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Electrooxidation-Ozonation: A Synergistic Sustainable Wastewater Treatment Process

Carlos E. Barrera-Díaz and Nelly González-Rivas

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Abstract

Advanced oxidation processes (AOPs) have shown to be very useful technologies for application in different wastewater treatment areas. These processes use the very strong oxidizing power of hydroxyl radicals to oxidize organic compounds to carbon dioxide and water. These procedures usually involve the use of O_3 , H_2O_2 , Fenton's reagent and electrolysis to generate the hydroxyl radicals. However, some recent investigations have found that the use of a coupled processes using O_3 /electrooxidation increases the effectiveness of the process and also could reduce the operating costs associated to the application of AOPs. In this chapter, there is a description of our work in the treatment of wastewater using an ozonation-electrooxidation combined process. The main parameters to control for having a successful application of such method are discussed. Several examples for different kinds of polluted water are addressed.

Keywords: organic pollutants, degradation, mass transfer, mineralization, removal

1. Introduction

Traditional wastewater treatments involve the addition of chemicals or the use of microorganisms to treat polluted water. However, in both processes, there is always a residue known as sludge. The sludge management and final disposal could represent up to 50% of the total wastewater treatment plant cost. Therefore, novel ways to deal with this issue should be developed. In this way, the use of advanced oxidation processes (AOPs), in which the $HO\bullet$ radical production is favored, could represent an interesting option for treat wastewater with less or without sludge production.

The final goal of AOPS is the complete degradation of the pollutants present in wastewater, aiming its final mineralization, yielding as final products: carbon dioxide, water and inorganic

compounds. These methodologies solve the problem of the final disposal of sludge; because when they are well developed, there is no production of sludge. Obviously, not always is possible the complete mineralization of contaminants. Nevertheless, most of the times, the final products of the destruction of contaminants are harmless compared to the original ones.

Electrochemical techniques use one of the cleanest reagents: "the electron." Thus, since the main reactive used in the oxidation process is green, this becomes sustainable. Oxidation of the organic compounds could occur at the interface of the anode/aqueous solution or in solution via intermediates. Electrochemical oxidation consists in the application of an external source of energy into an electrochemical cell that contains one or more pairs of electrodes. At the cathode, a reduction reaction occurs and the oxidation reactions takes places at the anode. The use of boron diamond doped anodes (BDD) allows the generation of $\text{HO}\bullet$ radicals, which reacts with organic compounds.

Electrochemical oxidation is considered a robust technology and is easy to use, for those reasons, it has been used for a diversity of wastewater treatments. The main advantages of this technology over other conventional treatments are as follows: the main reagent is the electron; many processes occur in the electrochemical cell; the addition of chemicals is not required; and the process is carried out at room temperature and atmospheric pressure.

Ozone is a powerful oxidant produced in gas phase, and by means of a diffuser, a mass transfer occurs to aqueous solution. A main advantage of ozone is that it oxidizes organic compounds without producing residual sludge. However, it was found that some compounds are ozone-resistant such as iopamidol, sucralose and atrazine-desethyl.

Combination of the ozonation processes with others, such as ozone/hydrogen peroxide, ozone with sand filtration and activated carbon filtration, have been used to remove ozone resistant contaminants; this allows enhancing the removal efficiency and reducing ozone dosage. Recent reports indicates that there are two reaction mechanisms for ozone oxidation: direct ozonation that takes place at acidic solutions and indirect $\text{HO}\bullet$ radical ozonation at basic solutions.

One of the major limitations for the use of ozone is the mass transfer from the gas phase to the liquid phase, the same behavior is observed at direct electrooxidation in which the $\text{HO}\bullet$ generation takes place at the anode surface. Thus, when both processes take place at the same time a synergy occurs, the process reaction time is decreased, this implies that the ozone and electricity consumption is also reduced.

In this chapter, there is a description of our work in the treatment of wastewater using an ozonation-electrooxidation combined process. The main parameters to control for having a successful application of such method are discussed. Several examples for different kinds of polluted water are addressed.

2. Characteristics of the hydroxyl radical

Advanced oxidation processes rely on the hydroxyl radical formation. The hydroxyl radical, $\text{OH}\bullet$ is a highly reactive radical, able to react unselectively and rapidly with organic

pollutants, including recalcitrant organic compounds, such as aromatic, chlorinated and phenolic compounds [1].

There are different technologies to produce hydroxyl radicals. Nevertheless, the most “greener” one is its electrochemical production direct from the treated water. Among all the electrodes used in the production of hydroxyl radicals, the BDD anodes have shown to be perhaps the most efficient ones. They also have some other useful characteristics that allowed his use in the wastewater treatment, such as the radicals are loosely retained in the surface of the electrode allowing its oxidative action close to the surface area.

No matter from which source the hydroxyl radicals are generated, they have some special characteristics that make the extremely useful in the treatment of wastewater polluted with recalcitrant organic compounds. Some of the characteristics of the hydroxyl radical are as follows:

- Powerful oxidant
- Highly reactive
- Easily generated
- Not selective
- Short reaction time
- Harmless

The hydroxyl radical has a high oxidation potential as shown in **Table 1**, it can be generated, chemically, electrochemically or by UV radiation combined with the presence of suitable catalyst. The major failure of the electrochemical oxidation is the high-energy consumption during the process of mineralization of pollutants.

Oxidant	Potential (V)
Fluorine	3.06
Hydroxyl radical	2.80
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36

Table 1. Oxidation potential for some common oxidants [2].

3. Ozone

Ozone is a pale blue gas with a pungent odor. It is generated from oxygen. The electric discharge method is the most common process for the preparation of ozone on laboratory and

industrial scale. The electrical discharge generates ionized oxygen atoms that react with oxygen molecules to producing ozone.

Ozone is a powerful oxidant and very highly unstable. For this reason, the gas should be produce *in situ* prior to its use on the wastewater treatment. Once the ozone is produced, a diffuser is used to transport the gas to aqueous solution trough a mass transfer process. A major advantage of ozone is that it fully degrades organic materials, leaving no residual sludge.

Ozone can oxidize and destroy the organics through two different pathways, the direct and the indirect ones. In the first, one of the molecules react directly with the ozone molecules. In the second case, the ozone reacts to generate oxidant species such as hydroxyl radicals that carried out the oxidation process. The oxidation pathway that operates in a particular oxidation depends on the reaction rate of ozone and the organic. Sometimes the product generated in the reaction could promote or inhibit the ozone decomposition modifying the initial oxidation mechanism.

It has been found that some compounds are resistant to the oxidation by ozone, such as iopamidol, sucralose and atrazine-desethyl. In order to overcome this limitations, the use of combined ozone processes, such as the UV light, metal oxides catalyst and hydrogen peroxides, have been proposed. In many cases, a remarkable procedure improvement was found [3–5]

Figure 1 shows an ozone bubble column reactor in which ozone is feed in the bottom part of the reactor, O_3 passes through a diffuser that allows the generation of small bubbles which reaches the wastewater contained inside the reactor.

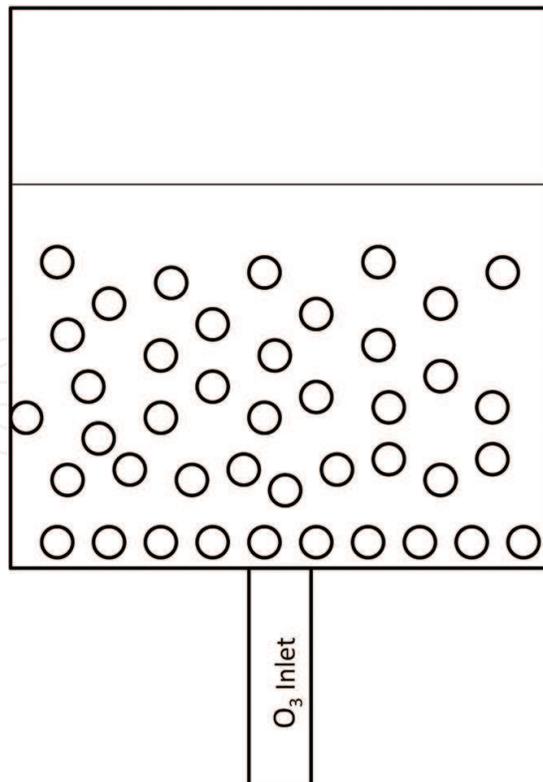


Figure 1. Schematic representation of a column bubble reactor in which ozone is feed in the bottom part.

The decomposition of ozone in water to form hydroxyl radicals, which occurs as are shown in Eqs. (1)–(6) [6]:



As observed, it takes six reactions to form one hydroxyl radical; now, a mass transfer from the gas phase to the aqueous phase should take place in order to have available hydroxyl radicals in aqueous solution. The process is often limited since only a part of ozone is effectively converted to hydroxyl radicals [7].

4. Electrooxidation

Electrochemical oxidation is considered a robust technology and easy to use, for that reasons, it has been used for a diversity of wastewater treatment areas. The main advantages of this technology over other conventional treatments are as follows:

- Electron is the main reagent.
- A simple electrochemical cell is required in the process.
- Addition of chemicals is not required.
- The process is carried out at room temperature and atmospheric pressure.

In 2003, Marselli et al. demonstrated that the production of hydroxyl radicals during conductive-diamond electrolysis of aqueous wastes is possible. Consequently, a very new class of oxidation processes, the electrochemical advanced oxidation processes (EAOP) were discovered [8].

In the direct electrooxidation, pollutants in the bulk of the wastewater must reach the electrode surface and the oxidation reaction takes places once they are adsorbed onto this surface. Thus, the electrode materials influence the selectivity and efficiency of the oxidation process and mass transfer becomes a very important process. **Table 2** shows some anodic materials that have been investigated for the oxidation of organic compounds.

Material	Oxygen evolution potential
Pt	1.60
Graphite	1.70
SnO ₂	1.90
PbO ₂	1.90
Boron doped diamond	2.30

Table 2. Oxygen evolution potential of some electrodic materials [9].

Figure 2 shows the general scheme of an electrochemical reactor. It contains an anode made of boron diamond doped in which hydroxyl radicals are produced. The cathode is made of stainless steel and allows water reduction.

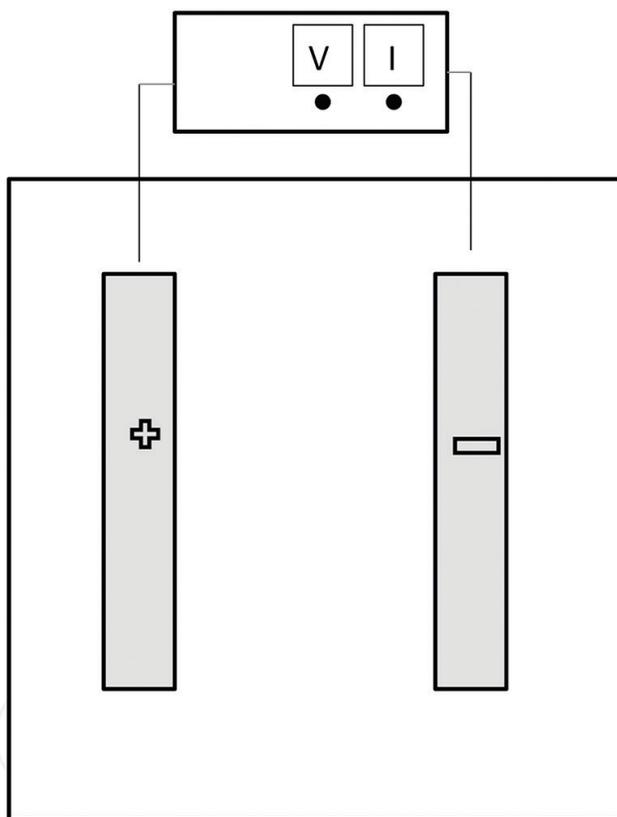
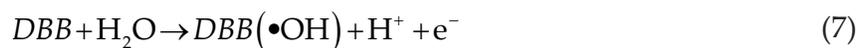
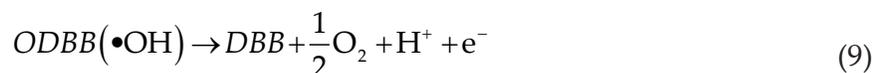
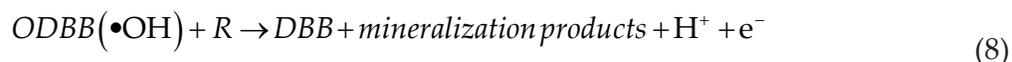


Figure 2. An electrooxidation reactor in which hydroxyl radicals are produced in the anode and water reduction takes place in the cathode.

The main reactions involved in the hydroxyl radicals production are shown in Eqs. (7)–(9)





Diamond anodes exhibits three outstanding properties as compared with other advanced oxidation technologies and with electrolysis with other anodes [10]:

- Robustness, because results found in this latter years demonstrate that it can attain the complete mineralization of almost any type of organic without producing refractory final products.
- Efficiency, because when it is operated under the no diffusion control, current efficiencies are close to 100%.
- Integration capability, because it can be easily coupled with other treatment technologies and it can be fed with green energy sources such as wind mills and photovoltaic panels.

However, as can be observed in **Figure 2**, the hydroxyl formation is limited to the anodic surface and also by the mass transfer from the liquid to the electrode.

5. Integrated ozonization-electrooxidation reactor

In order to have a synergistic effect of the two previously described processes, a couple treatment consisting in introducing electrodes inside the ozone reactor has been proposed.

Figure 3 shows an ozone bubble column reactor in which two electrodes are introduced. As can be observed, the bubbles generated by the addition of ozone in the bottom part of the reactor allowing a complete mixing of the solution.

In this reactor, the ozone and the electrooxidation reaction takes place at the same time, thus the hydroxyl radical concentration is enhanced, the mass transfer is limited and a large amount of bubbles provides an excellent mixing inside the reactor. There are several variables to control in the integrated process aiming to obtain a complete degradation of pollutants:

- Initial pollutants concentration
- Initial pH
- Current density
- Interelectrode distance
- Salt concentration (in case it is required to improve conductivity)
- Ozone flow rate
- Electrodes type

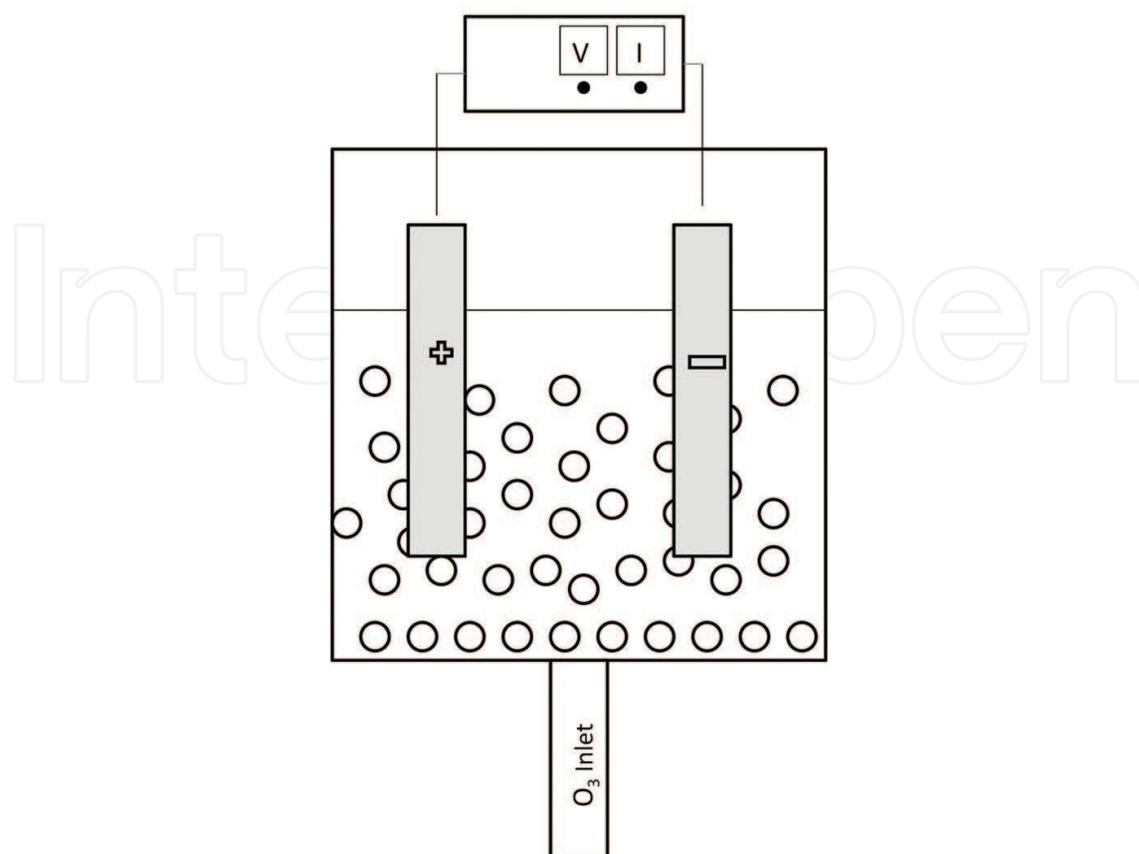


Figure 3. An electrooxidation reactor in which hydroxyl radicals are produced in the anode and water reduction takes place in the cathode.

With a set of well-optimized parameters, there is always an improvement in results compared with the two separated techniques. In **Table 3**, some samples are gathered in which the integrated ozone-electrooxidation process has been applied to different kinds of wastewater. As it is possible to observe, there is a significant improvement in the quality of the treated wastewater. In all the cases, the chemical oxygen demand (COD) is almost eliminated, and some other parameters are also decreased in an important amount. The most used parameters to control the quality of treated wastewater are as follows: conductivity, total organic carbon (TOC), color, turbidity and biochemical oxygen demand (BOD_5), the values of these parameters obtained before and after of the coupled treatment demonstrate the suitability of the proposed procedure to treat wastewater from different sources.

	Results	References
Industrial wastewater	Integration of the two processes at pH 7 and 20 mA cm^{-2} of current density greatly improved the reduction in COD (84%), BOD_5 (79%), color (95%), turbidity (96%) and total coliforms (99%)	[11]
Industrial wastewater	In the integrated electrochemical-ozone process with energy pulses, the COD reduction was observed to be 80% after 44 min of treatment. Initial pH was 7.5 at all experiments	[12]

	Results	References
Dye removal in denim effluents	Using the integrated process, 65% color removal, 76% turbidity removal and 37% COD reduction could be attained	[13]
Offset printing dyes	Optimal conditions are found when adding 20 mg L ⁻¹ AHC, followed by electrocoagulation at 4 A for 50 min, and finally, alkaline ozonation for 15 min, resulting in an overall color removal of 99.99% color and 99.35% COD	[14]
Industrial wastewater	In only 15 min, the integrated process reduced the COD by 83%, TOC by 78%, color by 93%, turbidity by 77% and conductivity by 27% at relatively low current density (12.5 mA cm ⁻²)	[15]
<i>p</i> -Nitrophenol solutions	Up to 91%, TOC was removed after 60 min of the electrolysis-O ₃ process	[16]
Industrial wastewater	COD is reduced by 99.9% along with most color and turbidity in about an hour. The coupled process practically eliminates the COD, color and turbidity without the addition of chemical and does not generate any sludge	[17]

Table 3. Examples of the electrooxidation-ozonation process applied to wastewater treatment.

6. Conclusions

Electrooxidation-ozonation is an efficient process for the treatment of different kinds of wastewater, since there is always a large reduction in COD, color, and turbidity, conductivity and BOD₅. The coupled process always has a superior performance compared with the application of separated processes. It is also noteworthy to mention that the coupled process is green, as it does not produce residual sludge. This coupled process has the potential to be used in wastewater in which other processes do not work well, including those with recalcitrant pollutants.

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Nomenclature

BOD₅ Biochemical oxygen demand

COD Chemical oxygen demand

TOC Total organic carbon

Author details

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