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### Full Length Article

# Synergic effect of ozonation and electrochemical methods on oxidation and toxicity reduction: Phenol degradation

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#### HIGHLIGHTS

- O<sub>3</sub>-EO enhances by 2.5 times the mineralization of phenol when compared to O<sub>3</sub> alone.
- O<sub>3</sub>-EO reduces by half the time to achieve a phenol mineralization >90%.
- Ozonation alone fails on phenol mineralization and on diminishing toxicity.
- Toxicity onto *Latuca sativa* is only eliminated by the coupled treatment (O<sub>3</sub>-EO).

#### ARTICLE INFO

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#### G R A P H I C A L A B S T R A C T



#### ABSTRACT

The degradation of phenol was studied under three chemical environments, ozonation  $(O_3)$ , electrooxidation (EO) and ozonation-electro-oxidation  $(O_3-EO)$  coupled process. The parent compound concentration was established by UV–Vis spectrophotometry while the by-products were identified by HPLC. This allowed proposing a mechanism of phenol oxidation during the coupled process. This coupled process was found to practically mineralize all phenol (TOC removal = 99.8%) under pH 7.0 ± 0.5 and at a current density of 60 mA cm<sup>-2</sup>, 0.05 L min<sup>-1</sup> flowrate, ozone concentration of 5 ± 0.5 mg L<sup>-1</sup>. Furthermore, it was found that the coupled process is practically twice faster than the EO process alone to achieve a high degree of mineralization. In this sense, it was concluded that ozone alone only partially mineralizes the phenol molecule and mainly leads to the formation of aliphatic compounds. In addition, the toxicities of phenol and its degradation products were established by using a bioassay with lettuce seeds. It was concluded that, unlike ozonation, the coupled oxidation process not only mineralizes the organic molecule but also completely eliminates the toxicity of the treated phenolic solution.

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#### 1. Introduction

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http://dx.doi.org/10.1016/j.fuel.2016.10.117 0016-2361/© 2016 Elsevier Ltd. All rights reserved. Some main organic pollutants of water are oil, gasoline, plastics, pesticides, solvents and detergents, among many other water-soluble and water-insoluble chemicals that threat human health

Please cite this article in press as: Amado-Piña D et al. Synergic effect of ozonation and electrochemical methods on oxidation and toxicity reduction: Phenol degradation. Fuel (2016), http://dx.doi.org/10.1016/j.fuel.2016.10.117 and damage aquatic life. Some of these substances can cause kidney disorders, birth defects and various cancers even at very small concentration. This is the case of phenolic compounds, which are used in a wide variety of industrial processes such as the production of pesticides, resins, nylon, antioxidants, plasticizers, drugs, dyes, explosives, oil additives and disinfectants [1–3]. In this context and due to its toxicity and persistence, phenol mineralization is of paramount importance for the environment protection. To achieve so, several technologies are available. However, among all these treatments, Advanced Oxidation Processes (AOP's) emerge as promising methods for wastewater treatment because they have been reported to be relatively simple, easy to control, and result in a high oxidation degree and compatibility with the environment [4–7].

Ozonation  $(O_{3})$  and electro-oxidation (EO) chemical methods can be found among these AOP's. Some information considered as relevant of each treatment and helpful to improve the understanding of the coupled treatment is below presented.

#### 1.1. Ozonation

Ozone  $(O_3)$  is a weak polar (0.53 D) and highly reactive molecule that exhibits a high redox potential (2.07 V vs. NHE) only below atomic oxygen (2.42 V vs. NHE) [8]. In wastewater treatment, ozone can play different roles and these are mainly: disinfectant or biocide, oxidant to remove organic pollutants, and as pre-or post-treatment agent to aid other processes, i.e. flocculation or sedimentation [9].

In ozonation, the oxidation of organic pollutants can occur via (a) direct electrophilic attack by molecular ozone (known also as ozonolysis) and this proceeds at acidic or neutral pH and is a selective reaction resulting in the formation of carboxylic acids as end products that cannot be oxidized further by molecular ozone and (b) indirect attack through the formation of stronger oxidant species like hydroxyl radicals (HO<sup>•</sup>) [10,11]. Therefore, the pH of the effluent is a major factor determining the efficiency of the ozonation process since it can alter both, the chemistry and kinetics of the oxidation process.

The generation of hydroxyl radicals occurs by the following reactions (1)-(11) [12],

$$O_3 + OH^- \to HO_2^- + O_2$$
 (1)

$$O_3 + HO_2^- \to HO_2^- + O_3^-$$

$$HO_2^{-} \rightarrow O_2^{-} + H^+ \tag{3}$$

$$O_{2}^{-} + H^{+} \to HO_{2} \tag{4}$$

$$0_3 + 0_2^{-} \rightarrow 0_3^{-} + 0_2$$
 (5)

$$O_3^- + H_2 O \to HO^- + O_2 + OH^-$$
 (6)

$$\mathbf{O}_3^{-} + H\mathbf{O}^{-} \to H\mathbf{O}_2^{-} + \mathbf{O}_2^{-}$$
(7)

$$O_3 + HO^{\bullet} \rightarrow HO^{\bullet}_2 + 20 \tag{8}$$

$$HO_2^- + H^+ \to H_2O_2 \tag{9}$$

$$H_2 O_2 \to H O_2^- + H^+$$
 (10)

$$O_3 + HO^{\bullet} \rightarrow O_3 + OH^{-} \tag{11}$$

These reactions are promoted either under alkaline conditions or under the presence of initiators like hydrogen peroxide or ultraviolet light. Yet, the improvement of ozonation efficiency is desirable in order to decrease ozone consumption and to fully oxidize compounds like humic substances or oxalic acid [8]. In this sense, the coupling of ozonation and electrochemical treatment has already been proven [13–16] to exert a positive synergic effect on oxidation rate and mineralization degree.

#### 1.2. Electro-oxidation

This process consists on the generation of highly oxidant species by electrolysis. The main operational variables affecting the efficiency of this process are pH, current density, electrochemical cell design, physicochemical properties of reacting solution, electrolyte type and concentration, pollutant concentration and nature, electrodes material and geometry. The most oxidizing specie produced during electro-oxidation is the hydroxyl radical (HO<sup>•</sup>) at the anode surface [17] by water oxidation. The availability of oxygen is also important since can be reduced to hydrogen peroxide or water at the cathode under acidic pH. The produced hydrogen peroxide can then react with the hydroxyl radicals at the anode to generate hydroperoxyle radicals (reaction (12)),

$$H_2O_2 + HO \rightarrow H_2O + HO_2 \tag{12}$$

Nevertheless, the low efficiency of the anode has motivated the assessment of a wide variety of electrode materials such as graphite [18], platinum [19], IrO<sub>2</sub> [20], RuO<sub>2</sub> [21], SnO<sub>2</sub> [22], PbO<sub>2</sub> [23] and boron-doped diamond (BDD) [17]. Among all these materials, PbO<sub>2</sub> and BDD electrodes are more attractive because of its high oxygen overpotential [24].

However, previously conducted research [25,26] suggests that caution must be taken when BDD electrodes are used for the oxidation of chloride-containing waters because BDD electrodes can form twice faster  $ClO_4^-$  than other electrodes, i.e. Pt, IrO<sub>2</sub>, IrO<sub>2</sub>, RuO<sub>2</sub>. This has been ascribed to the ability of the BDD electrodes to promote the interaction between  $ClO_3^-$  and HO<sup>-</sup> at high concentrations resulting in the production of  $ClO_4^-$ ,  $ClO_3^-$ , or  $ClO_2$ , chlorine ( $Cl_2$ ) and hypochlorous acid/hypochlorite (HOCl/OCl<sup>-</sup>) and other compounds (i.e. halogens). The detrimental effect of chlorides has been suggested [25] to be minimized by working at relative low current densities ( $\leq 50 \text{ Am}^{-2}$ ). Other disadvantage of using BDD electrodes is their high cost mainly due to the substrate (Nb, W, Ta) onto which the BDD film is deposited.

In the context of electrochemical technologies, it is of paramount importance to reduce the treatment time without sacrificing efficiency since many electrodes exhibit a relative short life and high cost. It should be kept on mind that electrochemical treatment time is directly correlated with energy consumption and therefore treatment cost. This has motivated the coupling with other treatments like ozonation.

#### 1.3. Ozonation-electrooxidation coupled process (O<sub>3</sub>-EO)

This process consists on the addition of ozone to the electrochemical cell where an oxidation is being conducted. If hydrogen peroxide is demonstrated to be *in-situ* produced then this treatment is also known as electroperoxonation. The *in-situ* hydrogen peroxide production is expected to occur, as abovementioned, by the cathodic reduction of oxygen under acidic conditions. The source of oxygen can be either the ozone stream or some ozone reactions (i.e. reactions (1), (5) and (6)). It has been shown [27] that when a carbon-PTFE electrode is used as cathode and other material as anode, a high hydrogen peroxide concentration is achieved.

Despite the disadvantages of BDD electrodes mentioned in Section 1.2, the anodic oxidation with this type of electrodes has received special attention [28,29]. Actually, high concentrations of hydrogen peroxide have also been achieved when BDD electrodes are used as anode and cathode.

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