DEGRADATION OF PESTICIDES IN AQUEOUS MEDIUM BY ELECTRO-FENTON AND RELATED METHODS. A REVIEW

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Key Words: Pesticides, electro-Fenton, photoelectro-Fenton, carbon-felt cathode, gas diffusion cathode, water treatment

ABSTRACT

This paper reviews the application of indirect electro-oxidation processes such as electro-Fenton, photoelectro-Fenton and peroxi-coagulation to decontaminate waters containing persistent pesticides. The fundamentals of these electrochemical advanced oxidation processes (EAOPs) are described. They are environmentally friendly technologies based on the electrogeneration of H2O2 at a carbonaceous cathode from the reduction of oxygen gas. In all cases, the main oxidizing species is the powerful oxidizing agent hydroxyl radical formed from Fenton’s reaction between added Fe2+ and electrogenerated H2O2. The characteristics of three- and two-electrode divided or undivided tank or flow cells using working cathodes such as carbon-felt, reticulated vitreous carbon or O2-diffusion and anodes such as Pt, boron-doped diamond (BDD) or iron for the treatment of pesticides in these EAOPs are analyzed. The effect of several operational parameters that have large influence on the degradation rate of these pollutants in different electro-Fenton systems is examined. Pesticides are quickly removed following pseudo first-order kinetics in most cases. Their degradation sequences are discussed from aromatic intermediates, short aliphatic acids and inorganic end products detected. Final carboxylic acids are completely destroyed using undivided Pt/carbon felt and BDD/O2 cells, whereas they are more difficultly oxidized in undivided Pt/O2 cell because of the formation of hardly oxidizable Fe(III)-oxalate complexes. These latter products can be rapidly photodecomposed by the action of UV light in photoelectro-Fenton or sunlight in solar photoelectro-Fenton, significantly enhancing the mineralization process. Peroxi-coagulation with a sacrificial Fe anode also leads to fast degradation with production of small quantities of Fe(III) complexes because organics are mainly retained in the Fe(OH)3 precipitate formed.

INTRODUCTION

Pesticides are chemical substances intended for preventing, destroying, repelling and mitigating any pest, although they can also be used as a plant regulator, defoliant or desiccant. Herbicides, insecticides and fungicides are the most common pesticides. The widespread use of thousands of tons of these compounds in domestic, industrial and agricultural activities throughout the world, especially in developed countries, generates large volumes of contaminated wastewaters, whose direct disposal into natural channels causes their accumulation in the environment. Although very low levels of pesticides, typically concentrations < 10 μg L⁻¹ [1], are detected as pollutants in surface and ground waters, most of them are hardly biodegradable and toxic for human beings and animals. Therefore, aiming to avoid the adverse effects of these contaminants on living organisms, the purification of wastewaters containing pesticides is needed, thus ensuring their reuse in human activities. Unfortunately, pesticides are considered as persistent organic pollutants (POPs), since they can not be removed by conventional oxidation methods in municipal sewage treatment plants.

As a response, a large variety of advanced oxida-
tion processes (AOPs) have been recently developed to remove POPs from waters. AOPs are environmentally friendly methods based on the in situ chemical, photochemical, photocatalytic or electrochemical production of •OH [1-7], which is the second strongest oxidant known after fluorine, with $E^\circ$($\cdot$OH/H$_2$O) = 2.8 V vs. NHE (normal hydrogen electrode). They are applied when conventional oxidation techniques become insufficient by kinetic reasons or because contaminants are refractory to chemical oxidation in aqueous medium or are partially oxidized yielding stable by-products showing even greater toxicity than the starting pollutants. In contrast, •OH generated in AOPs is able to non-selectively destroy most organic and organometallic pollutants until total mineralization. These radicals react rapidly with organics mainly either by abstraction of a hydrogen atom (dehydrogenation) or by addition to a non-saturated bond (hydroxylation). The latter reaction is typical of aromatic compounds, exhibiting second-order rate constants as high as $10^3$-$10^{10}$ M$^{-1}$ s$^{-1}$ [8].

Over the last decade, electrochemical AOPs (EAOPs) based on the cathodic electrogeneration of hydrogen peroxide are being successfully tested for the treatment of acidic wastewaters containing pesticides [1,5,6,9,10]. Among these emerging indirect electro-oxidation methods, the most popular technique is electro-Fenton (EF) that can be easily applied using divided or undivided electrolytic cells. In the first case, •OH is produced by the catalytic Fenton reaction between cathodically electrogenerated H$_2$O$_2$ and Fe$^{2+}$ whereas in the second one this radical is also formed, although to a much lesser extent, from water oxidation at the anode surface. The EF process in undivided cells can then take advantage of the oxidation reactions arising from the simultaneous participation of both anode and cathode, being more efficient for destruction of organics than classical anodic oxidation (AO). Other indirect electro-oxidation methods like photoelectro-Fenton (PEF) and peroxy-coagulation (PC) have been recently proposed to enhance the efficiency of EF from the catalytic action of UV light and the alternative use of a sacrificial iron anode, respectively.

This paper presents a review of the application of the above EAOPs to the degradation of pesticides in waters. Fundamentals of EF and related indirect electro-oxidation methods are initially described to analyze their characteristics and oxidation power.

**FUNDAMENTALS OF ELECTRO-FENTON PROCESS**

Hydrogen peroxide is a “green” chemical that leaves oxygen gas and water as by-products. It is widely utilized, e.g., to bleach pulp and paper and textiles, clean electronic circuits and delignify agricultural wastes, as well as for disinfection in medical and industrial applications and as an oxidant in synthesis and wastewater treatment [11,12]. However, the direct remediation of wastewaters with H$_2$O$_2$ is limited by its low oxidation power, since it can only attack reduced sulphur compounds, cyanides and certain organics such as aldehydes, formic acid and some nitro-organic and sulpho-organic compounds. For this reason, H$_2$O$_2$ is commonly activated in acidic effluents with Fe$^{2+}$ ion as catalyst (Fenton’s reagent) to produce homogeneous •OH as strong oxidant of organics [2-4]. This procedure is widely developed in the traditional chemical Fenton method.

It is known since 1882 that H$_2$O$_2$ can be accumulated in aqueous medium from the cathodic two-electron reduction of dissolved O$_2$ gas at carbonaceous electrodes with high surface area [13]. In acidic solutions, this reaction with $E^\circ$ = 0.68 V vs. NHE can be written as follows:

$$O_{2(g)} + 2H^+ + 2e^{-} \rightarrow H_2O_2 \quad (1)$$

and takes place more easily than the four-electron reduction of this gas to water ($E^\circ$ = 1.23 V vs. NHE). Hydrogen peroxide production and stability depend on factors such as cell configuration, cathode properties used and operational conditions. Electrochemical reduction at the cathode surface by reaction (2) and in much lesser extent disproportion in the bulk by reaction (3) are general parasitic reactions that result in the loss of oxidant or a lowering of current efficiency [14]:

$$H_2O_2 + 2e^{-} \rightarrow 2OH^- \quad (2)$$

$$2H_2O_2 \rightarrow O_{2(g)} + 2H_2O \quad (3)$$

When an undivided cell is utilized, H$_2$O$_2$ is also oxidized to O$_2$ at the anode via hydroperoxyl radical (HO$_2^•$) as intermediate by the following reactions [15]:

$$H_2O_2 \rightarrow HO_2^- + H^+ + e^- \quad (4)$$

$$HO_2^- \rightarrow O_2(g) + H^+ + e^- \quad (5)$$

The EF treatment of aqueous solutions of pesticides involves the continuous generation of H$_2$O$_2$ from O$_2$ directly injected as pure gas or compressed air, which is efficiently reduced at carbon felt [1,16-31], reticulated vitreous carbon (RVC) [32-34] and carbon-polytetrafluoroethylene (PTFE) gas diffusion [35-47] cathodes via reaction (1). The technique becomes operative if the acidic contaminated solutions contain a small catalytic quantity of Fe$^{2+}$ that reacts with electrogenerated H$_2$O$_2$ to form Fe$^{3+}$ and •OH according to the classical Fenton’s reaction [48]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^- \quad (6)$$

The optimum pH for reaction (6) is 2.8, where it can be propagated by the catalytic behaviour of the Fe$^{3+}$/Fe$^{2+}$ pair [48,51]. Table 1 collects the main reactions related to the Fenton system, along with their corresponding absolute second-order rate constant ($k_2$).
Table 1. Absolute second-order rate constant for the main general reactions involved in a Fenton system at pH ca. 3 [49]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k_2 ) (M(^{-1}) s(^{-1}))</th>
<th>Reaction No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initiation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- )</td>
<td>55</td>
<td>(6)</td>
</tr>
<tr>
<td><strong>Catalysis: Fe(II) regeneration</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \cdot\text{OH} )</td>
<td></td>
<td>(7)</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + \text{HO}_2^- \rightarrow \text{Fe}^{2+} + \cdot\text{O}_2^- + \text{H}^+ )</td>
<td>( 2.0 \times 10^7 )</td>
<td>(8)</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + \cdot\text{O}_2^- \rightarrow \text{Fe}^{2+} + \cdot\text{O}_2 )</td>
<td>( 5.0 \times 10^7 )</td>
<td>(9)</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + \cdot\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}_2 )</td>
<td>( 1.0 \times 10^7 )</td>
<td>(10)</td>
</tr>
<tr>
<td><strong>Propagation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^- )</td>
<td>( 2.7 \times 10^7 )</td>
<td>(11)</td>
</tr>
<tr>
<td>( \text{HO}_2^- \rightarrow \cdot\text{OH} + \text{O}_2^- )</td>
<td></td>
<td>(12)</td>
</tr>
<tr>
<td>( \cdot\text{OH} + \cdot\text{OH} \rightarrow \text{R}^* + \text{H}_2\text{O} )</td>
<td>( 10^7-10^9 )</td>
<td>(13)</td>
</tr>
<tr>
<td>( \text{ArH} + \cdot\text{OH} \rightarrow \text{ArHOH} )</td>
<td>( 10^9-10^{10} )</td>
<td>(14)</td>
</tr>
<tr>
<td><strong>Inhibition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + \cdot\text{OH} \rightarrow \text{Fe}^{2+} + \text{OH}^- )</td>
<td>( 3.2 \times 10^6 )</td>
<td>(15)</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + \text{HO}_2^- + \cdot\text{OH} \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 )</td>
<td>( 1.2 \times 10^6 )</td>
<td>(16)</td>
</tr>
<tr>
<td>( \cdot\text{O}_2^- + \text{HO}_2^- + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 )</td>
<td>( 9.7 \times 10^7 )</td>
<td>(17)</td>
</tr>
<tr>
<td>( \text{HO}_2^- + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 )</td>
<td>( 8.3 \times 10^9 )</td>
<td>(18)</td>
</tr>
<tr>
<td>( \text{HO}_2^- + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>( 7.1 \times 10^9 )</td>
<td>(19)</td>
</tr>
<tr>
<td>( \cdot\text{O}_2^- + \cdot\text{OH} \rightarrow \text{OH}^- + \text{O}_2 )</td>
<td>( 1.0 \times 10^{10} )</td>
<td>(20)</td>
</tr>
<tr>
<td>( \cdot\text{O}_2^- + \cdot\text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}_2^- + \frac{1}{2}\text{O}_2 )</td>
<td>( 9.7 \times 10^7 )</td>
<td>(21)</td>
</tr>
<tr>
<td>( \cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 )</td>
<td>( 6.0 \times 10^9 )</td>
<td>(22)</td>
</tr>
</tbody>
</table>

Thus, organics contained in the acidic solution are destroyed by \( \cdot\text{OH} \) from reactions (13) or (14), but also by action of heterogeneous \( \cdot\text{OH} \) produced at a high \( \text{O}_2 \)-overvoltage anode (M) from water oxidation by reaction (25) [7,52]:

\[
\text{M} + \text{H}_2\text{O} \rightarrow \text{M}(\cdot\text{OH}) + \text{H}^+ + \text{e}^- \quad (25)
\]

The degradative action of \( \text{M}(\cdot\text{OH}) \) is rather ineffective for classical electrodes such as Pt, being much more efficient when a BDD (boron-doped diamond) thin layer is used as anode. It has been found that operating at high current, within the water discharge region, reactive BDD(\( \cdot\text{OH} \)) is produced in much higher quantity than Pt(\( \cdot\text{OH} \)) and can mineralize completely aromatics and unsaturated compounds such as carboxylic acids [52]. Furthermore, the low adsorption ability of \( \cdot\text{OH} \) on BDD favours its dimerization to \( \text{H}_2\text{O}_2 \) by reaction (26). Also, when the iron sulphate salt is used to generate the catalyst (\( \text{Fe}^{2+} \) or \( \text{Fe}^{3+} \) ions) or the sulphuric acid is employed to set the solution pH, the high oxidation power of this anode facilitates the generation of other weaker oxidizing agents like \( \text{S}_2\text{O}_8^{2-} \) ion from oxidation of \( \text{SO}_4^{2-} \) and \( \text{HSO}_4^- \) ions by reactions (27) and (28), respectively, and ozone by reaction (29) [52-55]:

\[
2\text{BDD}(\cdot\text{OH}) \rightarrow \text{BDD} + \text{H}_2\text{O}_2 \quad (26)
\]
\[
2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2\text{e}^- \quad (27)
\]
\[
2\text{HSO}_4^- \rightarrow \text{S}_2\text{O}_8^{2-} + 2\text{H}^+ + 2\text{e}^- \quad (28)
\]
3H₂O → O₃ (g) + 6H⁺ + 6e⁻  

(29)

The use of a BDD anode is currently preferred in AO and comparison with EF can be made without Fe²⁺ or Fe³⁺ addition to the contaminated water, which corresponds to the method so-called AO with H₂O₂ (AO-H₂O₂).

A related EAOP is PEF, which consists in the simultaneous use of electrogenerated H₂O₂ in the presence of Fe²⁺ (EF conditions) and UVA (ultraviolet A) illumination of the solution to enhance the mineralization process. The degradation action of irradiation can be associated with: (i) higher regeneration of Fe²⁺ and production of additional 'OH from photoreduction of Fe(OH)²⁺, the predominant Fe³⁺ species in acidic medium [48], according to photo-Fenton reaction (30):

Fe(OH)²⁺ + hν → Fe²⁺ + 'OH  

(30)

and/or (ii) photodecarboxylation of complexes of Fe(III) with generated carboxylic acids. As an example, reaction (31) shows this photolytic processes for Fe(III)-oxalate complexes (Fe(C₂O₄)²⁺, Fe(C₂O₄)³⁻ and Fe(C₂O₄)₃³⁻) [56], which are formed as ultimate by-products of aromatics:

2Fe(C₂O₄)²⁺ + hν → 2Fe²⁺  

+ (2n − 1)C₂O₄²⁻ + 2CO₂  

(31)

A disadvantage of this method is the high electrical cost of lamps supplying UVA light. This can be solved by applying the solar PEF (SPEF) method in which the solution is directly irradiated with sunlight as a cheap and renewable energy source allowing the use of wavelengths longer than 300 nm [47].

Another related EAOP is the so-called PC process. It utilizes a sacrificial iron anode to treat a wastewater in an undivided cell containing a cathode that electrogenerates H₂O₂ from reaction (1). Fe²⁺ is continuously supplied to the solution from the oxidation of the Fe anode by reaction (32) [57]:

Fe → Fe²⁺ + 2e⁻  

(32)

Fe²⁺ thus formed is quickly oxidized by electrogenerated H₂O₂ according to the Fenton reaction (6) to give a Fe³⁺ saturated solution, while the excess of this ion precipitates as hydrated Fe(III) oxide (Fe(OH)₃). All produced hydrogen peroxide is then consumed allowing that organic pollutants can be removed from the wastewater by the combined action of their degradation with 'OH generated by Fenton reaction (6) and their coagulation with a great quantity of Fe(OH)₃ precipitate formed [43]. PC differs from classical electrocoagulation with a Fe anode, where soluble organics are not oxidized due to the absence of electrogenerated H₂O₂, although in some cases, they can be separated from the medium by precipitation of their complexes with injected iron ions.

**ELECTROCHEMICAL SYSTEMS**

Three-electrode divided [1,16-20,24] or undivided [21,32,34] tank cells and undivided flow cells [33], as well as two-electrode undivided tank reactors [22,23,25-31,35-46] or flow cells [47], have been tested for the treatment of different pesticides. In all these electrochemical systems, O₂ gas or compressed air is bubbled through the solution or directly injected to the carbonaceous cathode to produce H₂O₂ from reaction (1). Examples of two-electrode undivided cells with carbon felt [50] and O₂-diffusion [15] cathodes are depicted in Figs. 1a and 1b, respectively.

When solid cathodes are employed, pesticide solutions are usually saturated with pure O₂ or compressed air under vigorous stirring or high liquid flow rate to obtain the maximum production and sometimes, accumulation of H₂O₂. This is also achieved with an O₂-diffusion cathode if it is fed with an excess of pure O₂ gas. The initial pH of effluents treated by EF is normally regulated to a value near 3.0, close to the optimum pH of 2.8 for Fenton’s reaction (6) [48], to ensure the fastest generation of homogeneous 'OH.

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**Fig. 1.** Schemes of bench-scaled electrochemical systems with open and stirred two-electrode undivided tank reactors utilized for the EF treatment with H₂O₂ electrogeneration. (a) Carbon-felt cathode and bubbling of compressed air [50] and (b) carbon-PTFE diffusion cathode directly fed with pure O₂ [15].
Other parameters affecting the production of this radical such as the cathodic potential ($E_{\text{cat}}$) or current and Fe$^{2+}$ or Fe$^{3+}$ concentration are optimized in each system.

The use of a carbon-felt cathode with a large specific area only allows H$_2$O$_2$ accumulation in the medium if no iron ions are added to the electrolyzed solution, since this species is not detected when EF is applied [50]. In such system, Fig. 2a shows the change of iron ions concentration with time during the electrolysis of 200 mL of 0.05 M Na$_2$SO$_4$ with 0.2 mM Fe$^{3+}$ at pH 3.0 in the two-electrode cell of Fig. 1a with a 4.5 cm$^2$ Pt cylindrical mesh as anode and a 60 cm$^2$ carbon felt cathode. A very fast conversion of all initial Fe$^{3+}$ into Fe$^{2+}$ operating at 300 mA can be observed, reaching an Fe$^{2+}$ concentration close to 0.2 mM after 20 min of electrolysis. This makes it evident that the rate of reaction (23) is so high that Fe$^{2+}$ is rapidly regenerated from Fe$^{3+}$ reduction at the cathode, being able to readily remove all electrogenerated H$_2$O$_2$ from Fenton reaction (6). These results also corrobo-rate that a very small catalytic quantity of Fe$^{2+}$ or Fe$^{3+}$, even lower than 0.2 mM, is needed to obtain the maximum rate for OH production in this type of cells.

A very different behaviour can be seen in Fig. 2b for the electrolysis of 100 mL of 0.05 M Na$_2$SO$_4$ solutions at pH 3.0 in the two-electrode undivided Pt/O$_2$ cell of Fig. 1b equipped with a 10 cm$^2$ Pt anode and a 3 cm$^2$ carbon-PTFE O$_2$-diffusion cathode [35]. As can be seen, H$_2$O$_2$ is gradually accumulated for 3 h reaching an increasing steady concentration with rising applied current of 100 mA (curve e), 300 mA (curve b) and 450 mA (curve a). The steady H$_2$O$_2$ concentration is attained just when its electrogeneration rate from reaction (1) becomes equal to its oxidation rate to O$_2$ from reactions (4) and (5). When 1.0 mM Fe$^{2+}$ is added to this system (EF conditions), H$_2$O$_2$ destruction is accelerated by action of reactions (6), (7) and (11), as can be deduced by comparing curves b and c of Fig. 2b at 300 mA. The acceleration of H$_2$O$_2$ destruction mainly from Fenton reaction (6) owing to additional Fe$^{2+}$ regeneration under UVA illumination from photo-Fenton reaction (30), i.e., operating under PEF conditions, can be confirmed from the slight decay in steady H$_2$O$_2$ concentration observed by comparing curves c (without UVA light) and d (with 6 W UVA light) of Fig. 2b.

A trend for H$_2$O$_2$ accumulation similar to that of Fig. 2b has also been described by Badellino et al. [32] for a three-electrode undivided Pt/RVC cell operating under potentiostatic control at a constant $E_{\text{cat}}$ in the range between -0.5 and -1.7 V vs. saturated calomel electrode (SCE). At more negative cathodic potentials this species is unstable since it is reduced to OH$^-$ by reaction (2). These authors also showed that H$_2$O$_2$ production decays with increasing temperature as a result of the lower O$_2$ solubility in the aqueous solution. On the other hand, Oturan’s group applied a low constant $E_{\text{cat}} = -0.5$ V vs. SCE when using three-electrode cells [11,16-21], because such $E_{\text{cat}}$ value allowed enough H$_2$O$_2$ production for ensuring fast degradation of organic pollutants by EF.

**DEGRADATION OF PESTICIDES**

As explained above, several electrochemical systems with different oxidation properties have been applied to degrade pesticides by EF and related methods. This section is devoted to discuss the degradation of these contaminants in aqueous medium taking into account the characteristics of each system utilized, which have been mainly studied by the authors of this article. The most significant results obtained for divided and/or undivided Pt/carbon felt, Pt/RVC, Pt/O$_2$, BDD/O$_2$ and Fe/O$_2$ cells are described. The treatment of pesticides in the first type of electrolysis cells has been extensively studied by Oturan’s group, whereas their mineralization in the three latter systems has
been investigated by Brillas and co-workers.

1. Divided Pt/Carbon Felt Cell

Former studies by Oturan and co-workers [1,17-20] initially reported the mineralization process and the oxidation intermediates formed from several aromatic pesticides during their EF degradation in the cathodic compartment of a three-electrode divided cell with a carbon-felt working cathode of high specific surface surrounding the anodic compartment containing a Pt counter electrode and separated with a glass frit. A constant potential was applied to the carbon-felt electrode by using a SCE reference electrode. Its value was chosen to yield the efficient generation of both components of Fenton’s reagent (H₂O₂ and Fe²⁺), being ·OH produced from Fenton’s reaction (6) in the bulk. This allowed keeping an efficient concentration of Fe²⁺ in solution from reaction (23), giving rise to a rapid destruction of organic pollutants. Electrolyses were then carried out with 125-150 mL of O₂-saturated aqueous solutions acidified with H₂SO₄ in the presence of 0.5-2 mM Fe³⁺ or Fe²⁺ at pH 2-3 and \( E_{\text{cat}} = -0.5 \text{ V vs. SCE} \). The mineralization degree attained during the EF treatment was monitored from the abatement of total organic carbon (TOC) or chemical oxygen demand (COD) of the solution.

The pioneering work of Oturan in this matter [17] reported that the EF process with 1 mM Fe³⁺ allows the rapid and almost total mineralization (> 95% TOC decay) of an aqueous solution with 1 mM 2,4-D (2,4-dichlorophenoxyacetic acid) after the consumption of 2,000 C (Fig. 3a). In contrast, the decay kinetics of the initial chlorophenoxy herbicide was much faster, attaining total removal after the pass of only 700 C, as can be observed in the inset of Fig. 3b. Reversed-phase HPLC analysis of electrolyzed solutions revealed the generation of some primary hydroxylated derivatives, such as 2,4-dichlorophenol, 2,4-dichlororesorcinol, 4,6-dichlororesorcinol, 2-chlorohydroquinone and 1,2,4-trihydroxybenzene, formed at the early stages of the treatment. Figure 3b shows that the three first dichlorinated derivatives disappear after consuming 700 C, that is, they persist in the medium while 2,4-D is being destroyed. The presence of these derivatives in the reaction medium then confirms the attack of hydroxyl radical on the aromatic ring of the herbicide leading to the formation of its hydroxylated derivatives, along with other processes involving dechlorination and dehydrogenation. The primary derivatives can also react with ·OH, similarly to 2,4-D, to give polyhydroxylated compounds and quinones before undergoing the attack of the oxidant to open the benzene moiety producing short-chain carboxylic acids.

Further work [1] confirmed fast kinetic decay with formation of hydroxylated derivatives for other chlorophenoxy herbicides including 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), mecoprop (2-(4-chloro-2-methylphenoxy)propionic acid), 2-(4-chlorophenoxy)-2-methylpropionic acid and 2,4-DP (2-(2,4-dichlorophenoxy)propionic acid), as well as pesticides such as bendiocarb (2,3-isopropylidendioxy-phenyl-N-methylcarbamate), pirimiphos-methyl \((O-(2-diethylamino-6-methylpyrimidin-4-yl)-O,O-dimethylphosphorothioate), coumatetralyl (4-hydroxy-3-(1,2,3,4-tetrahydro-1-naphthy)coumarin) and cholorophacinon \((2-(2-(4-chlorophenyl)-2-phenylacetyl)inden-1,3-dione). For a polychlorinated pesticide like PCP (pentachlorophenol) [18], it was also observed the existence of hydroxylation followed by quick dechlorination of resulting by-products. A slow TOC abatement of 125 mL of a 0.03 mM PCP (saturated) solution of pH 3 in the three-electrode divided Pt/carbon felt cell up to achieving 82% mineralization was found after consumption of 1,500 C, attaining total release of all chlorine atoms as Cl⁻ ion at
Table 2. Absolute second-order rate constant \( (k_{2,P}) \) determined by the competition kinetics method for the reaction of several pesticides with homogeneous \( \cdot \)OH formed during the EF process in sulphuric acid solutions at room temperature using three- and two-electrode Pt/carbon felt cells

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>( C_0 ) (mM)</th>
<th>Experimental conditions</th>
<th>Current (mA)</th>
<th>( E_{\text{cat}} ) (V vs. SCE)</th>
<th>( k_{2,P} \times 10^{-9} ) (M(^{-1}) s(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Divided cell</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-D</td>
<td>1.0</td>
<td>150 mL, 0.01 M H(_2)SO(_4), 1 mM Fe(^{3+})</td>
<td>60</td>
<td>-0.50</td>
<td>35</td>
<td>[17]</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>0.10</td>
<td>125 mL, pH 3, 0.5 mM Fe(^{2+})</td>
<td>60</td>
<td>-0.50</td>
<td>5.4</td>
<td>[20]</td>
</tr>
<tr>
<td><strong>Undivided cell</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>0.03</td>
<td>125 mL, pH 3, 1 mM Fe(^{2+})</td>
<td>50</td>
<td></td>
<td>3.6</td>
<td>[18]</td>
</tr>
<tr>
<td>Ditetron</td>
<td>0.17</td>
<td>125 mL, pH 3, 0.5 mM Fe(^{3+})</td>
<td>100</td>
<td></td>
<td>4.8</td>
<td>[21]</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>0.13</td>
<td>150 mL, pH 3, 0.1 mM Fe(^{3+})</td>
<td>100</td>
<td></td>
<td>42</td>
<td>[25]</td>
</tr>
<tr>
<td>Chlortoluron</td>
<td>0.05</td>
<td></td>
<td>60</td>
<td></td>
<td>4.9</td>
<td>[26]</td>
</tr>
<tr>
<td>Carbofuran</td>
<td>0.05</td>
<td>150 mL, 0.05 M Na(_2)SO(_4), pH 3, 0.1 mM Fe(^{3+})</td>
<td>60</td>
<td></td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Bentazone</td>
<td>0.05</td>
<td></td>
<td>60</td>
<td></td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Imazaquin</td>
<td>0.10</td>
<td>125 mL, pH 3, 0.1 mM Fe(^{3+})</td>
<td>60</td>
<td></td>
<td>4.5</td>
<td>[28]</td>
</tr>
<tr>
<td>Picloram</td>
<td>0.125</td>
<td>150 mL, 0.05 M Na(_2)SO(_4), pH 3, 0.2 mM Fe(^{3+})</td>
<td>60</td>
<td></td>
<td>2.7</td>
<td>[29]</td>
</tr>
<tr>
<td>Propham</td>
<td>0.50</td>
<td>150 mL, 0.05 M Na(_2)SO(_4), pH 3, 0.5 mM Fe(^{3+})</td>
<td>60</td>
<td></td>
<td>2.2</td>
<td>[30]</td>
</tr>
</tbody>
</table>

Table 2 collects the \( k_{2,P} \)-value obtained for several pesticides using this method in different EF conditions involving both divided and undivided Pt/carbon felt cells under potentiostatic or galvanostatic operation mode. As can be seen, this parameter is always close to \( 10^9 \) to \( 10^{10} \) M\(^{-1}\) s\(^{-1}\), as expected for the hydroxylation reactions of aromatic compounds [8].

### 2. Undivided Pt/Carbon Felt Cell

More recently, Oturan’s group has extended its research to an undivided Pt/carbon felt cell using similar experimental conditions to those of the previous divided one. A three-electrode cell was firstly used to...
treat 125 mL of an O₂-saturated 40 mg L⁻¹ diuron solution with 0.5 mM Fe³⁺ in H₂SO₄ of pH 3 at 100 mA [21]. The herbicide disappeared in 10 min, whereas the solution TOC was reduced by 93% at 1,000 °C. A further work already reporting the use of a two-electrode cell as in Fig. 1a was devoted to soil extract solutions containing high PCP loads [22]. These extractions were made by adding hydroxypropyl-β-cyclodextrin (HPCD) to soil effluents, thus increasing up to 3.5 times the concentration of PCP during the water flush of the soil. Although the reaction of •OH with HPCD is more rapid than with PCP, it was found that a HPCD content of 5 mM in an O₂-saturated solution with 0.5 mM Fe³⁺ at pH 3 accelerated the decay rate of 0.1 mM PCP, probably due to the formation of a ternary PCP-HPCD-iron complex that is directly oxidized by this radical. Total disappearance of the pesticide and 90% COD abatement were achieved after 11 h of electrolysis of 125 mL of a soil extract solution with 0.15 mM PCP, 5 mM HPCD and 0.5 mM Fe³⁺ of pH 3 at 50 mA. Accumulation of short-chain carboxylic acids such as monochloroacetic, dichloromalenic, acetic, formic and oxalic was detected during the mineralization process.

The effect of different experimental parameters on the degradation power of EF was also investigated. Thus, this method showed an excellent ability for the decomposition of aqueous solutions of commercial formulations of pesticides containing Cu²⁺ ions such as Mistel GD (a fungicide of Novartis Agro) and Cuprofix (a fungicide of ELF Atochem Agri) [23]. Mistel GD is a mixture of the active principally cymoxanil and mancozebe along with additives, and Cuprofix contains cymoxanil, zinebe, CuSO₄ and surfactants as additives. Note that in the presence of H₂O₂ a catalytic behaviour of the Cu²⁺/Cu⁺ system is expected [58] involving the reduction of Cu²⁺ to Cu⁺ with HO₂⁻ by reaction (34) and/or with organic radicals R* by reaction (35):

$$\text{Cu}^{2+} + \text{HO}_2^- \rightarrow \text{Cu}^+ + \text{H}^+ + \text{O}_2(g) \quad (34)$$

$$\text{Cu}^{2+} + \text{R}^* \rightarrow \text{Cu}^+ + \text{R}^- \quad (35)$$

followed by regeneration of Cu²⁺ from oxidation of Cu⁺ with H₂O₂ according to the following Fenton-like reaction:

$$\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + ^\cdot \text{OH} + \text{OH}^- \quad (36)$$

HPLC analysis of a Mistel GD solution treated at 100 mA revealed that cymoxanil and mancozebe are rapidly and completely removed after electrolysis times of 90 and 120 min, respectively (Fig. 4a). Taking into account the complex consumption of •OH by the additives, these removal times seem reasonable. Figure 4a also illustrates that the use of either 1 mM Fe³⁺ or Cu²⁺ as catalyst gives practically the same decay rate, being slightly higher for the latter ion. In contrast, the catalytic action of Fe²⁺ on H₂O₂ is more effective than Cu⁺ for COD reduction, since 92 or 80% mineralization was attained for the Mistel GD containing 1 mM Fe³⁺ or Cu²⁺, respectively, after the consumption of 6,000 C at 300 mA. The positive catalytic action of Cu²⁺ in the EF method has been corroborated by treating a Cuprofix solution without Fe³⁺ addition. Under these conditions, zinebe and cymoxanil, the active principles of Cuprofix, are completely removed from the medium in 70 and 150 min, respectively, by applying a constant current of 100 mA. As can be seen in Fig. 4b, Cuprofix can be completely mineralized when electrolysis is prolonged up to the consumption of a charge of 10,000 C after 8 h of treatment at 350 mA, although the mineralization rate is slightly higher when Fe³⁺ is added as catalyst, thus confirming the synergistic action of Cu²⁺ and Fe²⁺.

The role of solution pH and the inorganic ion used to adjust this parameter on the effectiveness of EF was clarified by electrolyzing 150 mL of a 0.2 mM solution of the organophosphorus herbicide methyl parathion with 0.1 mM Fe³⁺ in a two-electrode undi-
Fig. 5. Effect of pH and medium on TOC removal of 150 mL of 0.2 mM methyl parathion aqueous solutions with 0.1 mM Fe<sup>3+</sup> by EF treatment in an undivided Pt/carbon felt cell at 150 mA and room temperature [25]. Initial pH: (∇) 1.0, (□) 3.0 and (△) 4.0 in H<sub>2</sub>SO<sub>4</sub> medium; (●) 1.0, (■) 3.0 and (▲) 4.0 in HClO<sub>4</sub> medium.

Fig. 6. Effect of Fe<sup>3+</sup> content and applied current on (a,c) TOC and (b,d) picloram concentration decays of 150 mL of pesticide solutions in 0.05 M Na<sub>2</sub>SO<sub>4</sub> of pH 3.0 at room temperature using an undivided Pt/carbon felt cell [29]. Initial picloram concentration: (a,c) 0.25 mM and (b,d) 0.125 mM. Fe<sup>3+</sup> concentration: (a,b) (○) 0.02 mM, (□) 0.05 mM, (△) 0.1 mM, (◇) 0.2 mM, (▽) 0.5 mM and (◁) 1.0 mM; (c) 0.2 mM and (d) 0.1 mM. Current: (a) 200 mA, (b) 60 mA and (c,d) (●) 30 mA, (■) 60 mA, (▲) 100 mA, (◇) 200 mA, (▽) 300 mA and (△) 500 mA.
ram solutions with 0.2-0.1 mM Fe\textsuperscript{3+} when current increases from 30 to 500 mA. Actually, similar results are obtained for 300 and 500 mA, suggesting that the system has already attained its maximum oxidation power at a certain applied current. At 300 mA, for example, picloram disappears in only 4 min; time gradually becomes longer with decreasing applied current.

Kesraoui-Abdessalem et al. [27] established the optimum operational conditions for the EF treatment of 150 mL of solutions of the pesticide chlortoluron (3-(3-chloro-4-methylphenyl)-1,1-dimethyleurea) in 0.05 M Na\textsubscript{2}SO\textsubscript{4} with 0.1 mM Fe\textsuperscript{3+} of pH 3.0 based on a novel procedure that uses a factorial design methodology and a Doehlert matrix to clarify the degradation kinetics and the mineralization rate, respectively, considering pesticide concentration, current and electrolysis time as experimental variables in both cases. The highest decay kinetics was attained for 0.05 mM chlortoluron at 60 mA, giving rise to complete disappearance in 4 min, whereas maximum mineralization efficiency with TOC removal of 98\% was achieved after 8 h of treatment of a 0.125 mM pesticide solution at 300 mA.

Several papers also calculated the mineralization current efficiency (MCE, in \%) for the EF process in an undivided Pt/carbon felt cell operating in galvanostatic control from the following equation:

\[
MCE = \frac{\Delta \text{TOC}_{\text{exp}}}{\Delta \text{TOC}_{\text{theor}}} \times 100 \tag{37}
\]

where \(\Delta \text{TOC}_{\text{exp}}\) denotes the experimental TOC decay in solution and \(\Delta \text{TOC}_{\text{theor}}\) represents the theoretically calculated TOC removal assuming that the applied electrical charge is only consumed to mineralize the pesticide under study according to the electrochemical oxidation reaction. For example, the \(\Delta \text{TOC}_{\text{theor}}\) values in Eq. 37 were calculated considering that total conversion into carbon dioxide and inorganic ions verifies reaction (38) for methyl parathion [25] and reaction (39) for propanil (phenylcarbamate acid isopropyl ester) [30]:

\[
\begin{align*}
\text{C}_8\text{H}_{15}\text{NO}_5\text{PS} + 22\text{H}_2\text{O} & \rightarrow 8\text{CO}_2 + \text{NO}_3^- \\
+ & \text{SO}_4^{2-} + \text{PO}_4^{3-} + 54\text{H}^+ + 48\text{e}^- \tag{38}
\end{align*}
\]

\[
\begin{align*}
\text{C}_{10}\text{H}_{17}\text{NO}_2 + 2\text{H}_2\text{O} & \rightarrow 10\text{CO}_2 \\
+ & \text{NO}_3^- + 55\text{H}^+ + 54\text{e}^- \tag{39}
\end{align*}
\]

For a 0.2 mM methyl parathion solution at pH 3 and 150 mA (Fig. 7), the efficiency decreased from 51\% at 10 min to 2.7\% after 9 h of treatment [25]. A sharp decay in MCE with prolonged electrolysis time was also found for the degradation of 150 mL of 0.25 mM propanil solutions in 0.05 M Na\textsubscript{2}SO\textsubscript{4} with 0.01-1.0 mM Fe\textsuperscript{3+} of pH 3 by applying 60-300 mA [30]. This behaviour can be associated with the progressive formation of oxidation by-products that are more difficultly destroyed with \(^1\text{OH}\) compared to the degradation of the initial pollutant.

GC-MS and HPLC analyses of EF treated solutions were employed to identify and quantify the aromatic and aliphatic intermediates formed during the degradation of some pesticides [21,25-31]. Released inorganic ions such as Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, NH\textsubscript{4}\textsuperscript{+}, SO\textsubscript{4}\textsuperscript{2-} and PO\textsubscript{4}\textsuperscript{3-} were also followed by ion chromatography. Figures 7a, 7b and 7c illustrate the time-course of aromatic compounds, carboxylic acids and inorganic ions found when a 0.12 mM methyl parathion solution in HClO\textsubscript{4} medium of pH 3.0 was degraded at 60 mA [25]. As can be seen in Fig. 7a, all aromatic intermediates such as methyl paraoxon, 4-nitrophenol, 4-nitroacetanilide, hydroquinone and p-benzoquinone are present in the medium during a time similar to that of
Fig. 8. General reaction sequence proposed for the mineralization of methyl parathion in aqueous acid medium by hydroxyl radical following EF process in an undivided Pt/carbon felt cell [25].

Several authors have investigated the degradation of some pesticides in three-electrode undivided Pt/RVC cells. Badellino et al. [32] electrolyzed 130 mL of 100 mg L\(^{-1}\) 2,4-D solutions in 0.3 M K\(_2\)SO\(_4\) at pH 3.5 and 10 °C in a tank reactor at \(E_{\text{cat}} = -1.6\) V vs. SCE, maintaining a content of 25 mg L\(^{-1}\) of dissolved O\(_2\), by means of different methods such as AO-H\(_2\)O\(_2\), EF with 1 mM Fe\(^{2+}\) and PEF with 1 mM Fe\(^{2+}\) under a 8 W UVC irradiation. Although UVC light photolyzes 2,4-D, the role of illumination was very poor during the degradation process, giving similar 67-69% mineralization after 90% of 2,4-D removal by EF and PEF, a value higher than 58% obtained for AO-H\(_2\)O\(_2\). The EF process is preferable since it needs a lower energy consumption of 0.05 in comparison to 0.98 kWh g\(^{-1}\) TOC for PEF. Aromatic intermediates like 2,4-dichlorophenol, 2,4-dichlororesorcinol, 4,6-dichlororesorcinol and 2-chlorophenol were identified in all processes. The same authors extended the above treatments to 3.5 L of the 100 mg L\(^{-1}\) 2,4-D solution in a flow cell operating under similar operational conditions [33]. In this system, the pH was adjusted to 2.5, the cathodic potential was taken as -1.6 V vs. Pt and the liquid flow rate was 300 L h\(^{-1}\). They confirmed that the degradation power increased in the sequence AO-H\(_2\)O\(_2\) < EF < PEF and that the PEF method led to ca. 95% TOC removal in 300 min, much greater than 64% obtained for EF.

More recently, Losito et al. [34] reported the EF degradation of 50 mL of 5 mg L\(^{-1}\) of phenyl-urea herbicides such as isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea), chlortoluuron and chloroxuron (N-[4-(4-chlorophenoxy)phenyl]-N,N-dimethylurea) in sulphuric medium of pH 3 with 0.017-0.024 mM Fe\(^{3+}\) (1:1 [substrate]:[Fe\(^{3+}\)]) at \(E_{\text{cat}} = -0.5\) V vs. Ag/AgCl.
Isoproturon was totally removed in 60 min, whereas the other two chlorophenyl-urea compounds were more refractory and disappear after about 180 min of electrosynthesis. Aromatic intermediates were detected by HPLC coupled to electrospray ionization single and tandem mass spectrometry. Single and multiple hydroxylation with substitution of H, alkyl groups or Cl, depending on the herbicide, and demethylation on the dimethylamino moiety, eventually followed by hydroxylation, were the most relevant processes found allowing to explain the generation of the different by-products.

4. Pt/O2 Cell

The degradation of several pesticides by AO-H2O2, EF and PEF with a Pt anode (denoted AO-H2O2-Pt, EF-Pt and PEF-Pt, respectively) has been studied by Brillas’ group using the open, thermostated, cylindrical and undivided Pt/O2 cell of Fig. 1b containing 100 mL of contaminated solution vigorously stirred with a magnetic bar. The anode was a 10 cm2 Pt sheet and the cathode was a 3 cm2 carbon-PTFE electrode placed at the extreme of a polypropylene holder and mounted onto a Ni screen that served as current distributor, in contact with a nichrome wire used as electrical connection. This electrode was directly fed with pure O2 at a flow rate of 12-20 mL min−1, which diffuses to the interface of its carbon surface with the liquid, where it is reduced to H2O2 by reaction (1). Under these conditions, the rate of H2O2 accumulation in the Pt/O2 cell is high enough (Fig. 2b) to destroy relatively concentrated solutions of organic contaminants.

Common chlorophenoxy herbicides present in the aquatic environment such as 2,4-D [35], 4-CPA (4-chlorophenoxyacetic acid) [36], 2,4,5-T [38], MCPA (4-chloro-2-methylphenoxyacetic acid) [40] and dicamba (3,6-dichloro-2-methoxybenzoic acid) [42], were degraded in this cell. The contaminated solutions contained 0.05 M Na2SO4 as background electrolyte and H2SO4 to adjust its pH in the range 2.0-6.0. Electrolyses were performed at constant current between 100 and 450 mA, keeping the temperature at 25 or 35 °C. EF-Pt and PEF-Pt were performed by adding 0.2-2.0 mM FeSO4 to the starting solutions. In the latter method, the solution was irradiated with UVA light of \(\lambda_{\text{max}} = 360\) nm supplied by a 6 W fluorescent black tube placed at 7 cm above its surface.

Figure 9a illustrates the comparative degradation behaviour for 190 mg L\(^{-1}\) of 4-CPA, at pH 3.0, 100 mA and 35 °C using the above treatments. As can be seen, their oxidation power increases in the sequence AO-H2O2-Pt < EF-Pt with 1 mM Fe\(^{2+}\) < PEF-Pt with 1 mM Fe\(^{2+}\). The low oxidation ability in AO that only allows 29% TOC reduction in 360 min can be ascribed to the small concentration of reactive Pt(\(\text{OH}\))\(^{•}\) formed at the anode surface from reaction (35), being considered the sole oxidizing species of organics because H2O2 is a comparatively much weaker oxidant. In contrast, EF-Pt with 1 mM Fe\(^{2+}\) yields a much faster TOC removal during approximately 120 min owing to the existence of quick homogeneous reactions of organics with the high quantity of \(\text{OH}\) produced from Fenton’s reaction (6), although at long electrolysis time the solution accumulates by-products that are hardly attacked by this radical, only giving 74% mineralization at 360 min. The photodecomposition of such by-products and/or the enhancement of the generation rate of \(\text{OH}\) by reaction (30) can account for the highest mineralization rate of PEF-Pt with 1 mM Fe\(^{2+}\), giving rise to total mineralization in about 180-240 min. Therefore, this method exhibits the greatest oxidation power in the Pt/O2 system.

The same relative oxidation power was found for the above EAOPs in the treatment of all herbicides, as deduced from the percentages of TOC removal after 1 and 3 h of electrosynthesis of solutions with 100 mg L\(^{-1}\) TOC of 4-CPA, MCPA, 2,4-D and 2,4,5-T at pH 3.0 and 100 mA summarized in Table 3. All initial chlorine atoms of these compounds was released as Cl\(^{-}\), as discussed below. The MCE was then determined from Eq. 37 assuming that the conversion of these compounds into carbon dioxide and chloride ion follows
Table 3. Percentage of TOC removal, mineralization current efficiency (MCE) and pseudo first-order rate constant determined for the degradation of 100 mL of solutions with 100 mg L\(^{-1}\) TOC of chlorophenoxyacetic acid herbicides in 0.05 M Na\(_2\)SO\(_4\) of pH 3.0 by different EAOPs at 100 mA [35,41,43,44]

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Method(^a)</th>
<th>T(ºC)</th>
<th>after 1 h of treatment</th>
<th>after 3 h of treatment</th>
<th>(k_1) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>%TOC removal</td>
<td>MCE %</td>
<td>%TOC removal</td>
</tr>
<tr>
<td>4-CPA</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td>35</td>
<td>18</td>
<td>16</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td></td>
<td>25</td>
<td>22</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>EF-Pt</td>
<td></td>
<td>48</td>
<td>42</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td></td>
<td>37</td>
<td>33</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td></td>
<td>78</td>
<td>70</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td></td>
<td>74</td>
<td>66</td>
<td>86</td>
</tr>
<tr>
<td>MCPA</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td>35</td>
<td>9.6</td>
<td>8.9</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td></td>
<td>24</td>
<td>23</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>EF-Pt</td>
<td></td>
<td>41</td>
<td>39</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td></td>
<td>49</td>
<td>47</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td></td>
<td>66</td>
<td>62</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td></td>
<td>68</td>
<td>64</td>
<td>85</td>
</tr>
<tr>
<td>2,4-D</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td>25</td>
<td>4.7</td>
<td>3.9</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td></td>
<td>27</td>
<td>22</td>
<td>57</td>
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<tr>
<td></td>
<td>EF-Pt</td>
<td></td>
<td>25</td>
<td>35</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td></td>
<td>35</td>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td></td>
<td>52</td>
<td>44</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td></td>
<td>56</td>
<td>47</td>
<td>76</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>AO-H(_2)O(_2)-Pt</td>
<td>35</td>
<td>4.8</td>
<td>3.7</td>
<td>21</td>
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<tr>
<td></td>
<td>AO-H(_2)O(_2)-BDD</td>
<td></td>
<td>20</td>
<td>16</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>EF-Pt</td>
<td></td>
<td>38</td>
<td>30</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>EF-BDD</td>
<td></td>
<td>49</td>
<td>38</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>PEF-Pt</td>
<td></td>
<td>64</td>
<td>50</td>
<td>99</td>
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<tr>
<td></td>
<td>PC</td>
<td></td>
<td>59</td>
<td>46</td>
<td>84</td>
</tr>
</tbody>
</table>

\(^a\)AO-H\(_2\)O\(_2\)-Pt = anodic oxidation with a Pt/O\(_2\) cell, AO-H\(_2\)O\(_2\)-BDD = anodic oxidation with a BDD/O\(_2\) cell, EF-Pt = electro-Fenton with a Pt/O\(_2\) cell and 1 mM Fe\(^{2+}\), EF-BDD = electro-Fenton with a BDD/O\(_2\) cell and 1 mM Fe\(^{2+}\), PEF-Pt = photoelectro-Fenton with a Pt/O\(_2\) cell, 1 mM Fe\(^{2+}\) and UVA light, PC = peroxi-coagulation with an Fe/O\(_2\) cell.

The effect of experimental parameters on the degradation rate of herbicides was also investigated. It was found that increasing current caused higher mineralization rate in all EAOPs by the concomitant production of more Pt(\(^{•}\)OH) from reaction (25) and/or \(^{•}\)OH in the medium from reaction (6) because more H\(_2\)O\(_2\) is accumulated (Fig. 2b). However, the MCE value gradually decreased at higher current because of the greater relative increase in rate of parasitic wasting reactions involving these radicals, like AO (in primis) to O\(_2\) as follows:

\[2M(\^{•}\text{OH}) \rightarrow 2M + O_{2(g)} + 2H^{+} + 2e^{-} \] (44)
as well as reactions (11) and (15). In contrast, a higher efficiency was obtained with raising initial herbicide content as a result of the quicker destruction of organics with hydroxyl radical and the concomitant decay in the rate of previous non-oxidizing parasitic reactions. All compounds were more effectively degraded at pH 3.0-4.0 by EF-Pt and PEF-Pt, near the optimum
Fig. 10. Evolution of the concentration of selected products detected during the degradation of 4-CPA solutions under the conditions shown in Fig. 9 by (●) AO-H$_2$O$_2$-Pt, (■) EF-Pt and (▲) PEF-Pt [36]. Plots correspond to: (a) 4-chlorophenol, (b) glycolic acid, (c) oxalic acid and (d) chloride ion.

pH of 2.8 for Fenton’s reaction (6), where it produces the major quantity of oxidant ‘OH. Note that this effect was not significant for the AO process. At pH 3.0, similar degradation rates were found up to 1 mM Fe$^{2+}$, whereas higher Fe$^{2+}$ contents caused a decrease in TOC removal due to the acceleration of reaction (15).

The decay kinetics for initial pollutants was followed by reversed-phase HPLC chromatography. As illustrated in Fig. 9b for 4-CPA, the herbicide concentration is removed very slowly in AO-H$_2$O$_2$-Pt for 360 min, in agreement with the low oxidation ability of electrogenerated Pt(‘OH). A much faster decay of this compound and similar disappearance in 25 min can be observed for EF-Pt and PEF-Pt because of the production of very high quantities of ‘OH from Fenton’s reaction (6). This indicates that the participation of photo-Fenton reaction (30) is insignificant, without photodecomposition of the initial herbicide by the action of UVA light. All concentration decays for the aforementioned herbicides agreed with the kinetics equation related to a pseudo first-order reaction. The corresponding pseudo first-order rate constants ($k_1$) are summarized in the last column of Table 3, being about two magnitude orders higher for EF-Pt and PEF-Pt than for AO-H$_2$O$_2$-Pt.

GC-MS and HPLC analyses of electrolyzed solutions allowed detecting aromatic intermediates like: (a) hydroquinone and $p$-benzoquinone for 4-CPA, (b) 4-chloro-$o$- cresol, methylhydroquinone and methyl-$p$-benzoquinone for MCPA, (c) 2,4-dichlorophenol, 4,6-dichlororesorcinol, chlorohydroquinone and chloro-$p$-benzoquinone for 2,4-D, and (d) 2,4,5-trichlorophenol, 2,5-dichlorohydroquinone, 4,6-dichlororesorcinol and 2,5-dihydroxy-$p$-benzoquinone for 2,4,5-T, which remained in solution while the starting herbicide was being removed. A high number of short-chain carboxylic acids coming from the cleavage of the benzenic ring of aromatics and the release of aliphatic lateral chains were identified by ion-exclusion HPLC analysis of electrolyzed solutions.

As an example, Fig. 10 presents the time-course of selected compounds detected during the treatment of 190 mg L$^{-1}$ 4-CPA solutions of pH 3.0 at 100 mA. The primary by-products, 4-chlorophenol (Fig. 10a) and glycolic acid (Fig. 10b) are slowly destroyed by AO-H$_2$O$_2$-Pt, but very quickly degraded by EF-Pt and PEF-Pt. The evolution of 4-chlorophenol is very similar in the two latter processes, as expected if aromatics are not photodecomposed by UVA light. However, glycolic acid disappears more rapidly in PEF-Pt, probably due to the fast photodegradation of its complexes with Fe(III). The same trends were found for the other intermediates, except oxalic acid that is accumulated in EF-Pt and rapidly photodecarboxylated in PEF-Pt (Fig. 10c). These tendencies can be associated with the formation of a high proportion of Fe(III)-oxalate complexes, owing to the high amounts of Fe$^{3+}$ produced from Fenton’s reaction (6). The low oxidation ability of ‘OH to destroy the Fe(III)-oxalate complexes formed renders a slow TOC abatement at the end of EF-Pt (Fig. 9a), while the fast photodecarboxylation of such complexes by UVA light [56] accounts for the total mineralization achieved in PEF-Pt, thus explaining the highest oxidation power of this
procedure. Mineralization of 4-CPA causes the loss of its initial chlorine as chloride ion. As can be seen in Fig. 10d, all Cl\(^-\) ions are released after 30-40 min of EF-Pt and PEF-Pt, when chlorinated by-products are totally destroyed. In contrast, the progressive Cl\(^-\) accumulation in AO-H\(_2\)O\(_2\)-Pt for 360 min is indicative of a slower removal of chlorinated intermediates.

From the results obtained for 4-CPA degradation, the reaction sequence shown in Fig. 11 is proposed for the different EAOPs tested in a Pt/O\(_2\) cell. The initial breaking of the lateral chain of 4-CPA via C(1)-O bond gives 4-chlorophenol and glycolic acid. Hydroxylation on C(2)-position of 4-chlorophenol leads to 4-chlorocatechol, while parallel \(^\cdot\)OH attack on its C(4)-position yields hydroquinone with loss of Cl\(^-\). Hydroquinone is subsequently dehydrogenated to p-benzoquinone. Further oxidation of 4-chlorocatechol, with release of Cl\(^-\), and p-benzoquinone produces a mixture of malic, maleic, and fumaric acids, which are oxidized to oxalic acid. This acid can also be formed from dehydrogenation of the initially generated glycolic acid, followed by hydroxylation of the resulting glyoxylic acid. Parallel oxidation of both glycolic and glyoxylic acids produces formic acid, which is transformed into CO\(_2\). Oxalic acid is slowly mineralized to CO\(_2\) by AO-H\(_2\)O\(_2\)-Pt, whereas in the EAOPs with iron ions, it forms complexes with Fe(III). These species are slowly destroyed in EF-Pt and quickly photodecarboxylated, with loss of Fe\(^{3+}\), in PEF-Pt.

The degradation of a solution with 100 mg L\(^{-1}\) TOC of the herbicide amitrole (3-amino-1,2,4-triazole) at pH 3.0 in the Pt/O\(_2\) cell of Fig. 1b was further studied by Da Pozzo et al. [45]. Complete decontamination was achieved by EF-Pt with 1 mM Fe\(^{2+}\), although with low accumulation of released NO\(_3^-\) and NH\(_4^+\) ions as expected if volatile N-products are lost during the mineralization process. A similar behaviour was found by treating the same amitrole solution by direct AO using Pt/stainless steel and BDD/stainless steel cells, but EF-Pt gave the fastest TOC removal due to the higher production of \(^\cdot\)OH from Fenton’s reaction (6).

5. BDD/O\(_2\) Cell

The influence of a BDD anode, with much higher oxidation power than Pt, on the AO-H\(_2\)O\(_2\) and EF treatments of several chlorophenoxy herbicides was studied to compare the oxidation power of Pt/O\(_2\) and BDD/O\(_2\) cells [44]. Solutions with 100 mg L\(^{-1}\) TOC of 4-CPA, MCPA, 2,4-D and 2,4,5-T of pH 3.0 were then electrolyzed at 100 mA and 35 °C in an undivided BDD/O\(_2\) cell like Fig. 1b equipped with a 3 cm\(^2\) BDD thin layer deposited on a conductive Si sheet as anode. Figure 12a depicts the TOC decay as function of consumed specific charge (in Ah L\(^{-1}\)) obtained for such trials for 10 h by AO-H\(_2\)O\(_2\)-BDD and EF-BDD with 1 mM Fe\(^{2+}\). As can be seen, all herbicide solutions are degraded at similar rate in each procedure, attaining total mineralization after 9-10 h (specific charge 9-10 Ah dm\(^{-3}\)) of the former treatment and 6-8 h (specific charge 6-8 Ah L\(^{-1}\)) of the latter one. A very fast degradation at the first stages (up to ca. 2 Ah L\(^{-1}\)) of EF-BDD can be observed, although just a slightly shorter time compared to AO-H\(_2\)O\(_2\)-BDD is required for achieving overall mineralization. Both methods with BDD are then much more efficient than the homologous ones with Pt (Table 3), which do not
allow total decontamination under comparable conditions (Fig. 9a). This can not be related to a faster reaction of aromatic intermediates with the higher amount of reactive BDD(•OH) expected from reaction (25), since initial herbicides always followed a pseudo-first-order decay with a quite similar $k_1$-value for each method in both Pt/O$_2$ and BDD/O$_2$ cells, as can be seen in Table 3. Worth highlighting, these results confirm the quicker reaction of these herbicides with •OH in the medium rather than on Pt or BDD surface.

Analysis of generated carboxylic acids in the above trials revealed the presence of large amounts of oxalic acid. Figure 12b shows the evolutions of this acid during 4-CPA degradation. The persistence of Fe(III)-oxalate complexes in EF-BDD can not be related to their oxidation with homogeneous •OH because they are stable in EF-Pt (Fig. 10c) and hence, they are mineralized by reaction with BDD(•OH). The slow destruction of such complexes on the latter anode accounts for the long time needed for the total decontamination of herbicides by EF-BDD. This occurs at similar times to those needed using AO-H$_2$O$_2$-BDD in which oxalic acid is accumulated at lower concentrations (Fig. 12b) because it is practically removed at the same rate as produced. It was also found that Cl$^-$ ion released in all treatments was slowly oxidized to Cl$_2$ on BDD [58] as follows:

$$2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^- \quad (45)$$

Recently, the great oxidation power of EAoPs with BDD was confirmed by studying the degradation of herbicide 2,4-DP in the electrolytic cell of Fig. 1a [46]. It was found that AO with a BDD anode and a graphite cathode, EF-BDD with 1 mM Fe$^{2+}$ and PEF-BDD with 1 mM Fe$^{2+}$ led to complete mineralization, with overall loss of chloride ion, of 100 mL of 217 mg L$^{-1}$ 2,4-DP solutions (equivalent to 100 mg L$^{-1}$ TOC) in 0.05 M Na$_2$SO$_4$ of pH 3.0 at 300 mA and at 35 °C. This is feasible by the high generation of oxidant BDD(•OH) favouring the destruction of final carboxylic acids, although the greater production of •OH in the bulk from Fenton’s reaction (6) destroyed more rapidly aromatic products, thus making the EF-BDD and PEF-BDD processes to be much more efficient than AO. Again, UVA light in PEF-BDD had little effect on the degradation rate of pollutants. The comparative procedures with Pt led to slower decontamination because of the lower oxidizing power of this anode. In all cases, chlorohydroquinone and chloro-p-benzoquinone were detected as primary aromatic intermediates, further on being oxidized to maleic, fumaric, malic, lactic, pyruvic, acetic, formic and oxalic acids.

A further study was focused to clarify the viability of the SPEF method with BDD (SPEF-BDD). This was made with the flow plant schematized in Fig. 13a in which a one-compartment filter-press BDD/O$_2$ cell with electrodes of 20 cm$^2$ area and a solar photoreactor of 600 mL of irradiation volume were coupled to treat 2.5 L of mecoprop solutions in 0.05 M Na$_2$SO$_4$ of pH 3.0 at 25 °C and flow rate of 180 L h$^{-1}$. Figure 13b illustrates the fast degradation of 100 mg L$^{-1}$ of this herbicide at 50 mA cm$^{-2}$ by SPEF-BDD with 0.5 mM Fe$^{2+}$ compared to AO-H$_2$O$_2$-BDD and EF-BDD with 0.5 mM Fe$^{2+}$. In the first method, however, TOC is very slowly removed after being reduced by 82% at 100 min (specific charge 0.67 Ah L$^{-1}$), attaining 96% mineralization at 9 h (specific charge 3.6 Ah L$^{-1}$). This suggests the presence of final species that can only be oxidized with BDD(•OH), but not photodecomposed by solar light. The degradation rate and efficiency of SPEF-BDD process calculated from Eq. 37 increased strongly with rising herbicide content up to 0.64 g L$^{-1}$, when it was observed a decay of the efficiency from
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37 to 93% along 9 h of electrolysis, confirming the efficient photodecomposition of Fe(III) complexes. At the end of this trial, 96% TOC removal was also achieved with 46 kWh m⁻³ energy cost. The decay kinetics of mecoprop in SPEF-BDD revealed its rapid reaction with ·OH in the bulk to yield 4-chloro-o-cresol, 2-methylhydroquinone and 2-methyl-p-benzoquinone as primary reaction products. Fe(III)-oxalate and Fe(III)-acetate complexes were detected as the most persistent final products. It was concluded that overall mineralization can be attained because Fe(III)-oxalate complexes are efficiently photodecomposed by solar irradiation, whereas Fe(III)-acetate complexes are slowly but progressively destroyed by BDD(·OH).

6. Fe/O₂ Cell

The degradation of acidic solutions containing herbicides such as 4-CPA, MCPA, 2,4-D, 2,4,5-T and dicamba has also been studied using a Fe/O₂ cell without (PC process) and with UVA irradiation (photoperoxi-coagulation process) [37,39,41,43] under experimental conditions comparable to those used with Pt and BDD anodes. Since the sacrificial Fe anode is quantitatively oxidized to Fe²⁺ by reaction (32) and large amounts of Fe(OH)₃ precipitate are produced, the solution pH increases continuously and periodic regulation with H₂SO₄ is required during electrolysis to make it possible the participation of Fenton’s reaction. For each pollutant, the same by-products and released inorganic ions were detected using EF, PEF and PC because ·OH formed from Fenton’s reaction (6) is always the main oxidant. Note that photoperoxi-coagulation only led to a slightly faster TOC removal than by means of PC, indicating that UVA light is mainly absorbed (or dispersed) by the Fe(OH)₃ precipitate in suspension, thus inhibiting the extra production of ·OH by the action of photo-Fenton reaction (30). Therefore, for the sake of simplicity only the characteristics of the PC process for the treatment of these compounds are examined hereafter.

Figure 14a presents the comparative TOC-time plots determined for 100 mg L⁻¹ TOC of the above herbicides at pH 3.0 and 100 mA under pH regulation. A quick reduction of soluble TOC can be observed during the first 2 h, whereupon degradation becomes much slower due to the presence of hardly oxidizable products. At 3 h of electrolysis, 76-86% TOC removal with 21-27% current efficiency was found for the chlorophenoxyacetic herbicides. These values are higher than those obtained for EF-Pt and EF-BDD but lower than the ones determined for PEF-Pt (Table 3). Figure 14b shows that the four chlorophenoxyacetic compounds are removed at similar rate with disappearance in ca. 30-40 min. These compounds undergo the attack of ·OH on the C(1) position of their benzenic rings causing the breaking of the C(1)-O bond to yield their phenol derivative and glycolic acid, as stated above (Fig. 11). In contrast, the chlorophenoxybenzoic herbicide dicamba is more rapidly destroyed, suggesting the existence of direct hydroxylation on its benzenic ring. All these compounds also followed a pseudo first-order decay kinetics in PC giving quite similar k₁-values to those obtained for EF-Pt, EF-BDD and PEF-Pt under comparable conditions (Table 3), as expected if the main oxidant is ·OH produced from Fenton’s reaction (6).

The fast TOC removal at the first stages of the PC process of all herbicides (Fig. 14a) can also be
related to the coagulation of some intermediates with the Fe(OH)₃ precipitate formed. The existence of this process was confirmed by determining the percentage of TOC removal and percentages of coagulated and mineralized TOC after 6 h of electrolysis, which are summarized in Table 4. These data show that both coagulation and mineralization paths compete at 100 mA, but increasing current accelerates TOC abatement with predominance of coagulation. The faster generation of $^\bullet$OH when current raises then enhances the oxidation of herbicides (Section 4) yielding a larger proportion of by-products retained by the greater quantity of Fe(OH)₃ precipitate produced, utterly avoiding their mineralization. Low contents of oxalic acid were detected in the final electrolyzed solutions, indicating that their Fe(III) complexes are very slowly removed by coagulation. On the other hand, the percentage of chloride ions released after 6 h of electrolysis at 100 mA was 86% for 4-CPA, 76% for MCPA, 100% for 2,4-D and dicamba and 90% for 2,4,5-T. This can be explained by the fact that most chlorinated organics formed from herbicides oxidation are destroyed with loss of Cl⁻, whereas the resulting organic products are the species mainly retained in the Fe(OH)₃ precipitate.

**CONCLUSIONS**

The EF method is a very attractive EAOP due to its ability to efficiently destroy acidic waters contaminated with environmentally hazardous POPs such as pesticides. It is an ecological technique because it can remove organic pollutants without the external addition of harmful chemical reagents and without production of neither dangerous wastes nor iron sludge, being also an environmentally friendly method and inexpensive due to its low operational energy cost. The degradation process is usually performed in divided or undivided cells containing a Pt anode, although other anodic materials such as BDD with much higher O₂-overvoltage can also be utilized. Different catalysts including salts of Fe²⁺, Fe³⁺ and Cu²⁺ alone or combined can be used to produce $^\bullet$OH by Fenton’s reaction with H₂O₂ electrogenerated at a carbonaceous cathode like carbon-felt, RVC or O₂-diffusion ele-

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**Table 4.** Percentages of TOC removal and of coagulated and mineralized TOC obtained after 6 h of peroxi-coagulation treatments of 100 mL solutions of chlorophenoxyacetic and chlorobenzoic acids solutions with an herbicide concentration equivalent to 100 mg L⁻¹ TOC in 0.05 M Na₂SO₄ of pH 3.0 at 35 °C in a Fe/O₂ cell at different current values and under pH regulation [43].

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Current (mA)</th>
<th>%TOC removal</th>
<th>% coagulated TOC</th>
<th>% mineralized TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CPA</td>
<td>100</td>
<td>91</td>
<td>48</td>
<td>43</td>
</tr>
<tr>
<td>MCPA</td>
<td>100</td>
<td>92</td>
<td>49</td>
<td>43</td>
</tr>
<tr>
<td>2,4-D</td>
<td>100</td>
<td>81</td>
<td>38</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>92</td>
<td>45</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>92</td>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td>dicamba</td>
<td>100</td>
<td>94</td>
<td>48</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>94</td>
<td>94</td>
<td>0</td>
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<tr>
<td></td>
<td>450</td>
<td>94</td>
<td>94</td>
<td>0</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>100</td>
<td>93</td>
<td>54</td>
<td>39</td>
</tr>
</tbody>
</table>
trode. The reaction of this radical with pesticides obeys a pseudo-first-order kinetics in most cases, allowing determining its absolute second-order rate constant in the Pt/carbon felt cell by the competitive kinetics method. In this cell, all intermediates formed during EF treatment are degraded and the final electrolyzed solutions only contain inorganic ions, along with short-chain carboxylic acids when overall mineralization is not attained. In the Pt/O₂ cell, however, complexes of Fe(III) with final carboxylic acids such as oxalic are formed, being hardly oxidized by both ·OH generated in the bulk and at the anode surface from water oxidation, thus limiting the mineralization of pesticides. The use of a BDD/O₂ cell always gives overall mineralization, although long electrolysis times are required. The related PEF process becomes much more efficient because total decontamination is accelerated mainly by the rapid photodecomposition of Fe(III)-oxalate complexes under the action of UVA irradiation. Preliminary studies with sunlight as alternative UVA source in SPEF have shown that this EAOP could be very attractive at industrial scale because operational time and cost are significantly reduced. Peroxi-coagulation with a sacrificial Fe anode is also very effective, although separation of pollutants in the precipitate formed usually predominates over their mineralization.

REFERENCES


Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.

Manuscript Accepted: February 3, 2009