

Chimia 49 (1995) 23–27
 © Neue Schweizerische Chemische Gesellschaft
 ISSN 0009–4293

Electrochemical Treatment of Industrial Organic Effluents

André Savall*

Abstract. The anodic oxidation of organics is a potentially powerful technique of controlling pollutants in industrial waste waters. Based on a fundamental analysis, this paper summarizes recent results in this field. Direct electrochemical processes catalyzed by the oxygen-transfer reaction are discussed for several anode materials. Ti/SnO₂ is particularly efficient for cold combustion of aromatic pollutants. Potential candidate processes involving the electrochemical generation of oxidizer reactants (O₃, H₂O₂), or the electrochemical regeneration of metallic redox couples are discussed.

1. Introduction

The treatment of organic effluent poses a serious problem in the chemical industries. Over the last twenty years, ever-greater efforts have been made by industry to limit this type of pollution at source by improving processes, recycling products, and controlling the treatment of waste at the production stage. However, despite the large amounts of liquid industrial effluent treated to retrieve certain solvents, for example, inevitably there are residues requiring a final transformation which is often delicate. Traditional incineration methods, for their part, pose problems of corrosion and, more seriously, of emissions if the conditions are not perfectly controlled.

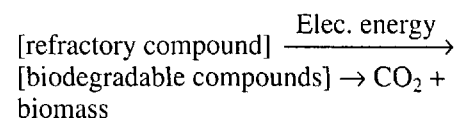
When an industry is confronted with such a problem, it must be examined as a whole, since there is no universal and simple method in this area. The great variety of industrial discharges means that a diversification of techniques must be sought with a view to adapting the treatment as well as possible to each situation. In spite of the efforts made to develop ever-cleaner processes, the increasingly severe environmental laws should encourage the search for better-performing treat-

ments making it possible to obtain environmentally compatible effluents.

Electrochemical technique has often been considered to be a way of eliminating the toxic compounds contained in certain effluents and waste waters [1]. Electrochemistry has proven its efficiency in processes used for destroying effluents as noxious as cyanides [2] by oxidation, or for retrieving heavy metals by cathodic reduction [3]. It also has a contribution to make in the treatment of certain industrial organic pollutants [4–9]. However, it is recognized that electrochemical techniques encounter difficulties when it comes to achieve the complete oxidation of organic species. Indeed, it is often only possible to complete oxidation under special conditions: concentrated acid or alkaline medium, at 80°, and on platinum-plated titanium electrodes [3].

Many industrial effluents are formed from waste water containing organic pollutants which must be mineralized by oxidation in CO₂, H₂O, Cl⁻, SO₄²⁻, etc. Of all the organic pollutants, the most toxic are the chlorinated and aromatic solvents, pesticide residues, phenols, polychlorinated biphenyls, etc. It is now accepted that a simple modification of the molecular structure can considerably reduce the toxicity of a compound [8]. Electrochemistry then has its part to play as a treatment preceding a biological process to destroy refractory pollutants that bacteria have great difficulty in digesting. To ensure the good operating condition of biological treatment installations, it may be practical to include in the industrial strategy an

electrochemical pretreatment stage where the pollutants are degraded into smaller molecules that the bacteria can easily assimilate in a purification station [8–10]. In practice, the following treatment scheme could be envisaged:



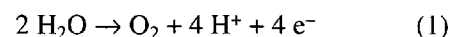
This paper deals with the most recent developments in direct or indirect electrochemical techniques with a view to treating organic pollutants contained in certain industrial effluents.

2. Anodic Oxidation by Oxygen Transfer

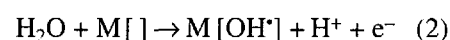
2.1. Electrocatalysis by Oxygen Transfer Anodic Reaction

The oxidation reactions of organic compounds by O₂ in CO₂ and H⁺ (or H₂O) are spontaneous transformations: however, the rate of these reactions is only appreciable at high temperatures or in the presence of a catalyst. Using electrochemical techniques with a view to degrading organic compounds by anodic oxidation in the aqueous phase is, therefore, theoretically possible if, on the one hand, the electrode is at a potential sufficient to cause the discharge of the H₂O molecule on the anode, and if, on the other hand, the electrode has a catalytic activity sufficient to lower the activation energy of the O-atom transfer reaction for each oxidation stage. The anodic oxidation of an organic compound in the aqueous phase first of all involves the irreversible transfer of an O-atom from the H₂O molecule to the substrate; this transfer then takes place on the intermediaries. In depollution applications, as in electrosynthesis, high overpotential oxygen anodes must be chosen. This is because the oxygen-transfer reaction must be encouraged while minimizing the unwanted co-discharge of oxygen.

The discharge of oxygen on an anode in an aqueous medium:

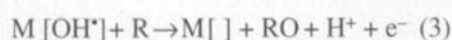


has been the subject of a large number of studies [11], and it is widely accepted [11–14] that the first step in this oxidation is the discharge of the water which leads to the hydroxyl radical adsorbed on the electrode:

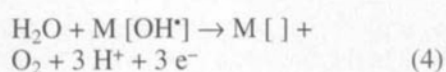


*Correspondence: Prof. A. Savall
 Laboratoire de Génie Chimique et
 Electrochimie
 URA 192 CNRS
 Université Paul Sabatier
 118, route de Narbonne
 F-31062 Toulouse

At a high overpotential, this step is limiting in all cases [11]. Furthermore, certain authors have suggested that the adsorbed OH* radicals are the intermediaries responsible for the transfer of oxygen in the anodic oxidation of a great number of organic molecules [10][12–15]:

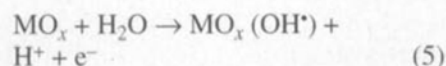


After step (2), the following competitive reaction leads to O₂:



where M[] represents a site that is deficient subsequent to the transfer of oxygen (3), or to the discharge of O₂ (4); this site is repopulated with the oxygen (OH*) by the anodic discharge of H₂O (2).

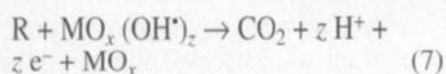
Cominellis has studied the oxidation of organics by using several anode materials and has proposed a generalized scheme of the electrochemical conversion/combustion on an oxide anode (MO_x) [10]. In the first step, H₂O is discharged:



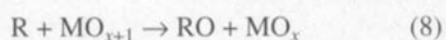
and in a second step, the adsorbed OH* radicals may interact with the oxygen already present in the oxide anode to form the higher-oxide MO_{x+1}:



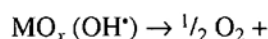
In the presence of oxidizable organics it is assumed [10] that the physisorbed radicals OH* should cause predominantly their complete degradation into CO₂, H₂O, or H⁺:



On the other hand, the chemisorbed active oxygen (MO_{x+1}) participates in the formation of selective oxidation products:



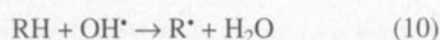
For the degradation (combustion) of organics, a high concentration of OH* radicals on the anode surface is necessary. This is the case when the rate of the reaction (5) is faster than the oxygen transfer into the oxide lattice (6). The current efficiency for the combustion of organics depends on the relative rate of the reaction (7) to the rate of the oxygen evolution:



For the selective oxidation (8) the concentration of adsorbed OH* radicals on the anode surface must be very low. This means that the rate of the oxygen transfer into the oxide lattice must be faster than that of the OH*-radical formation (5). According to this scheme, the SnO₂ anode favors the complete degradation of organics, contrary to the IrO₂ or Pt anodes which favour the selective oxidation reaction (8) [10].

In addition, it is probable that dioxygen contributes also in the oxidation scheme according to the following steps:

i) formation of organic radicals:



ii) formation of peroxide and hydroperoxide:



These intermediates are instable and lead, after molecular breakdown, to subsequent products with lower carbon numbers. This degradation continues until the formation of CO₂ and H₂O.

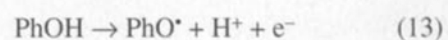
In summary, the anodic oxidation of an organic compound by the transfer of oxygen from H₂O requires an electrode material that, in order to be efficient, must encourage reaction (2) but limit reactions (4) or (9). The goal of research, currently being carried out, is to define electrodes whose activity on the M[] sites encourages the transfer of oxygen (3) from the labile form M[OH*]. The recent use of Ti electrodes coated with SnO₂ has made it possible to undertake fruitful research on the oxidation of phenol.

2.2. Phenol Oxidation

The petrochemical, paint, textile, industries *etc.* produce residual waters that can contain high concentrations of phenol. It is difficult to extract this pollutant from water, when its concentration is lower than 2000–4000 ppm; it must, therefore, be destroyed. It is generally considered that discharge waters must not contain more than 20 ppb [16]. Under these conditions, phenol is considered to be a model molecule, and the study of its electrochemical degradation has been the subject of many works [16–25]. Platinum is a reference material, but vitreous C elec-

trodes [16] and Ti electrodes coated with oxides of metallic elements such as IrO₂, RuO₂, PbO₂, and SnO₂ have also been used [9][17][18][24].

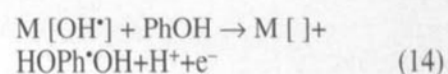
The works carried out to the pilot stage in the 70s and 80s did not reach the industrial stage due to the slowness and inefficiency of the oxidation on the electrodes used at the time. The contamination of the anodes by the products of polymerization was the main cause. The PhO* radical formed during the first step:



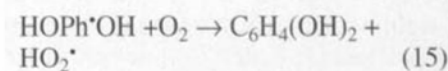
tended to give coupling products [16][19]. This problem can be reduced by operating at a temperature higher than 50°. The second problem relative to the detoxification of effluents containing phenol is the result of the slowness of the oxidation of the reaction products; the total organic carbon decreases very slowly during electrolysis carried out through a flow-by electrochemical reactor employing carbon anode [16]. This remark is highly significant, since the main products formed, quinones, are even more toxic than phenol [28]. Using high potentials also causes considerable corrosion of carbon anodes [16].

The study of the influence of the classic parameters (pH, temperature, initial concentration) on the electrochemical degradation of phenol on a Pt anode has revealed that its mineralization reaches a limit around 60% [19].

The results given in [18][21][27] show that the process is not limited by the transfer of matter to the anode. Oxidation takes place by the electrophilic attack of the OH* radical formed by reaction (2) on the aromatic nucleus:



followed by the formation of the hydroquinone [19]:



Analysis of the intermediates formed during the anodic oxidation of phenol in a 0.02 mol dm⁻³ solution at pH 3 and at 70° led Cominellis and Pulgarin [10][19] to propose a mechanism in which the reaction takes place *via* two possible pathways:

- chemical oxidation identical to step (3) initiated by the chemisorbed active oxygen MO_{x+1} formed by reaction (8),
- direct degradation to the CO₂ stage of

the adsorbed phenol and/or of the aromatic intermediates (hydroquinone, catechol, benzoquinone) by the physisorbed OH[•] radicals formed by reaction (5).

Using Ti electrodes coated with IrO₂, RuO₂, or PbO₂ gives low current efficiency values (14–18%), comparable with those observed on Pt [18][27]. These modest values are due to the current losses caused by the discharge of oxygen on these oxides.

Recent studies on electrode materials for anodic oxidation, ozone generators have led Kötzt *et al.* [20] to demonstrate that SnO₂ deposited on Ti raised to a temperature of 550°, by a technique that involves spraying a solution of SnCl₄ (+ SbCl₃) in MeOH, provides electrodes with a high oxygen discharge overpotential. Kötzt *et al.* [20], Stucki *et al.* [21], and Cominellis [17][18] have tested these Ti/SnO₂ electrodes doped with antimony. These works have shown that they have remarkable properties:

- high chemical and electrochemical stability,
- high electrical conductivity by introducing doping agents (Sb, F),
- high oxygen discharge overpotential.

The oxygen discharge overpotential is *ca.* 600 mV higher than that of Pt; furthermore, it is not very sensitive to variations in the concentration of the doping agent [20][21]. These electrode coatings provide a current efficiency of at least 58% (4). Asea Brown Boveri has constructed a pilot installation that has a two-pole electrode reactor; the specific power consumption is estimated to be *ca.* 50 kWh (kgD-CO)⁻¹ for concentrations comprised between 500 and 15 000 ppm [21]. A pilot plant with an anode surface of 1.6 m² has been developed at the Ecole Polytechnique Fédérale in Lausanne, Switzerland.

2.3. Predicting Electrochemical Mineralization Method [9][26]

The type of organic compound has a significant effect on the current efficiency value, defined by the electrochemical oxidation index [17–19][27]. The EOI corresponds to the intrinsic oxidability of a compound. Measurements performed on Pt electrodes have made it possible to compare the behavior of a series of monosubstituted compounds of benzene with phenol (R = –OH, –NH₂, –COO[–], –SO₃[–], –NO₂). The experimental EOI values are available as Hammett's correlation. Cominellis' work [9] has shown that the oxidation reaction is slowed down by electron-attracting substituents (–NO₂) and promoted by electron-donating groups

(–OH, –NH₂). This suggests that the limiting stage in the oxidation of aromatic compounds is an electrophilic substitution. Among the aromatic compounds, those that carry the amino group can be treated electrochemically in the most economical way. It should be noted that the nitrated derivatives electrolyzed in a cell without a separator are efficiently eliminated due to the cathodic reduction of the NO₂ group into the NH₂ group [29].

3. Electrochemical Regeneration of a Redox Mediator

The possibilities in this area are far more limited than in electrosynthesis. The mediator redox couple used must not introduce any additional toxicity into the discharged effluent. Heavy metals that catalyze oxidation reactions must, therefore, be excluded when treating liquid effluents, except in certain special cases.

Iron, which is not very toxic, can be used as mediator, provided it can be eliminated by precipitation in a later stage of the process. However, it can be efficient, at low concentrations, for catalyzing the transfer of oxygen when degrading detergents in aqueous solutions [30].

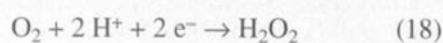
Let us consider the case of a mixture of Fe²⁺ and H₂O₂ which forms *Fenton's* reagent whose oxidizing action is very powerful due to the formation of OH[•] radicals by a homogeneous reaction:

These radicals oxidize an aromatic compound by electrophilic attack: reactions (10) and (11). In fact, the sequencing of the reactions is extremely complex [31–33], and the overall process is not self-maintaining [25][33]. The classic chemical reaction is difficult to control due to the loss of the OH[•] radicals [27][32].

The electrochemical regeneration of Fe²⁺:



and the formation of H₂O₂ by the simultaneous cathodic reduction of O₂ in solution allow the rate of hydroxyl radicals generation to be controlled [25][32][33]:



Given the low solubility of oxygen in an aqueous medium, the productivity of (18) is low; it is worthwhile injecting H₂O₂ directly into the solution at a suitable flow rate [33]. Sudoh *et al.* [25] have

degraded the phenol (initial concentration 260–2600 ppm) in oxalic acid and CO₂ by more than 60%, by forming *Fenton's* reagent in the effluent at pH 3 and saturated with O₂. According to these authors, the destruction of the intermediaries, hydroquinone, catechol, and *p*-quinone, is virtually total. It may be considered that the electrochemical *Fenton's* reagent could only be applied to the treatment of polluted waters with electrodes with a large specific surface area, due to the low value of the optimum iron concentration [32], and, therefore, to the low value of the reduction limit currents for step (18).

In a recent work, Farmer *et al.* [34] suggested that the degradation of benzene by anodic oxidation of Ag⁺ in an acid aqueous solution, could be initiated through to the quinone step by the OH[•] radicals formed by the action of Ag²⁺ electrically generated in H₂O. The Ag²⁺ ions, which are particularly powerful oxidants, are then capable of pursuing the degradation of the quinone through to complete mineralization in CO₂. This process is particularly interesting in the nuclear industry for dissolving and mineralizing contaminated materials and various products.

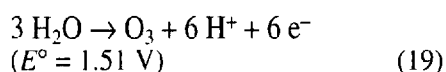
Metals (Ce, Cr, Ag, ...) at their higher degree of oxidation can be used to oxidize liquid or gaseous effluents after being absorbed by an electrolytic aqueous solution. A mixture of metal ions is used in the *Electrocinerator*TM process [35]. The use of heavy metals is justified, when the pollutant products are in the gaseous phase; these metals remain confined in the apparatus through which the gaseous flow to be treated passes. The electrochemical treatment is performed on the solution obtained after absorption by the electrolytic solution of the organic compounds contained in the gaseous effluent. Several tens of different organic compounds can be treated in this way by the process developed by *Electrocinerator Technologies Inc.* [36].

The classic generation of hypochlorite by anodic oxidation of chloride in a neutral or base medium can be performed in small- or medium-sized commercial cells and apparatuses [37][38].

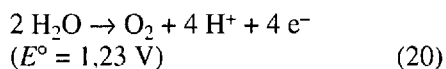
Recently, Cominellis and Nerini reported that the electrochemical oxidation on Ti/IrO₂ anodes of phenol in the presence of NaCl is catalyzed by the electro-generated ClO[–] anion [24]. Analysis of the oxidation products under these conditions has shown that, initially, organo-chlorinated compounds are formed in the electrolyte which are further oxidized to volatile organics (CHCl₃).

4. Electrochemical Generation of Oxidants without Residue

Oxidants such as H_2O_2 and O_3 can be produced on a small scale on the utilization site by electrochemical methods. The electrochemical production of O_3 is particularly interesting, since it can be obtained at higher concentrations than with traditional processes involving electrical discharges in air or oxygen [39]. The *Membrel*[®] process developed by *Asea Brown Boveri (ABB)* produces O_3 by oxidizing H_2O [40]:



But the competing production of O_2 has the advantage:



To prevent the preponderant formation of O_2 and to ensure that as much O_3 as possible is produced, a high oxygen overpotential anode must be used. The anodes developed by *ABB* meet stringent requirements, since they inhibit the formation of O_2 , have good electrical conductivity, and catalyze the formation of O_3 . They are made of $\beta\text{-PbO}_2$. The O_3 is produced, using solid electrolytes, from demineralized pure water directly in solution in the water. The efficiency in terms of current of *Membrel*[®] cells is of the order of 20% at 3 V and 1 A cm^{-2} [40]. This process has applications in sterilization and purification by oxidation of high purity water systems in the pharmaceuticals industry.

It should also be noted that *ICI* is studying an electrochemical process for generating O_3 that should allow O_3 concentrations in water to be obtained that are 10 to 20 times higher than those obtained by electrical discharge [41].

The electrochemical generation of H_2O_2 could be interesting for the on-site treatment of effluents. The production of alkaline solutions of H_2O_2 by electroreduction of dissolved oxygen according to reaction (18) on carbon electrodes is one of the best known methods [42–45]:

The solution formed under these conditions is unstable and has to be used on the site. Production is limited by the rate of the oxygen transfer in the solution [42]. The on site production of H_2O_2 by the old persulfate process [42] could be reinvestigated in a near future due to the increasing applications' number.

5. Conclusion

In certain cases, electrochemical techniques may provide economically viable solutions for treating industrial effluents containing organic compounds.

Ti/SnO_2 electrodes efficiently catalyze the oxygen-transfer reaction; they are promising in the area of the pretreatment of refractory aromatic compounds.

Processes based on the use of redox mediators are operational for treating gaseous effluents containing organic vapors.

The electrochemical production of O_3 is particularly interesting when a high concentration of this reagent in aqueous solution is required.

Received: October 20, 1994

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Chimia 49 (1995) 27–32
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ISSN 0009–4293

Development of Rechargeable Monopolar and Bipolar Zinc/Air Batteries

Stefan Müller^{a)}*, Franziska Holzer^{a)}, Otto Haas^{a)}, Christian Schlatter^{b)}, and Christos Comninellis^{b)}

Abstract. For the development of a rechargeable zinc/air battery, $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ -catalyzed (perovskite) bifunctional oxygen electrodes and pasted zinc electrodes were prepared and tested in monopolar zinc/air cells. In addition, a bipolar Zn/air stack was tested using reticulated copper foam as substrate for the zinc deposit. The cells were cycled in moderately alkaline ZnO-saturated electrolytes with KF as an electrolyte additive. The maximum power as well as the cycle life of the cells was investigated. The differences in porosity of the zinc electrode before and after the long-term test were analyzed using mercury porosimetry.

1. Introduction

In metal/air batteries only the metallic active material has to be stored in the negative electrode, while oxygen is continuously provided to the positive electrode from the ambient air. These cells offer very attractive specific energy and power data. For zinc/air cells, the theoretical specific energy is 1085 Wh/kg,

based on the molecular weight of ZnO (658 Ah/kg) and the theoretical cell voltage (1.65 V). Practical values of 90–300 Wh/kg for secondary and primary batteries, have already been demonstrated [1][2].

Since cheap and nontoxic batteries with a high energy density are a prerequisite for electric vehicles, we think that investigation of these batteries will prove very rewarding.

About 25 years ago, GM and other companies gave up their Zn/air battery projects, since their oxygen electrodes had a very short life time and were not bifunctional, *i.e.*, could not be used for the charging process. In fact, the service life of their Zn/air module was only *ca.* 200 h. In one of their studies, they came to the conclusion that the Zn/air battery would only be interesting for private electric car applications, if the battery could be recharged electrically, but not, if it was recharged mechanically by replacing the Zn electrodes. For an electrically rechargeable Zn/air battery, bifunctional oxygen electrodes and Zn electrodes with minor shape change [3] and no dendrite formation are necessary. More recently, LBL (Lawrence Berkeley Laboratory) developed a pasted zinc electrode with a high cycle life [4], mainly for the Zn/NiOOH battery.

With the pasted Zn electrode, more than 500 cycles could be demonstrated in a Zn/NiOOH battery; moreover, the cycle life of this battery was not limited by the Zn electrode. Shape change, which typically degrades Zn electrodes, was not the major problem in these cells, since they used moderately alkaline ZnO-saturated electrolyte and electrode or electrolyte

*Correspondence: S. Müller^{a)}

^{a)} Paul Scherrer Institut
CH–5232 Villigen PSI

^{b)} Swiss Federal Institute of Technology
CH–1015 Lausanne