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Electrolytic and electro-irradiated processes with diamond anodes for the oxidation of persistent pollutants and disinfection of urban treated wastewater

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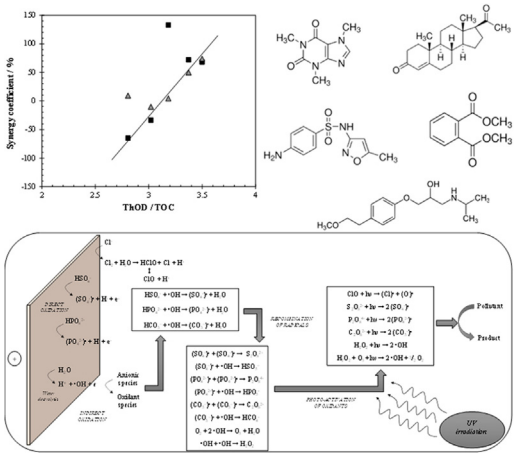
HIGHLIGHTS

- Coupling UV with electrolysis does not always result in synergism for the removal of organics.
- Oxidation state seems to be important parameter to foresee the synergism of photo-electrolysis.
- For high ThOD/TOC ratios, UV irradiation improves results attained by electrolysis.
- Photo-electrolysis improves the disinfection as compared to the additive effect of both single technologies.
- UV irradiation contributes to prevent the formation of hazardous species during electrolysis.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper analyzes the advantages and drawbacks of the combination of UV irradiation with electrolysis with the aim to give insight about the feasibility of the application of this technology for the reclaiming of conventionally-treated wastewater. The oxidation of synthetic solutions containing five selected model complex pollutants has been compared, showing that UV irradiation improves the results of electrolysis for progesterone, metoprolol and caffeine and deteriorates the performance for the degradation of sulfamethoxazole and dimethyl-phthalate. Differences observed becomes lower when mineralization is compared showing that the effects of UV irradiation are diluted when a mixture of species is oxidized. Results suggest that high ThOD/TOC (Theoretical Oxygen Demand/Total Organic Carbon) ratios improve the synergistic coupling of technologies while low values lead to a clear antagonistic effect. Because during oxidation progress this ratio is decreased, the observed effect on mineralization is much lower than in the oxidation of the raw molecule. Opposite to this low effect on the oxidation of organics, the improvement in the performance of the disinfection by coupling UV to electrolysis is much clearer.

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In addition, UV irradiation modifies significantly the chlorine speciation and helps to prevent the formation of hazardous species such as chlorate and perchlorate during the electrochemical processes.

1. Introduction

Conductive Diamond Electrochemical Oxidation (CDEO) has been proven efficient for the treatment of different types of wastewater [1–9]. According to recent literature [10–16], process efficiency seems to be improved by coupling the electrochemical process to other advanced oxidation processes such as ultraviolet (UV) irradiation, because of the rise in the generation of oxidizing agents and their better activation.

In this context, the role of peroxocompounds seems to be very important in order to fully understand the efficiency of the treatment. It is well-known that the electrochemical oxidation of wastewater with high concentration of sulfate leads to the formation of peroxosulfate [17,18] by the direct oxidation of the anion on the anode surface (Eq. (1)), followed by the recombination of the free sulfate radicals (Eq. (2)).

$$HSO_4^- \rightarrow (SO_4^-)^\bullet + H^+ \quad (1)$$

$$(SO_4^-)^\bullet + (SO_4^-)^\bullet \rightarrow S_2O_8^{2-} \quad (2)$$

In addition to this direct electrolytic mechanism, it is known that conductive-diamond anodes promotes the production of free hydroxyl radicals at high current densities (Eq. (3)). These species have a huge oxidation capability and they can react with sulfate anions (Eqs. (4) and (5)) forming sulfate radicals [17], which can be recombined afterwards, forming peroxodisulfate (Eq. (2)) and/or peroxomonosulfate anions (Eq. (5)).

$$H_2O \rightarrow {}^\bullet OH + H^+ + e^- \quad (3)$$

$$HSO_4^- + {}^\bullet OH \rightarrow (SO_4^-)^\bullet + H_2O \quad (4)$$

$$(SO_4^-)^\bullet + {}^\bullet OH \rightarrow HSO_5^- \quad (5)$$

Similar reactivity to that observed for sulfate anions is reported for other species such as phosphates and carbonates, typically contained in urban wastewater. This fact explains the formation in the reaction media of peroxophosphates and peroxocarbonates [19–21] during electrolysis with diamond anodes. These peroxocompounds also coexist during electrolysis with hydrogen peroxide (Eq. (6)) and ozone (Eq. (7)) produced by the recombination of hydroxyl radicals or by the reaction of this radical with oxygen.

$$2{}^\bullet OH \rightarrow H_2O_2 \quad (6)$$

$$O_2 + 2{}^\bullet OH \rightarrow O_3 + H_2O \quad (7)$$

In addition to all these oxidants, oxidation of chlorides contained in wastewater leads to the formation of hypochlorite, chlorate and perchlorate during electrolysis [22]. Opposite to the formation of peroxocompounds, occurrence of these species is not always considered to be positive and often it is even aimed to be prevented.

Consequently, in actual wastewater with a high content of different anions, such as urban wastewater, a cocktail of different oxidants species is expected to be formed during electrolyses. Recent studies have shown that the efficiency of in-situ electrogenerated oxidants is much higher than that obtained when commercial oxidants are added [23] and the differences may only be explained by some sort of activation of the oxidants added/produced. In this context, UV irradiation is considered as a potential activation technology [13–15,24–27] because it favors the formation of radical species by decomposition of more stable oxidants (Eqs. (8)–(10)).

$$S_2O_8^{2-} \xrightarrow{hv} 2(SO_4^-)^\bullet \quad (8)$$

$$H_2O_2 \xrightarrow{hv} 2{}^\bullet OH \quad (9)$$

$$H_2O_2 + O_3 \xrightarrow{hv} 2{}^\bullet OH + O_2 \quad (10)$$

This activation enhances the reaction rate of the process and, as an example, the radical sulfate reacts typically 10^3–10^5 times faster than the anion peroxosulfate [28]. Same behavior is expected for peroxophosphates and peroxocarbonates. Likewise, UV irradiation also favors the activation of hypochlorite to form chlorine radical and oxygen (Eq. (11)) [29–31].

$$ClO^- \xrightarrow{hv} (Cl)^\bullet + (O^-)^\bullet \quad (11)$$

It is important to note that, opposite to single electrolytic process, the effect of these radicals (such as sulfate and chlorine) can be extended to the bulk in a photo-electrolytic process because, in spite of their short lifetime, radicals are produced not on the anodic surface but in the bulk by decomposition of more stable oxidants [14,15]. This fact can minimize the well-known negative effect of the mass transfer limitations in low-concentrated systems.

Several authors have studied the effect of the coupling of UV irradiation on chemical and electrochemical processes for the treatment of wastewater by photo-chemical oxidation [16], photo-electro catalysis processes [32–34], processes based on Fenton's reaction chemistry [35–38] or photo-electrolysis [39,40]. In these studies, interesting results were obtained, observing significant improvements on the process efficiency for the removal of different organic compounds, which often may be explained taking into account the role of the different types of oxidants produced. At this point, it is also important to take in mind that combination of UV irradiation and electrolysis has not only been evaluated for the oxidation of organics but also in disinfection [41,42]. The results obtained showed that the combination of both techniques allowed attaining a complete disinfection, avoiding the bacterial regrowth.

With this background, the goal of this work is to evaluate the effect of coupling UV irradiation and CDEO for the treatment of synthetic and actual wastewater polluted with persistent pollutants (metoprolol, progesterone, sulfamethoxazole, dimethyl-phthalate and caffeine) and for the disinfection of treated wastewater in only one stage, trying to evaluate the effect of radical species on the performance of the combined treatment and to clarify the conceptual model proposed in Fig. 1 which summarizes the main reactions expected (related to oxidants production and activation).

At this point, it is important to note that, when the effluent of the secondary treatment of a municipal wastewater treatment plant is treated by electrochemical oxidation for the degradation of persistent pollutants looking for wastewater reclamation, both removal of organics and disinfection take place simultaneously and hence, the electrochemical oxidation of persistent pollutants from a real wastewater entails the disinfection process. This could open up the way for an efficient reclamation of urban wastewater. In this context, this manuscript looks for the clarification of the mechanisms of photo-electrochemical oxidation of reclaimed wastewater trying to elucidate if the irradiation of UV can lead to improvements in the efficiency of the treatment.

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