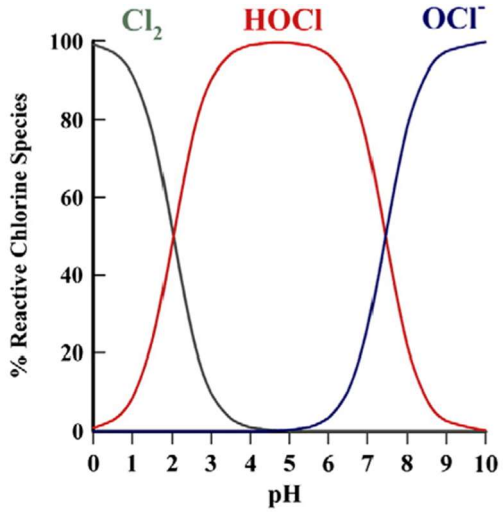

Fig. 1. Relative concentrations of Cl_2 (green), HOCl (red) and ClO^- (blue) calculated at 140 mM chloride using K = 1.3×10^{-3} for reaction 2 and a pKa of 7.44 for the reaction 3 [15].

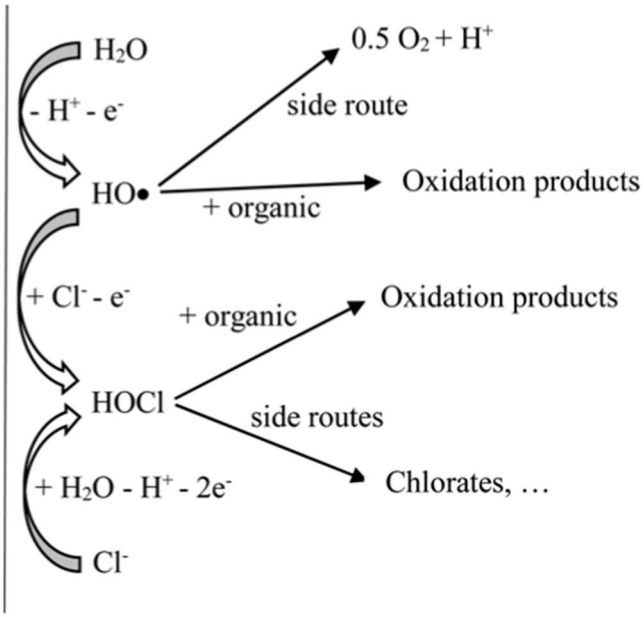

Figure 2. Scheme of main reaction pathways for the electrochemical oxidation of organics in water in the presence of chlorides [16].

Chlorides can be also converted in Cl_2O and ClO_2 by chemical or anodic routes (eqs. (4) and (5)) that can contribute as well to the organics oxidation and to disinfection.

$$Cl^- + 2H_2O \rightarrow ClO_2 + 4H^+ + 5e^- \quad (4)$$

$$2Cl^- + 2H_2O \rightarrow Cl_2O + 2H^+ + 4e^- \quad (5)$$

In particular, ClO_2 is a powerful oxidant which, unlike chlorine, does not lead to the formation of chlorinated byproducts [17,18] while Cl_2O is likely to be one of the most active species [19].

Oxidation of organics and disinfection

It has been shown that electro-generated active chlorine can be used effectively, using suitable anodes and operative conditions, for various kinds of waters including industrial wastewaters with highly refractory organics and high salts content [20], reverse osmosis concentrates [21], landfill leachates [22], wastewater contaminated by pharmaceutical residues, olive-mill, dairy and textile wastewater [23, 24], tannery effluents [25], drinking water [26], etc. Furthermore, it has been shown that electro-generated active chlorine can inactivate a large variety of microorganisms ranging from bacteria to viruses and algae [12].

The performances of these processes drastically depend on various operating conditions including the nature of the anode. In particular, metal oxide anodes yield usually higher removal of organic pollutants with respect to graphite and Pt. To better evaluate the role of the anode (and in particular of metal oxide ones), it is worth to mention that in the absence of chlorides, the organics oxidation and the disinfection takes place mainly by hydroxyl radicals generated by the anodic oxidation of water (eq. (6)) [3].

$$H_2O \rightarrow HO\bullet + H^+ + e^- \quad (6)$$

In particular, in the absence of chlorides, active anodes, such as Ir- and Ru-based electrodes (where the anodic oxidation of water results in the formation of chemisorbed hydroxyl radicals), usually give lower current efficiencies than nonactive ones, such as SnO_2, Boron Doped Diamond (BDD) or PbO_2 (where the anodic oxidation of water results in the formation of physical adsorbed hydroxyl radicals). Conversely, in the presence of high concentrations of chlorides, among metal oxides, active anodes, such as Ir- and Ru-based electrodes, usually give higher current efficiencies than nonactive ones, such SnO_2 and PbO_2 [3]. In this frame, García-Espinoza and co-authors [27] have shown that, for a concentration of NaCl of 14 mM, BDD gave a faster production of active chloride with respect to IrO_2. However, Scialdone et al. [28] found that, in the presence of high concentrations of NaCl and high current densities, higher current efficiencies for the removal of organics can be obtained at Ir-based anodes with respect to that achieved at BDD.

More in general, provisional results present in the literature indicate that, for large amounts of chlorides and organic pollutants easily oxidized by electrogenerated active chlorine, metal oxide anodes (particularly active anodes, such as RuO_2 and IrO_2) seem more suitable due to the high current efficiency for the active chlorine generation, the low formation of chlorate and perchlorate (as detailed in the following section), high porosity, as well as relatively low costs. Conversely, for organics resistant to active chlorine, the utilization of nonactive anodes (such as BDD), which are particularly effective for the mineralization of a very large number of pollutants) would be preferable if the formation of toxic chlorinated products can be avoided. For what concerns the disinfection, it has been shown that various anodes can be used, involving IrO_2 and RuO_2 based anodes and BDD, and, in particular, the employment of BDD guarantees a relevant inactivation of microorganisms [13].

It was also shown that many other operating parameters affect the removal of organics and pathogen microorganisms including the pH, the nature and the concentration of organic pollutants, the current density, and the flow dynamic conditions. In particular, it has been shown that the effect of one

parameter often depends on the value of other ones [3]. Hence, in many cases, the optimization of this process is rather complex.

Formation of toxic chlorinated compounds.

One relevant problem of electrochemical treatment by electrogenerated active chlorine consists in the potential formation of undesired toxic chlorinated derivatives, including highly toxic chlorinated amines [29, 30], trihalomethanes (THMs), haloacetic acids (HAAs) [21, 31-34], chlorinated oligomers [55] and ClO_3^- and ClO_4^-, which are suspected of exerting toxic effects on humans [35,36]. The formation of undesired halogenated organic compounds is due to reactions of substitution and addition between the organics and the active chlorine species (fig. 3) and/or chlorine radicals [37].

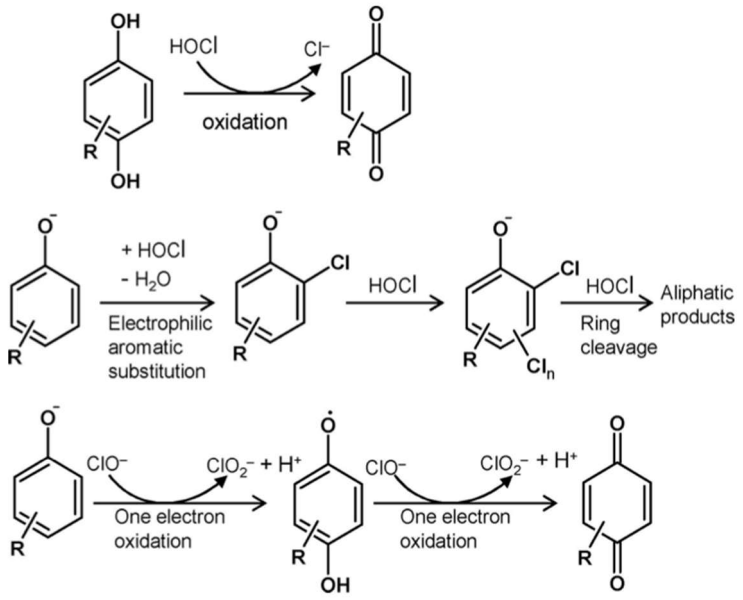

Figure 3. Scheme of main reaction pathways for the reaction between organic aromatic compounds and active chlorine [38].

As an example, the treatment by electro-generated active chlorine of a mixture of dyes with a Ti/TiO_2-RhOx anode in 100 mM NaCl at pH 4.0 gave rise to the formation of a high number of mono/dichlorinated intermediates, such as 2-chloroethenylbenzene, 2-chloro-2-methylbutane, cis-3-chloropropanate, cis-1,3-dichlor-ocyclopentane and trans-1,2-dichlorocyclopentane [39]. Similar

results were found by many other authors; although, in many of these cases, organochlorinated compounds were progressively removed at long electrolysis times [10,38-41].

According to various studies [35,42], chlorate and perchlorate are generated via a multistep oxidation pathway from chloride, as shown in reaction (7).

$$Cl^- \rightarrow OCl^- \rightarrow ClO_2^- \rightarrow ClO_3^- \rightarrow ClO_4^- \quad (7)$$

Moreover, on some anodes (such as BDD) the formation of perchlorate may proceed also through reaction paths involving the hydroxyl radicals generated by the oxidation of water [43-46] as shown in eqs. (8) and (9).

$$ClO^- + 2HO\bullet \rightarrow ClO_3^- + 2H^+ + 2e^- \quad (8)$$

$$ClO_3^- + HO\bullet \rightarrow ClO_4^- + H^+ + e^- \quad (9)$$

In order to enhance the applicability of electro-generated active chlorine, it is mandatory to find a set of operative conditions that allows to remove organic pollutants and/or minimize pathogen microorganisms avoiding or minimizing the formation of toxic chlorinated compounds.

It was shown that the formation of perchlorate strongly depends on the nature of the anode; in particular, BDD gave drastically higher perchlorate formation with respect to Pt and IrO_2 based anodes [26]. Furthermore, a significantly higher formation of total HAAs and THMs was observed using BDD anode with respect to that achieved at both Ti/SnO_2-Sb and Ti/Pt-IrO_2 for a similar charge passed for the electrochemical treatment of reverse osmosis concentrate [47]. In the case of Pt/Ti anodes, the formation of ClO_3^- and ClO_4^- increased with the initial Cl^- concentration and with the pH [42]. It is wort to mention that the perchlorate production at BDD was decreased using a lower current density and a higher flow rate, that can, however, give rise to slower removals of organics

[26] and a higher concentration of organics [46] that causes a depletion of hydroxyl radicals. In particular, for BDD anodes, the group of Serrano [48] has shown that, if the applied current density is close to the limiting current density, chlorides were oxidized almost only to hypochlorite; conversely, at higher current densities than that the limiting one, ClO^- was converted in ClO_4^-. Similarly, the group of Rodrigo has shown that, during the disinfection of an effluent of a municipal wastewater treatment plant by electrolysis at BDD anodes, the utilization of low current densities allows to avoid the formation of perchlorate [49]. Furthermore, these authors have shown that $CHCl_3$, $C_2H_4Cl_2$, C_2HCl_3, $CHBrCl_2$, $CHBr_2$-Cl, C_2Cl_4, $CHBr_3$ concentrations were below the detection limit of the technique used (2 ppb) at any electrolysis-time.

Another possible strategy to avoid the formation of chlorates and perchlorates may consist in the utilization of undivided cells equipped with carbon felt cathodes. These electrodes favor the cathodic reduction of oxygen to hydrogen peroxide that can, from one hand, contribute to the oxidation of organic pollutants and to the disinfection and, from the other hand, favor the conversion of chlorates to chlorine dioxide. Indeed, as reported by the group of Rodrigo [50], chlorine dioxide is considered a good disinfectant and oxidant with no tendency to form disinfection by-products for both DSA and BDD anodes. In this frame, since the cell design is a key factor [51-54], recently, the group of Rodrigo proposed also another route to avoid the formation of chlorate and perchlorate consisting in the utilization of a PEM-electrolyzer, equipped with diamond anodes, which involves very short hydraulic residence time [54].

Advantages and disadvantages and key aspects to be addressed

On overall, the treatment of wastewater contaminated by organic pollutants and/or pathogen microorganisms by electro-generated active chlorine at suitable anodes presents various advantages with respect to chemical chlorination routes. First, a fast removal of organic matter and

microorganisms occurs in the electrochemical cell due to the presence of various oxidation routes, involving both the homogeneous phase and the anode surface; second, the avoidance of transport and storage of dangerous chlorinated oxidants; and, third, the decrease of overall costs caused by the low operation costs that compensate the higher investment costs. In this frame, it is useful to remember that the electrolytic production of such oxidants become more interesting in the last years, due also to the decrease of the electric energy cost in many countries and the availability of electrodes with good performances.

This method presents some advantages also with respect to direct electrochemical oxidation (carried out in the absence of chlorides) such as i) the potential utilization of less expensive electrodes with respect to BDD ones (that are the elective anodes for such processes) and ii) high current efficiency achieved even in the presence of low concentrations of organic pollutants, since the oxidation process with electro-generated active chlorine is not kinetically limited by the mass transport of the organics toward the anode surface. Furthermore, lower energetic consumptions are often reported. However, the utilization of electro-generated active chlorine presents also some relevant disadvantages with respect to the chlorination such as i) the utilization of less conventional reactors and ii) the difficult optimization of the process given by the presence of various oxidation routes. Moreover, both chemical and electrochemical chlorination present the critical disadvantage of a potential formation of undesired toxic chlorinated derivatives as detailed in the previous paragraph.

On overall, in spite of the large number of papers devoted to this topic in the last two decades and the very promising results achieved, more studies are still necessary to determine a set of operative conditions that can guarantee a fast removal of organics and/or pathogen microorganisms coupled with the absence/minimization of toxic chlorinated substances at the end of the electrolysis at various kind of anodes, including DSA ones. In addition, a more detailed study of the effect of operating parameters on other relevant aspects such as the service life of anodes, especially in highly corrosive systems as concentrated chloride solutions, and on overall costs would be necessary.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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