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# Anodic, cathodic and combined treatments for the electrochemical oxidation of an effluent from the flame retardant industry

**Daniele Montanaro · Elisabetta Petrucci · Carlo Merli**

**Abstract** The electrochemical oxidation of an effluent from the manufacture of phosphorus based flame retardants was studied. To reach a residual concentration of reduced phosphorus lower than 10 mg L$^{-1}$, in compliance with Italian law for industrial wastewater disposal, anodic oxidation using a boron-doped diamond (BDD) anode and electro-Fenton (EF) treatment were tested. The effects of some factors are optimised and a comparison of the reaction pathways is also presented. A combined treatment using EF with BDD conducted in an undivided cell is shown not to enhance the data obtained with BDD while a novel combined treatment using EF and BDD in a divided cell shows promising results when an anionic membrane is used as separation. In this last case the cell operates as two different batch reactors working with the same current. The anodic compartment, fed with raw effluent, provides partial oxidation, while the cathodic compartment, fed with the partially anodically oxidised solution, completes the treatment. When the effluent is transferred in the cathodic compartment, the anodic one is fed with fresh untreated solution. The advantage of this kind of coupling consists in the simultaneity of the two treatments which allows total oxidation with notable saving of charge and time.

**Keywords** Electro-Fenton · Boron-doped diamond electrode · Hydroxyl radical · Combined treatment · Phosphorus compounds · Flame retardants

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## 1 Introduction

Electrochemical technologies are currently considered as a promising alternative for treating industrial wastewaters containing pollutants recalcitrant to traditional removal methods [1–3].

Several examples of integration of electrochemical processes with chemical or biological treatment are known [4–7], while scant information is available regarding the possible combination of only electrochemical processes of either cathodic or anodic type. Such a coupling is particularly appealing when realised at the same time, that is exploiting the same current, with clear economic benefits.

The simultaneous action of efficient anodes and oxidant species indirectly electrogenerated at the cathode can significantly increase the oxidation rate of pollutants.

Currently, boron-doped diamond (BDD) is the most promising anodic material for many applications [8–11] due to its high stability, wide potential window of water discharge and low background current [12–17].

The anodic oxidation takes place via hydroxyl radicals generated by water discharge on the BDD surface according to Eq. 1:

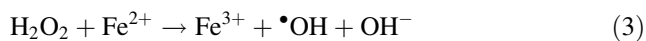$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^- \tag{1}$$
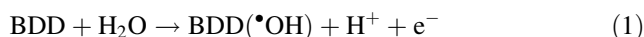
A gas diffusion electrode has been used as the cathode for the in situ generation of hydrogen peroxide [18–19] via electrochemical reduction of oxygen (Eq. 2).

$$O_2 + 2H_3O^+ + 2e^- \rightarrow H_2O_2 + 2H_2O \tag{2}$$
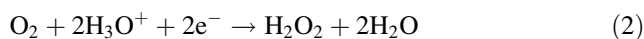
In acidic conditions, active free radicals with hard oxidizing properties [20–25] may be produced by simply adding ferrous ions according to Fenton's reaction (Eq. 3).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (3)$$

Unlike what is observed in chemical Fenton treatment, ferrous ions are continuous supplied by the simultaneous cathodic reduction of $Fe^{3+}$ (Eq. 4).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$

A combined treatment can be performed by the concomitant occurrence of direct oxidation on a BDD anode and an indirect cathodic oxidation via electro-Fenton (EF) reaction.

This can be performed either in an undivided cell, where the effluent is oxidized by the hydroxyl radicals generated by both the anode and the cathode, or alternatively in a divided two-chamber cell. In the latter case the effluent is fed and partially oxidized in a first compartment and then pumped into the second compartment where oxidation is completed while, at the same time, in the first compartment fresh untreated effluent is supplied.

Recent papers indicate a growing interest in the investigation of this kind of treatments where electro-Fenton reaction is combined with direct anodic oxidation [26–27].

In this study the efficiency of both direct and indirect electrochemical oxidation processes, alone and in combination, was investigated to treat an effluent from the manufacture of phosphorus based flame retardants.

Flame retardants are an important group of plastic additives which are commonly used to enhance the resistance to ignition and flame propagation of many everyday items. Unlike the traditional halogenated flame retardants, typically based on bromine, phosphorus compounds are known to overcome environmental concerns, because of the prevention of toxic gases and smoke release in case of fire [28–29].

Wastewaters from the manufacture of phosphorus flame retardants contain an overall phosphorus load ranging from 0.6 to 2.0 g $L^{-1}$, mainly as hypophosphites, phosphites and phosphates, together with red suspended phosphorus.

In the treatment of these effluents, for which effective remediation methods are not already available, strong oxidation agents are needed to transform all the phosphorus compounds into phosphates. After flocculation and precipitation the bulk limit of 10 mg $L^{-1}$ of residual phosphorus has to be reached in compliance with the Italian Regulation limits for industrial wastewater disposal [30].

## 2 Experimental

### 2.1 Materials

The industrial effluent, whose average composition is given in Table 1, came from an Italian plant for the manufacture of phosphorus derivatives. In the Fenton reaction bivalent iron was added as solid heptahydrate iron sulphate ($FeSO_4 \cdot 7H_2O$).

All the reagents were reagent grade from Merck and Aldrich and were used in their commercially available form with no further purification.

### 2.2 Electrochemical treatment procedure

All the electrolyses were performed under galvanostatic conditions using a potentiostat (AMEL 2051). An undivided thermostated cell 100 mL stirred with a magnetic bar was used, except for the sequential coupling treatment where a two-chamber cell was adopted. The two compartments, of 100 mL volume each, were separated by an anion exchange membrane (Neosepta supplied by Tokuyama corporation), thermostated and stirred with a magnetic bar.

In the electro-Fenton treatment a platinum electrode was used as anode while a carbon Vulcan gas diffusion electrode (GDE), was used as cathode. This electrode, described in detail in previous work [19], had a geometric area of about 5 $cm^2$.

Electrolyses were conducted after pH adjustment by means of sulphuric acid under air flow. 150 mg $L^{-1}$ of iron was added (as heptahydrate iron sulphate $FeSO_4 \cdot 7H_2O$) at the start of the electrolysis.

In anodic treatments a commercial BDD electrode (supplied by CSEM) with a geometric area of about 5 $cm^2$ was used as anode and a platinum electrode was used as cathode. Unless differently specified no pH adjustment was needed.

In combined treatments a GDE cathode and a BDD anode were used as electrodes.

Phosphates were removed through flocculation and precipitation by adding calcium hydroxide up to pH = 8.5 and a few drops of anionic flocculant (Floxan 9924, Misan Chimica). All the tests were carried out at least in triplicate.

The oxidation extent was expressed according to Eq. 5 where the different oxidation states of the reduced phosphorus compounds are taken into account:

**Table 1** Composition of the industrial effluent

| pH | Conductivity/mS | [P]hypoph./mg $l^{-1}$ | [P]phosphites/mg $l^{-1}$ | [P]phosphates/mg $l^{-1}$ | TOC/mg $l^{-1}$ | $Cl^-$/mg $l^{-1}$ | $SO_4^{2-}$/mg $l^{-1}$ |
|---|---|---|---|---|---|---|---|
| 6.8 | 7–8 | 500 | 500 | 500 | 20 | 800 | 400 |

$$\text{oxidation (\%)} = \left\{ 1 - \frac{\left( 2[P]_{\text{hypoph}} + [P]_{\text{phosphites}} \right)_t}{\left( 2[P]_{\text{hypoph}} + [P]_{\text{phosphites}} \right)_0} \right\} \times 100 \tag{5}$$

In accordance with Eq. 6, the apparent current efficiency (ACE) was expressed by the ratio between the charge theoretically required for the oxidation to phosphates at a given time t, and that actually consumed, considering that the charge passed is exclusively used for the phosphorus oxidation:

$$\text{ACE(\%)} = \frac{F[(4\text{mol}_{\text{hypoph}} + 2\text{mol}_{\text{phosphite}})_0 - (4\text{mol}_{\text{hypoph}} + 2\text{mol}_{\text{phosphite}})_t]}{JAt} \times 100 \tag{6}$$

where

$F$ = Faraday constant (96485 C mol$^{-1}$)
4 = number of electrons required for the oxidation of one mol of hypophosphite to phosphate
mol$_{\text{hypoph}}$ = number of mols of hypophosphite
2 = number of electrons required for the oxidation of one mol of phosphite to phosphate
mol$_{\text{phosphite}}$ = number of mols of phosphite
$J$ = current density (A m$^{-2}$)
$A$ = electrode surface (m$^2$)
$t$ = electrolysis time (s)

## 2.3 Analysis

pH was measured with a Crison GLP 421 pH meter. The ionic species concentration was determined by means of a Dionex 120 ionic chromatograph equipped with an IONPAC AS12A anionic column. The concentration of total residual phosphorus was determined by a UV-VIS spectrophotometer according to standard methods [31]. The concentration of hydrogen peroxide and iron was determined reflectometrically by means of a Merck specific analytical test based on a peroxidase and a Ferrospectral®/ 2,2′ bipyridine reagent respectively.

## 3 Results and discussion

### 3.1 Electro-Fenton treatment

To oxidize the industrial effluent a preliminary electro-Fenton treatment was performed using a current density of 100 A m$^{-2}$, pH 2.5 and an initial ferrous ions concentration of 150 mg L$^{-1}$. The reaction, after weak oxidation, did not proceed at all because of the rapid disappearance of iron in solution. As reported in Fig. 1, where the hypophosphite removal is presented, further additions of 100 mg L$^{-1}$ of iron every 150 min of electrolysis led to a poor improvement in the oxidation yield and only for a restricted time when iron remained available in solution after dosage. Since this effluent is rich with phosphates, the low concentration of iron was attributed mainly to the formation of iron phosphates whose solubility was affected by the working pH. To evaluate the influence of pH on the treatment a series of tests were then performed in a pH range varying from 1.5 to 2.5.

Figure 2, where the effect of pH on iron concentration is reported, shows that the residual concentration of iron increased with decreasing pH while total precipitation was confirmed at pH 2.5. However, although in the runs conducted at pH 2 a low amount of iron remained available in solution, a maximum oxidation of 20% was achieved, as shown in Fig. 3. In this case a noteworthy fouling of the cathode, affecting the hydrogen peroxide production, accounted for the low performance of the electro-Fenton treatment.

To reach quantitative oxidation of the reducing system a pH of 1.5 had to be adopted even though working at such a low pH involved two main disadvantages: higher treatment cost, due to the high acid dosage required by a solution rich in buffer systems, and concentration of sulphates or chlorides at the end of the process exceeding the legal limits. In these conditions 100% oxidation was achieved after about 1300 min.
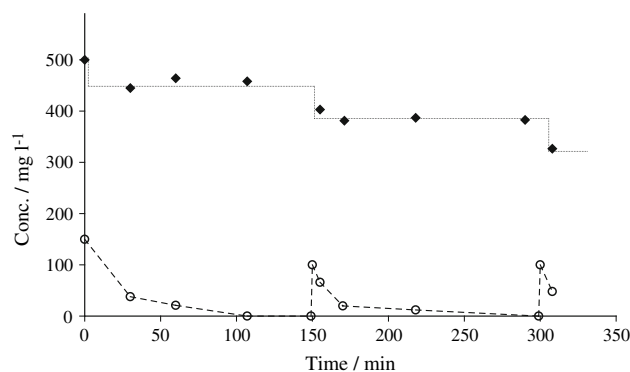


**Fig. 1** Concentration of hypophosphites (◆) and total iron (○) as a function of the time in an electro-Fenton treatment. pH = 2.5, $J = 100$ A m$^{-2}$, [Fe$^{2+}$]$_0$ = 150 mg L$^{-1}$
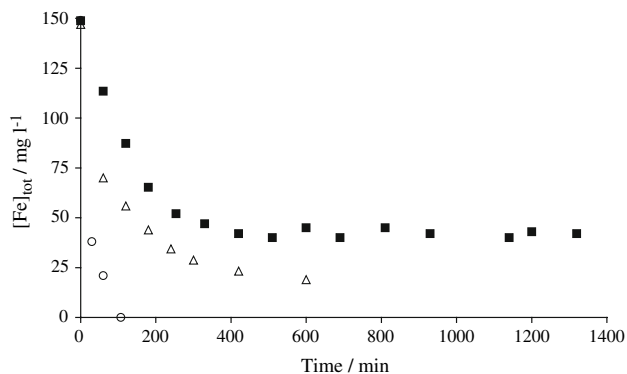
**Fig. 2** Iron concentration as a function of the time in an electro-Fenton treatment: pH 1.5 (■), pH 2.0 (△), pH 2.5 (○), $J = 100$ A m$^{-2}$, $[Fe^{2+}]_0 = 150$ mg L$^{-1}$
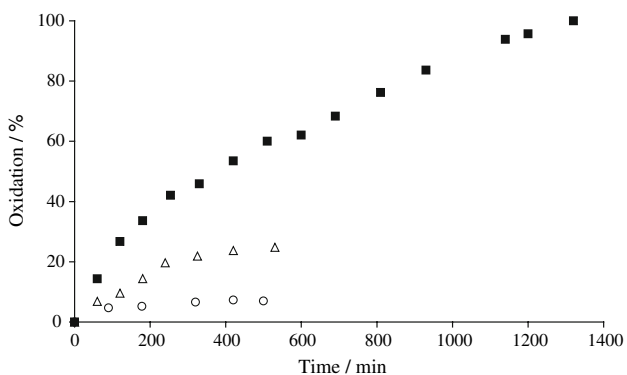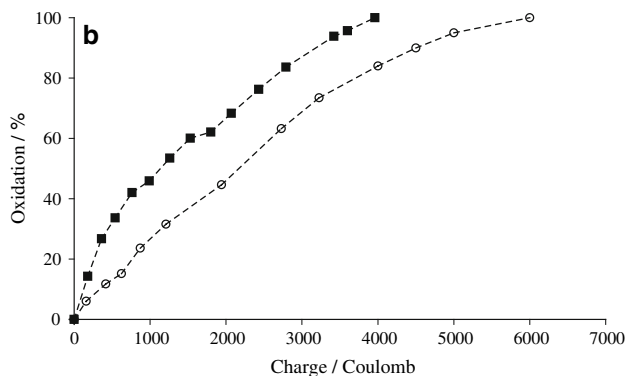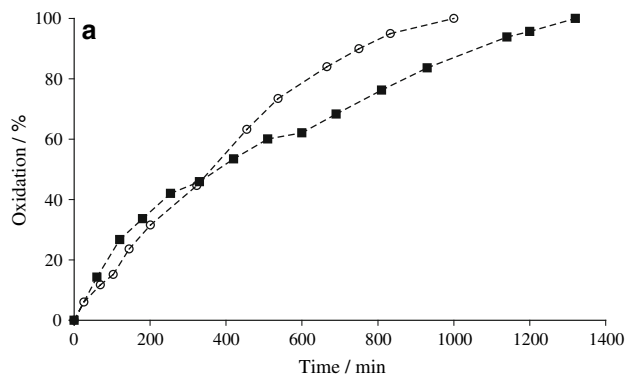


**Fig. 3** Oxidation as a function of the time in an electro-Fenton treatment: pH 1.5 (■), pH 2.0 (△), pH 2.5 (○), $J = 100$ A m$^{-2}$, $[Fe^{2+}]_0 = 150$ mg L$^{-1}$

To accelerate the electro-Fenton treatment a current density of $J = 200$ A m$^{-2}$ was also tested. As can be seen in Fig. 4, doubling the current density produced a 25% reduction of electrolysis time while the charge required for the total transformation increased by about 50%. This loss of efficiency was caused by the occurrence of two main side reactions leading to hydrogen evolution and water production which negatively affected the electrogeneration of hydrogen peroxide and ferric iron reduction (Eqs. 2 and 4).
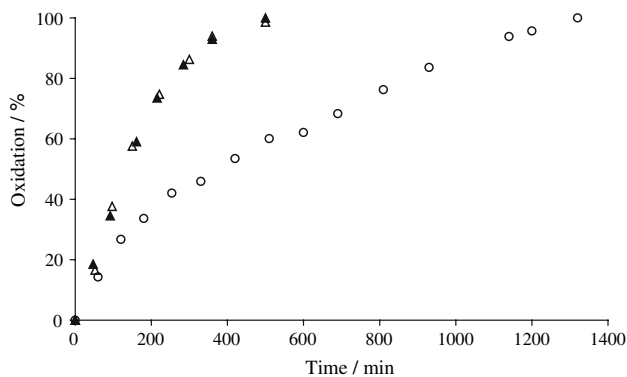
### 3.2 Anodic oxidation on BDD

Since electro-Fenton treatment required continuous monitoring of iron and pH, an alternative oxidation process, carried out using a direct anodic oxidation on BDD electrode, was then tested.

To make a comparison with the electro-Fenton treatment a series of tests were conducted at a pH of 1.5. Data shown
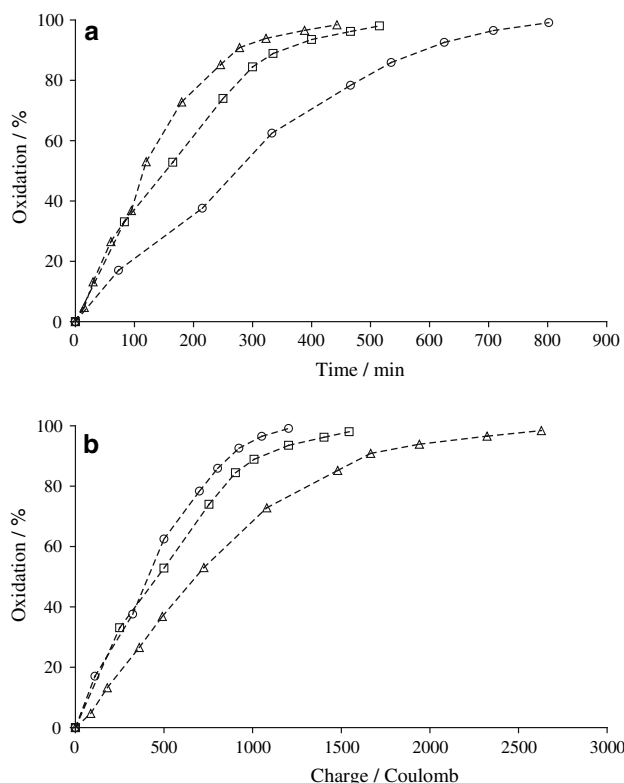


**Fig. 4** Influence of the current density on oxidation in an electro-Fenton treatment versus time (**a**) and charge (**b**): $J = 100$ A m$^{-2}$ (■), $J = 200$ A m$^{-2}$ (○), pH = 1.5, $[Fe^{2+}]_0 = 150$ mg L$^{-1}$



**Fig. 5** Oxidation as a function of the time in an electro-Fenton treatment (○) pH 1.5 and $[Fe^{2+}]_0 = 150$ mg L$^{-1}$, and in a BDD treatment pH 1.5 (▲), pH 6.8 (△), $J = 100$ A m$^{-2}$

in Fig. 5 indicate that anodic treatment on BDD occurred in a notably shorter time than electro-Fenton producing total oxidation in 500 min.

From further runs conducted at pH 6.8, whose results are included in the same figure, it was also observed that BDD anodic oxidation was insensitive to pH making it possible to treat the effluent without preliminary acidification with considerable saving in terms of reagents.

Fig. 6 Influence of the current density on oxidation in a BDD treatment: versus time (**a**) and charge (**b**) $J = 50$ A m$^{-2}$ ($\bigcirc$), $J = 100$ A m$^{-2}$ ($\square$), $J = 200$ A m$^{-2}$ ($\triangle$), pH 6.8

The influence of current density in the range from 50 to 200 A m$^{-2}$ was also evaluated and is reported in Fig. 6. An increase in current density from 100 to 200 A m$^{-2}$ produced a remarkable waste of charge, about 50%, without causing a significant decrease in electrolysis time which was reduced by only 14%. This behaviour is clearly explained by considering that higher values of current density imply a higher incidence of side reactions such as oxygen evolution. On the contrary, a decrease in the current density from 100 to 50 A m$^{-2}$ involved comparable consumptions of charge in a notably higher time. According to these results the value of 100 A m$^{-2}$ was considered the best current density to be adopted in the anodic treatment of this effluent.

Comparing the species evolution, depicted in Fig. 7 as a function of electrolysis time, an outstanding difference in the reaction pathway was observed between an EF and a BDD treatment. During oxidation of the industrial effluent hypophosphites disappeared with an almost identical trend while phosphites differed remarkably. In particular EF involved accumulation of phosphites reaching a maximum concentration of about 700 mg L$^{-1}$ after 300 min of electrolysis while BDD led to such a rapid disappearance of phosphites to suggest a direct oxidation of hypophosphites to phosphates.
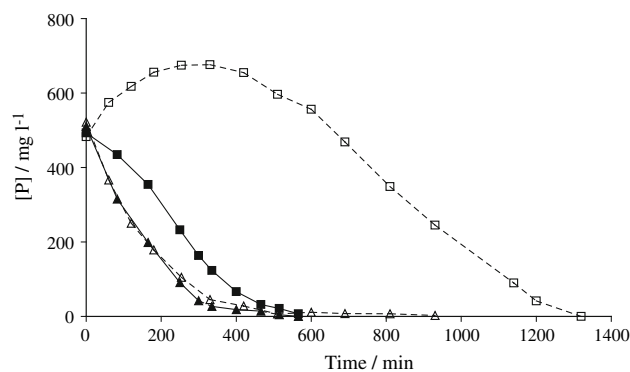


Fig. 7 Evolution of the concentration of hypophosphites ($\blacktriangle$ $\triangle$) and phosphites ($\blacksquare$ $\square$) during the oxidation of industrial effluent by Electro-Fenton (empty symbols) at pH = 1.5 and [Fe$^{2+}$]$_0$ = 150 mg L$^{-1}$ and BDD (full symbols), $J = 100$ A m$^{-2}$

### 3.3 Combined treatment

#### 3.3.1 Parallel coupling

To enhance the effluent oxidation a coupled treatment using electro-Fenton with BDD in an undivided cell was investigated. For these trials the pH was adjusted to 1.5, as required by electro-Fenton, while an initial iron concentration of 50 and 100 mg L$^{-1}$ was tested. Higher iron dosage was not further investigated since, with increasing values, a persistent deposition of ferric compounds on the anodic surface was observed.

Data obtained are presented in Fig. 8 where a comparison in terms of ACE variation with time is presented for all the treatments so far investigated. The last point of each curve corresponds to the complete oxidation of the reducing species.

For BDD anodic oxidation, initially constant ACE values near 100% were obtained denoting that the process was
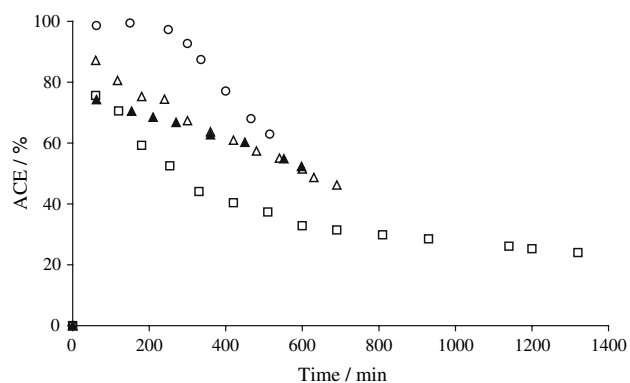


Fig. 8 ACE variation with electrolysis time. BBD: $J = 100$ A m$^{-2}$, pH = 6.8 ($\bigcirc$); Electro-Fenton: $J = 100$ A m$^{-2}$, [Fe$^{2+}$]$_0$ = 150 mg L$^{-1}$, pH = 1.5 ($\square$); Electro-Fenton with BDD in undivided cell [Fe$^{2+}$]$_0$ = 50 mg L$^{-1}$ ($\triangle$) and [Fe$^{2+}$]$_0$ = 100 mg L$^{-1}$ ($\blacktriangle$). Curves stopped at 100% oxidation

under current control. For an electrolysis time longer than 300 min, when more than 80% oxidation was achieved, the current efficiency dropped dramatically indicating that the process was under mass transfer control.

EF treatment showed the lowest current efficiency with an initial decay up to 30 % after 600 min followed by a constant trend until the end of the run at 1320 min. This process was strictly controlled by mass transfer of iron whose concentration in the bulk represented the actual driving force of the system as highlighted by the similar trend of [Fe$_{tot}$] (Fig. 2) and ACE with time.

The results of Fig. 8 also clearly indicate that no beneficial effect was obtained from BDD anodic oxidation combined with EF treatment. In this case the initial ACE was lower than that observed in BDD alone and dropped almost linearly with a slope affected by iron concentration. Although a larger amount of iron initially showed worse current efficiencies nonetheless a shorter electrolysis time was needed for complete oxidation (600 instead of 700 min). This can be probably explained considering that at the beginning of the electrolysis when the reducing phosphorus content was still high and the BDD oxidation was under current control, the oxidation of iron represented a competitive reaction whose negative effect increased with increasing concentration. In contrast, when a lower reducing phosphorus content remained in solution, EF, positively affected by increasing iron concentration, counterbalanced the rapid decay of ACE in BDD and the overall oxidizing ability.

### 3.3.2 Sequential coupling

A further coupling treatment using EF and BDD was thus proposed. In this case a divided cell was needed in order to perform two different oxidation steps in the two separate compartments at the same time.

The sequence involved partial oxidation of the industrial effluent on the anodic compartment by means of the BDD electrode. The solution thus obtained, after precipitation of the accumulated phosphates, then underwent complete oxidation by means of electro-Fenton treatment in the cathodic compartment. At the same time fresh untreated effluent was fed at the anode so that in each electrolysis raw effluent is used as anolyte whereas partially anodically oxidised solution is used as catholyte. A block diagram of the process is given in Fig. 9. The choice of carrying out the first oxidation step on BDD derived from consideration of its high efficiency at high concentration of oxidizable species. Moreover, BDD being unaffected by the pH, no preliminary adjustment was required. In addition, adopting this scheme, the EF took advantage by treating a solution where the concentration of phosphates was strongly
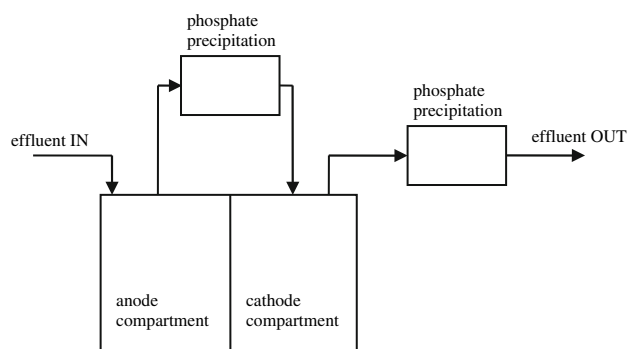


**Fig. 9** Block diagram of the coupling treatment in a divided cell

reduced by the intermediate clariflocculation of the anodically treated solution thus overcoming the limit correlated to iron precipitation.

Although an increase in catholyte pH (due to hydrogen peroxide production) and a simultaneous decrease in anolyte pH (due to water discharge and the oxidation of phosphorus compounds) were expected, in a first series of tests, where the electrolytic cell was equipped with a cationic membrane, an excessive pH variation was noticed. Particular problems arose in the cathodic compartment where high pH resulted in a fatal precipitation of iron that stopped the electro-Fenton treatment. This behaviour was attributed to the notable amount of ions present in the anolyte, mainly Na$^+$, which, being in competition with hydrogen ions, hindered their transfer towards the catholyte. This drawback was easily overcome by using an anionic membrane which allowed the passage of the hydroxides ions from the cathode to the anode thus maintaining the catholyte pH below critical values.
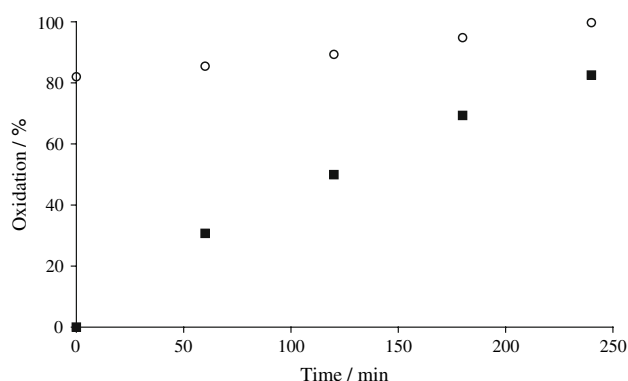
Several trials were then carried out to find an electrolysis time ensuring that the residual concentration of reduced phosphorus from the anodic treatment was totally oxidized at the cathode in a process lasting the same time. Thus tests were conducted by feeding the industrial effluent to the anode compartment while the cathode compartment was supplied with a solution whose composition was determined by the extent of anodic pre-treatment in a range from 69 to 91%.

Table 2 shows that the best result was obtained for an electrolysis time of 240 min. during which the anodic treatment was able to oxidise 82% of the solution content, while, in the same period, the electro-Fenton provided oxidation from 82% to 100%, as shown in Fig. 10 where the extent of oxidation is given as a function of the time.

A shorter electrolysis time, as in runs 1 and 2, led to a milder anodic oxidation resulting in solutions that could not be completely oxidized by EF in the same time. On the other hand, an increasing electrolysis time, as in runs 4 and 5, represented an excessive consumption of electrical

**Table 2** Coupling treatment in a divided cell separated by an anionic membrane: oxidation percentage (ox.%), phosphorus content and time required for the oxidation of 100 mL of the industrial effluent on a BDD electrode ($J = 100$ A m$^{-2}$) and time required by the simultaneous electro-Fenton treatment ([Fe$^{2+}$]$_0$ = 150 mg L$^{-1}$, pH = 1.5) for the complete oxidation of 100 mL of solution anodically pre-treated

| Run | Anodic oxidation (BDD) | | | | Cathodic oxidation (elettro-Fenton) |
|---|---|---|---|---|---|
| | ox.% | [P]$_{hypophosphite/mg\,l^{-1}}$ | [P]$_{phosphite/mg\,l^{-1}}$ | Time required/min. | Time required to complete oxidation/min. |
| 1 | 69 | 89 | 275 | 180 | 400 |
| 2 | 75 | 64 | 241 | 210 | 350 |
| 3 | 82 | 41 | 183 | 240 | 240 |
| 4 | 86 | 24 | 156 | 270 | 200 |
| 5 | 91 | 17 | 98 | 300 | 180 |



**Fig. 10** Oxidation as a function of the time in a sequential treatment: BDD anodic oxidation without pH adjustment (■), $J = 100$ A m$^{-2}$; simultaneous electro-Fenton treatment of an anodically pre-treated solution (○), pH 1.5 and [Fe$^{2+}$]$_0$ = 150 mg L$^{-1}$

charge since the solution obtained at the anode compartment did not require such a long time to complete the oxidation treatment in the cathode compartment.

## 4 Conclusions

All the electrochemical treatments examined in this work enabled total oxidation of the investigated effluent to be achieved.

In the Electro-Fenton treatment an initial pH no higher than 1.5 was required to prevent iron ions from precipitating while anodic oxidation using a BDD electrode could be successfully carried out in a wide range of working pH. Both these treatments showed better performance at a current density of 100 A m$^{-2}$. The study of species evolution revealed different reaction pathways.

A combined treatment using EF with BDD conducted in an undivided cell at pH 1.5 and [Fe]$_0$ = 100 mg L$^{-1}$, requiring 600 min electrolysis, did not improve the performance obtained by BDD that led to complete oxidation in about 500 min as opposed to the 1320 min required by EF.

A novel combined treatment using EF and BDD in a divided cell separated by an anionic membrane was tested where the anolyte was the effluent and the catholyte the anodically pre-treated solution. The simultaneous occurrence of both the anodic and cathodic processes allowed complete oxidation of the effluent in 240 min with clear saving of charge.

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