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Oxidation efficiency in the electro-Fenton process

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Abstract

An electro-Fenton treatment of a solution containing phosphorus compounds using a graphite electrode is described. Different operating conditions are tested to investigate the influence of the reagent ratio on the oxidative efficiency. Results show that electro-Fenton's reagent is able to provide a powerful conversion of the phosphorous compounds into phosphate. As hydrogen peroxide is continuously provided by the cathodic reduction of oxygen, the crucial step appears to be the iron dosage whose optimal concentration is found in the range 50–150 mg l^{-1}. Quantitative oxidation is not reached for concentration lower than 50 mg l^{-1}. Nonetheless, an excess of both iron and hydrogen peroxide in the bulk is found to negatively affect the oxidation yield because of the occurrence of undesired side reactions.

1. Introduction

In recent years there has been growing interest in electrochemical technologies for their application in the field of water and wastewater treatment [1, 2]. Besides direct electrochemical treatments [3–6], which allow the anodic or cathodic transformation of pollutants, indirect treatments [7] promoting the electrochemical generation of strong oxidants, such as the hydroxyl radical, have also undergone rapid development.

The hydroxyl radical

$$HO^{\bullet} + H^{+} + e^{-} \leftrightarrow H_2O \quad E^0 = 2,8\,\mathrm{V} \tag{1}$$

is one of the most powerful oxidising species which can effectively and non-selectively react with a wide range of compounds of environmental concern, even leading to their mineralisation.

Chemically, this radical can be produced by the addition, under acidic conditions, of hydrogen peroxide and ferrous ions, the so-called Fenton's reagent [8], which has been proven effective for the treatment of a wide range of pollutants [9–14].

The reaction mechanism can be described by means of the following reactions [15]

initiation step

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad k = 51\,\mathrm{M^{-1}\,s^{-1}} \tag{2}$$

propagation steps

$$OH^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \quad k = 10^{7} \div 10^{10}\,\mathrm{M^{-1}\,s^{-1}} \tag{3}$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \tag{4}$$

$$R^{+} + H_2O \rightarrow ROH + H^{+} \tag{5}$$

An alternative way of generating hydroxyl radicals is offered by electrochemistry. In particular, one method involves the addition of ferrous iron with the simultaneous electrochemical production of hydrogen peroxide by the cathodic reduction of dissolved oxygen on a graphite electrode, according to the following reaction:

$$O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O_2 \tag{6}$$

which is the result of a complex process involving the formation of the superoxide anionic radical $O_2^{\bullet}$ and the hydroperoxide radical $HOO^{\bullet}$.

This method is called the electro-Fenton process and has been studied for the oxidation of a wide range of biorefractory organic compounds [16–36].

If compared with the conventional chemical process, the electro-Fenton has the advantage of allowing a better control of hydroxyl radical production. Moreover, at least theoretically, the continuous production of hydrogen peroxide and the simultaneous regeneration of ferrous iron due to the cathodic reduction of the resulting ferric iron, enables Fenton's reaction to occur continuously, thus generating a higher concentration of hydroxyl radicals. Actually, numerous competitive reactions occur determining the reduction of the hydroxyl radical concentration, thus decreasing the oxidising efficiency of the system.

termination steps

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad k = 3 \times 10^{8}\ M^{-1}\ s^{-1} \tag{7}$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad k = 3.3 \times 10^{9}\ M^{-1}\ s^{-1} \tag{8}$$

$$2OH^{\bullet} \rightarrow H_2O_2 \quad k = 2.7 \times 10^{7}\ M^{-1}\ s^{-1} \tag{9}$$

In particular, reactions 7 and 8 severely affect the propagation of the Fenton reaction since they both consume the hydroxyl radical and the reagents that can produce it.

The limitation of one of the reagent concentrations can slow down the degradation rate of the Fenton's reaction. Therefore, the optimal molar ratio between hydrogen peroxide and iron has to be achieved for each concentration of reducing reagent in order to maximise the process yield.

Reagent minimisation, which also contributes towards lowering the costs of materials and sludge disposal, allows a reduction in the overall operating costs, thus increasing the economic feasibility of this technology.

The aim of this work was to enhance the efficiency of an electro-Fenton oxidation in the conversion of a hypophosphite solution to phosphates. The adopted inorganic reducing agent was chosen because of its linear two-step oxidative pathway and rapid analytical determination. In addition, as shown in preliminary tests, the oxidation rate due to hydrogen peroxide alone is very low and a negligible oxidative contribution from this species can be assumed.

In order to maximise the yield of the oxidation, electrolyses were conducted at controlled potential whose value was optimised and reported in a previous paper [37].

Different values of molar ratio were investigated, whereby the molar ratio R is defined here as the ratio between the initial molar concentration of the added iron and the molar concentration of the electrogenerated hydrogen peroxide.

Furthermore, the possibility of an external supply of hydrogen peroxide was evaluated: results were compared to those obtained in experiments where an initial amount of hydrogen peroxide was electrogenerated *in situ*. Moreover, the addition of iron as ferric instead of ferrous ions was also investigated.

2. Experimental details

2.1. *Materials*

Hypophosphite salt of sodium monohydrate (NaH_2PO_2 H_2O at 98% by weight) was used to prepare the sample solution in laboratory conditions.

Bivalent iron was added as solid heptahydrate iron sulphate ($FeSO_4 \cdot 7H_2O$).

All the reagents were supplied by the Carlo Erba Company and used in their commercially available form with no further purification.

2.2. *Cell apparatus*

The apparatus, including a potentiostat (AMEL 2051) coupled with a programmable function generator (AMEL 568), was employed for controlled potential electrolyses, and was carried out in a glass cylindrical cell of 100-ml useful volume (Figure 1).

The anodic compartment was constituted by a glass tube, in which an agar–H_2O–NaCl plug sintered-glass disk was used to separate the two compartments, and this was then filled with a saturated NaCl solution.

A commercial graphite cathode, cylindrical in shape and with a geometric area of about 2.5 cm^2, was used as a working electrode, while a platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) was used as a reference electrode.

2.3. *Procedure*

The experiments were carried out on a hypophosphite aqueous solution with an initial phosphorus concentration of 100 mg l^{-1}. Electrolyses were carried out on an aqueous solution which was continuously saturated with oxygen by bubbling the gas inside the cell at a flow of

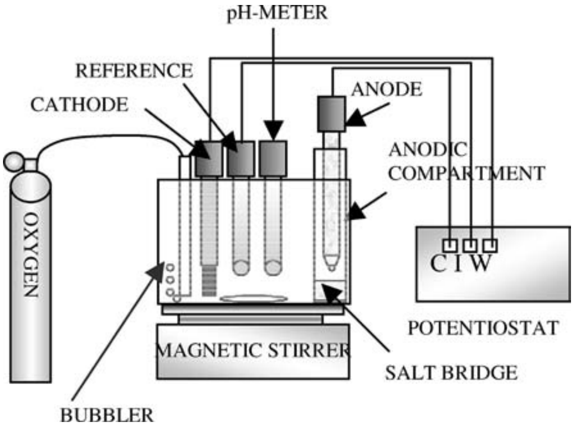

Fig. 1. Detail of the electrochemical cell.

130 ml min^{-1}, at a working potential of −0.9 V and a pH = 1.8–2.0 kept constant by means of a Na_2SO_4/$NaHSO_4$ buffer solution.

The solution was agitated at a constant rate of 1250 rpm by means of a magnetic stirrer and maintained at 25 °C with a recirculating water bath.

Under the adopted conditions, with an average current density of about 6 mA cm^{-2}, 100 ml of solution was subjected to electrochemical treatment consisting of two main steps: the electrogeneration of hydrogen peroxide in the absence of iron and the Fenton reaction between ferrous ions and the electrogenerated hydrogen peroxide.

All the reagents, except where otherwise specified, were added to the solution in the following order: hypophosphites, hydrogen peroxide (electrogenerated or introduced as a 35% by weight solution at the beginning of the electrolytic process) and ferrous iron.

To determine the influence of the reagent on the reaction yield a concentration range of 25–328 mg l^{-1} (0.45–5.87 mM) was investigated for iron ions, while a concentration range of 0–150 mg l^{-1} (0–4.41 mM) was investigated for hydrogen peroxide.

All the experiments were conducted at least in triplicate.

2.4. *Procedure analysis*

The reactions were monitored by using a continuous pHmeter (Crison 421).

Hypophosphites, phosphites and phosphates were 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 in accordance with standard methods [38].

The concentration of hydrogen peroxide and iron was determined reflectometrically by means of a Merck specific analytical test based on peroxidase and Ferrospectral®/2,2′-bipyridine reagent respectively.

3. Results and discussion

3.1. *Electrogeneration of hydrogen peroxide*

A first series of experiments, aimed at determining the hydrogen peroxide production under the adopted working conditions, was carried out both in the presence and absence of the studied substrate. In all these tests iron was not added in order to prevent hydrogen peroxide from being consumed in the Fenton reaction. The results obtained, in the charge range of 0–200 C, are reported in Table 1.

The lower hydrogen peroxide concentration measured in the presence of hypophosphite can be explained by its consumption due to a slight pre-oxidation of the reducing species by the different oxidative electrogenerated species.

3.2. *Effect of Fe^{2+}/H_2O_2 molar ratio on oxidation yield*

In order to study the effect of the reagent dosage on the extent of oxidation, several series of tests were conducted on solutions containing 100 mg l^{-1} of phosphorus as hypophosphites.

In each series of tests, the initial hydrogen peroxide concentration was fixed while ferrous salt was dosed to obtain a molar ratio respectively in peroxide excess, in iron excess and in stoichiometric ratio, according to Fenton's reaction 2.

The degradation pathway of hypophosphite proceeded through the formation of the phosphite as intermediate species.

Figure 2, where, for the sake of clarity, only the hypophosphite and phosphate curves were reported, shows the results of the first series of experiments conducted with an initial electrogenerated hydrogen peroxide concentration of 50 mg l^{-1}. The data were reported starting from the ferrous ions addition, thus not considering the electric charge needed for the production of hydrogen peroxide.

The oxidation increased with the increase in the molar ratio $R = [Fe^{2+}]/[H_2O_2]$, reaching a maximum for a ferrous ion concentration of 150 mg l^{-1}, which corresponded to a molar ratio of about 2, and without any significant improvement with further increases in the iron dosage. In particular, when a molar ratio of 0.3 was adopted, a residual concentration of hypophosphite was detected even after the passage of 250 C, while the production of phosphate was still negligible. In contrast, an almost complete transformation was obtained by using higher R values. It is also worth noting the delayed start of the production of phosphates at a R value of 1: it seems that, as soon as the needed Fe^{2+} concentration was restored by electro-reduction of Fe^{3+}, the

Table 1. Hydrogen peroxide concentration as a function of the charge

Charge/C	In the absence of hypophosphites	In the presence of hypophosphites	
	$[H_2O_2]$ /mg l^{-1}	$[H_2O_2]$ /mg l^{-1}	$[P]_{hypophosphites}$ /mg l^{-1}
0	0	0	100
50	35	35	99
100	80	70	98
150	120	110	97
200	155	135	96

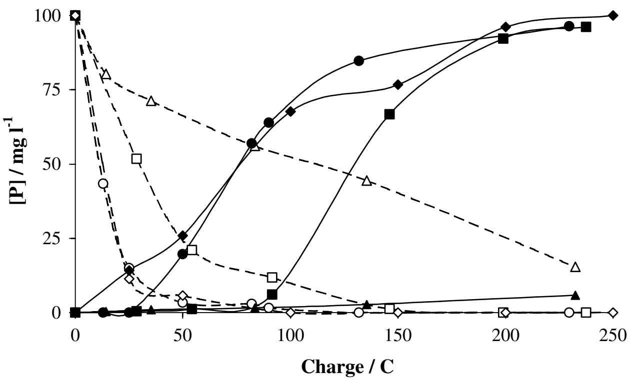

Fig. 2. Influence of molar ratio on phosphorus oxidation at $[H_2O_2]_{in} = 50$ mg l^{-1}. $R = 0.3$: hypophosphites (△), phosphates (▲); $R = 1$: hypophosphites (□), phosphates (■); $R = 2$: hypophosphites (○), phosphates (●); $R = 4$: hypophosphites (◇), phosphates (◆).

phosphites oxidation proceeded with a slope comparable to those observed for higher R values.

These results were confirmed by a further series of experiments carried out with an initial concentration of electrochemically generated hydrogen peroxide equal to 100 mg l^{-1} (Figure 3) where, however, for the same R values a faster and more effective transformation was observed. This is particularly evident when considering the $R = 0.3$ run, whose final phosphate concentration rose from 5 to 80 mg l^{-1}. Also in this case, the best molar ratio appeared to be $R = 2$. The higher oxidation rate was also proved by the trend of phosphites which did not accumulate because they were oxidised as soon as they were formed.

The addition of ferrous ions in the presence of hydrogen peroxide involves the sudden occurrence of the 'chemical' Fenton reaction whose contribution can be minimised by adding the reagents in a different sequence. In particular a series of tests was performed adding ferrous ions at the start of the electrolysis before any initial hydrogen peroxide electro-generation. Several concentrations of iron, ranging from 25 to 328 mg l^{-1}, were tested and the results are shown in Figure 4, in which only the phosphate curves were reported. As can be observed, in the studied range of iron concentration, apart from the run conducted with 25 mg l^{-1} of ferrous ions, an almost quantitative oxidation yield was reached. An increasing concentration of iron enhanced the oxidation rate up to a maximum, beyond which it notably worsened.

The run conducted using 25 mg l^{-1} of added ferrous ions, after the passage of 150 C, corresponding to the production of 30 mg l^{-1} of phosphorus as phosphates, slowed down to such an extent that a further passage of charge did not lead to a significant improvement. This behaviour can be explained by the probable iron depletion, this effect becoming critical only when a scarce quantity of iron was dosed. In fact, the curve corresponding to the run with $[Fe^{2+}]$ = 50 mg l^{-1} despite a limited rate, showed an almost linear trend, resulting in a quantitative transformation of the substrate after 300 C. A further increase in the iron concentration led to higher oxidation rates and complete transformation of the reducing substrate within a charge of 200 C. The corresponding curves did not show a linear trend presenting a plateau which, with increasing iron concentration, appeared to shift towards the lowest values of charge.

By far, larger amounts of iron did not favour the studied reaction, as illustrated by the trend of $[Fe^{2+}]$ = 328 mg l^{-1} curve, where, after a more extended initial plateau, the reaction started with a rate not comparable to those obtained in the best runs.

Figure 5 reports the concentrations of ferrous ions and hydrogen peroxide monitored during the previous series of experiments. The worst tests were characterised by an overdosage of one of the reagents whose excess, giving rise to side reactions, reduced the oxidation efficiency. The main reactions involved are those described in Equations 7 and 8, where hydrogen peroxide and ferrous ions became competitive with hypophosphite as oxidable species. In particular, an overdosage of hydrogen peroxide, as in the

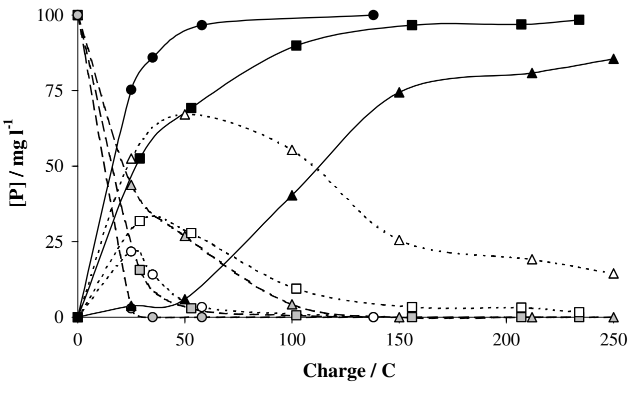

Fig. 3. Influence of molar ratio on phosphorus oxidation at $[H_2O_2]_{in} = 100$ mg l^{-1}. $R = 0.3$: hypophosphites (◬), phosphites (△), phosphates (▲); $R = 1$: hypophosphites (▣), phosphites (□), phosphates (■); $R = 2$: hypophosphites (◉), phosphites (○), phosphates (●).

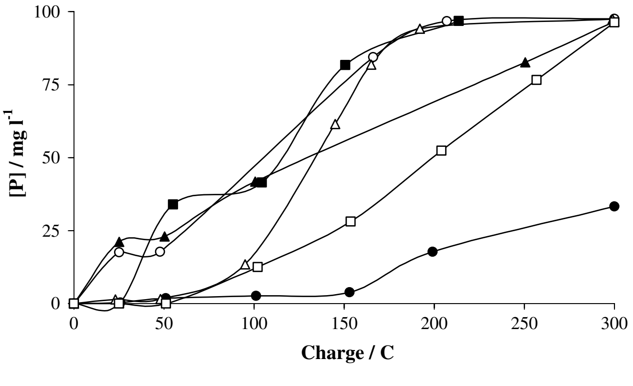

Fig. 4. Influence of iron on phosphate concentration at $[H_2O_2]_{in} = 0$ mg l^{-1}. $[Fe^{2+}]$ = 25 mg l^{-1} (●), $[Fe^{2+}]$ = 50 mg l^{-1} (▲), $[Fe^{2+}]$ = 100 mg l^{-1} (■), $[Fe^{2+}]$ = 150 mg l^{-1} (○), $[Fe^{2+}]$ = 200 mg l^{-1} (△), $[Fe^{2+}]$ = 328 mg l^{-1} (□).

$[\mathrm{Fe}^{2+}] = 25\ \mathrm{mg\ l^{-1}}$ run, led to a definite hindrance of the oxidation, since this reagent was continuously produced. For the same reason an overdosage of ferrous ions, as in the $[\mathrm{Fe}^{2+}] = 150$ and $200\ \mathrm{mg\ l^{-1}}$ runs, did not seem to compromise the oxidation yield because the continuous production of the other reagent tended to minimise this excess, although this caused slowdowns that in some tests, such as $[\mathrm{Fe}^{2+}] = 328\ \mathrm{mg\ l^{-1}}$, were particularly meaningful.

Conversely, optimal results were obtained when the concentration of the reagents was kept at a minimum level which in this case was realised by adding iron in a range 50–150 $\mathrm{mg\ l^{-1}}$.

To better understand this behaviour, a test with a stoichiometric ratio, realised with 100 $\mathrm{mg\ l^{-1}}$ of initial electrogenerated hydrogen peroxide and 164 $\mathrm{mg\ l^{-1}}$ of ferrous ions, was compared with two different experiments, in which respectively, firstly the same amount of hydrogen peroxide reacted with a larger amount of ferrous ions ($[\mathrm{H_2O_2}] = 100\ \mathrm{mg\ l^{-1}}$ and $[\mathrm{Fe}^{2+}] = 328\ \mathrm{mg\ l^{-1}}$, $R = 2$), and afterwards a larger initial hydrogen peroxide concentration reacted with the same ferrous ions concentration ($[\mathrm{H_2O_2}] = 150\ \mathrm{mg\ l^{-1}}$ and $[\mathrm{Fe}^{2+}] = 164\ \mathrm{mg\ l^{-1}}$, $R = 0.7$). As shown in Figure 6, referring to the concentration of produced phosphates, an increase in iron concentration to $R = 2$, at a given charge, led to an improvement in the reaction, both in terms of rate and yield. In contrast, an additional amount of hydrogen peroxide from $R = 1$ to 0.7 did not affect the overall trend of the reaction.

The explanation for this behaviour can be found in Figure 7, where the concentrations of the reagents, monitored along the experiments, were reported. In the experiment with a stoichiometric ratio of $[\mathrm{H_2O_2}] = 100\ \mathrm{mg\ l^{-1}}$ and $[\mathrm{Fe}^{2+}] = 164\ \mathrm{mg\ l^{-1}}$, a hydrogen peroxide excess with respect to the ferrous ions in the solution, which always remained below the detectable limit (0.5 $\mathrm{mg\ l^{-1}}$), was observed. The same figure shows that a hydrogen peroxide increase from 100 to 150 $\mathrm{mg\ l^{-1}}$, did not enhance the reaction efficiency, because it only produced an increase in the imbalance. The following experiment was conducted with the same concentration of hydrogen peroxide, $[\mathrm{H_2O_2}] = 100\ \mathrm{mg\ l^{-1}}$, increasing the iron concentration to 328 $\mathrm{mg\ l^{-1}}$, obtaining a molar ratio equal to $R = 2$. In this case an inversion of trend was observed since the hydrogen peroxide was the species that always remained below the detectable limit (0.2 $\mathrm{mg\ l^{-1}}$), while the Fe^{2+} concentration immediately dropped to very low values and, after an increase due to the electrogeneration, was finally consumed when the almost complete oxidation of the reducing agent was achieved. The results suggest that in order to achieve a higher oxidation efficiency it is necessary to work in the conditions of a slight overdosage of iron. This can be explained mainly by considering the reaction of hydrogen peroxide production being favoured in comparison with bivalent iron electroregeneration and besides taking into account that iron concentration may be reduced by other side reactions,

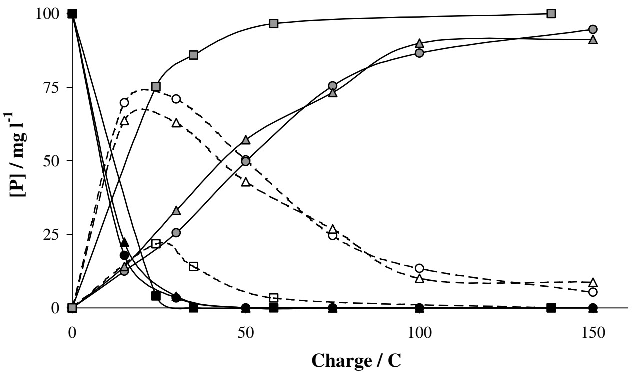

Fig. 6. Influence of iron and hydrogen peroxide concentration on phosphorus oxidation. $[\mathrm{H_2O_2}]_{\mathrm{in}} = 100\ \mathrm{mg\ l^{-1}}$, $[\mathrm{Fe}^{2+}] = 164\ \mathrm{mg\ l^{-1}}$: hypophosphites (●), phosphites (○), phosphates (◍) $[\mathrm{H_2O_2}]_{\mathrm{in}} = 150\ \mathrm{mg\ l^{-1}}$, $[\mathrm{Fe}^{2+}] = 164\ \mathrm{mg\ l^{-1}}$: hypophosphites (▲), phosphites (△), phosphates (◬) $[\mathrm{H_2O_2}]_{\mathrm{in}} = 100\ \mathrm{mg\ l^{-1}}$, $[\mathrm{Fe}^{2+}] = 328\ \mathrm{mg\ l^{-1}}$: hypophosphites (■), phosphites (□), phosphates (▣).

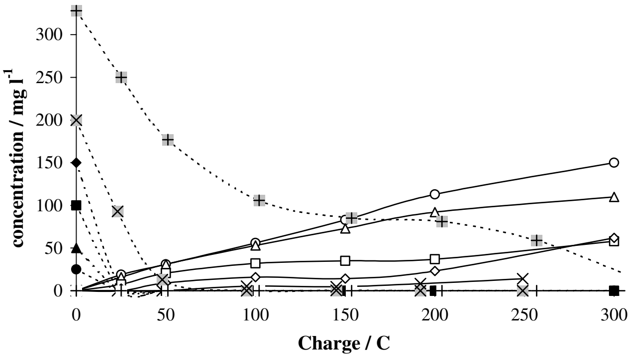

Fig. 5. Hydrogen peroxide and ferrous ion concentrations during experiments of Figure 4. $[\mathrm{H_2O_2}]$ (○), $[\mathrm{Fe}^{2+}]$ (●) at $[\mathrm{Fe}^{2+}] = 25\ \mathrm{mg\ l^{-1}}$; $[\mathrm{H_2O_2}]$ (△), $[\mathrm{Fe}^{2+}]$ (▲) at $[\mathrm{Fe}^{2+}] = 50\ \mathrm{mg\ l^{-1}}$; $[\mathrm{H_2O_2}]$ (□), $[\mathrm{Fe}^{2+}]$ (■) at $[\mathrm{Fe}^{2+}] = 100\ \mathrm{mg\ l^{-1}}$;$[\mathrm{H_2O_2}]$ (◇), $[\mathrm{Fe}^{2+}]$ (◆) at $[\mathrm{Fe}^{2+}] = 150\ \mathrm{mg\ l^{-1}}$; $[\mathrm{H_2O_2}]$ (×), $[\mathrm{Fe}^{2+}]$ (⊠) at $[\mathrm{Fe}^{2+}] = 200\ \mathrm{mg\ l^{-1}}$; $[\mathrm{H_2O_2}]$ (+), $[\mathrm{Fe}^{2+}]$ (⊞) at $[\mathrm{Fe}^{2+}] = 328\ \mathrm{mg\ l^{-1}}$.

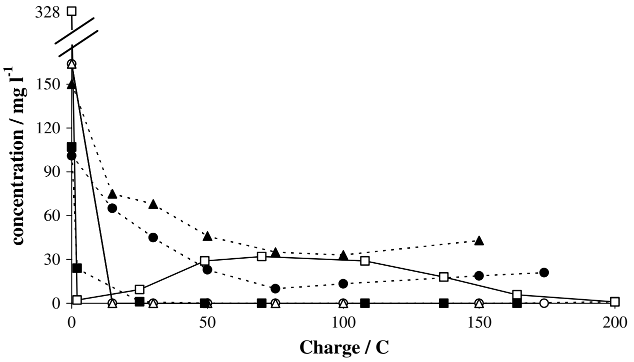

Fig. 7. Hydrogen peroxide and ferrous ion concentrations during experiments of Figure 6. $[\mathrm{H_2O_2}]$ (●), $[\mathrm{Fe}^{2+}]$ (○) at $[\mathrm{H_2O_2}]_{\mathrm{in}} = 100\ \mathrm{mg\ l^{-1}}$ and $[\mathrm{Fe}^{2+}] = 164\ \mathrm{mg\ l^{-1}}$; $[\mathrm{H_2O_2}]$ (▲), $[\mathrm{Fe}^{2+}]$ (△) at $[\mathrm{H_2O_2}]_{\mathrm{in}} = 150\ \mathrm{mg\ l^{-1}}$ and $[\mathrm{Fe}^{2+}] = 164\ \mathrm{mg\ l^{-1}}$; $[\mathrm{H_2O_2}]$ (■), $[\mathrm{Fe}^{2+}]$ (□) at $[\mathrm{H_2O_2}]_{\mathrm{in}} = 100\ \mathrm{mg\ l^{-1}}$ and $[\mathrm{Fe}^{2+}] = 328\ \mathrm{mg\ l^{-1}}$.

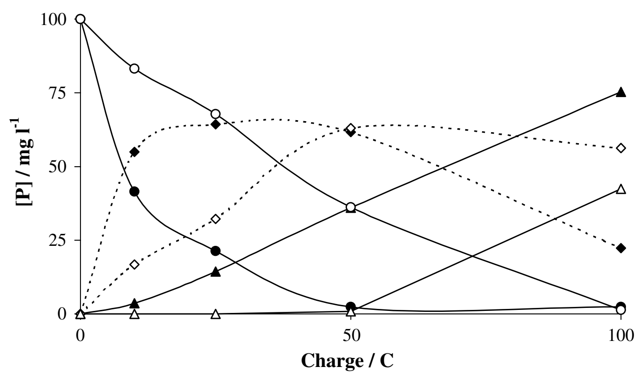

Fig. 8. Comparison between the addition of iron as ferrous and ferric ions. $[H_2O_2]_{in} = 100$ mg l^{-1}, $[Fe^{2+}]$ = 164 mg l^{-1}: hyphophospites (●), phosphites (◆), phosphates (▲); $[H_2O_2]_{in} = 100$ mg l^{-1}, $[Fe^{3+}]$ = 164 mg l^{-1}: hyphophospites (○), phosphites (◇), phosphates (△).

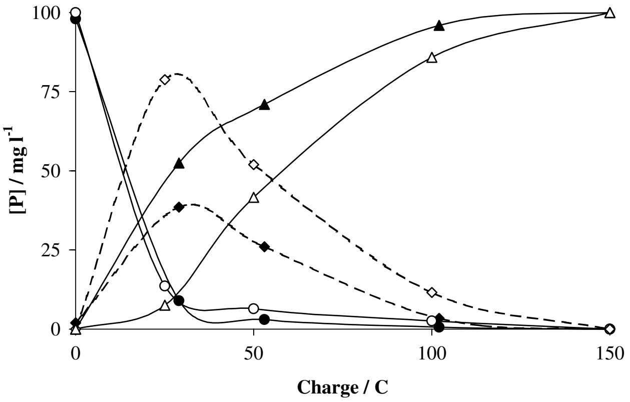

Fig. 9. Comparison between electro-generation and external addition of the initial H_2O_2 at $[H_2O_2]_{in} = 100$ mg l^{-1} and $[Fe^{2+}]$ = 164 mg l^{-1}. Electrogenerated H_2O_2: hyphophospites (●), phosphites (◆), phosphates (▲); external H_2O_2: hyphophospites (○), phosphites (◇), phosphates (△).

such as the formation of electro-inert compounds and the reduction of iron ions to metal.

3.3. *Addition of ferric ions*

To better understand the fate of the added ferrous ions additional tests were carried out by adding ferric instead of ferrous ions in accordance with the usually adopted procedure. Electrolyses were conducted with an initial hydrogen concentration of 100 mg l^{-1} and an added ferric ion concentration of 164 mg l^{-1} in parallel with runs where the same amount of iron was added as ferrous iron.

The results, reported in Figure 8, show that when ferrous iron was dosed a quick oxidation of the hypophosphite occurred with an almost immediate production of phosphates and high oxidation efficiency (75% in the studied range of charge). However, when ferric ions were dosed, the oxidation started more slowly and the production of phosphates was observed only after the passage of 50 C, leading to a lower final oxidation efficiency.

This behaviour can be explained by the absence of an immediate reaction occurring between ferrous ions and the available hydrogen peroxide.

To quantify this effect, chemical tests were performed with the same amount of reagents, as reported in Table 2. A reaction time of 10 min was required to achieve a complete chemical reaction.

Under these conditions, the chemical reaction conducted with ferric ions led to a negligible oxidation of the studied reducing agent, thus suggesting very little regeneration of ferrous ions. Therefore the oxidation yield observable in the electrochemical treatment when ferric ions were dosed was indicative of the ferrous ions regeneration rate.

In addition, the data indicate that the electrochemical treatment using ferrous ions showed a higher efficiency than that with ferric ions, without being comparable with the corresponding chemical Fenton reaction, at least in the reaction time employed. Therefore, not all the ferrous ions reacted in a chemical-like reaction but, presumably, most were quickly transformed into ferric ions once they were added to the solution. For this reason a more correct way of describing the oxidative system is an electro-Fenton process involving hydrogen peroxide and the Fe^{2+}/Fe^{3+} system.

3.4. *Preliminary addition of hydrogen peroxide*

A further series of tests were performed to investigate the possibility of substituting the initial amount of electrogenerated hydrogen peroxide with the same amount of a commercial hydrogen peroxide which was added externally.

Runs were carried out where the initial amount of 100 mg l^{-1} of hydrogen peroxide was added just prior to the addition of 164 mg l^{-1} of ferrous ions and compared with similar runs where the same initial amount of hydrogen peroxide had been electrogenerated. The comparison is shown in Figure 9 where data are reported starting from the ferrous ion addition.

The results show that only a very slight pre-oxidation was observed when hydrogen peroxide was electrogenerated, confirming the recalcitrance of this reducing species to oxidation by hydrogen peroxide alone. A similar rate of oxidation was observed for the hypophosphites, while the oxidation of phosphites to phosphates proceeded at a higher rate in the case of previously electrogenerated H_2O_2. This suggests a possible synergetic effect of species, presumably radicals, deriving from the complex mechanism of electro-reduction of dissolved oxygen which, in the presence of iron, favours the electro-Fenton oxidation yield.

3.5. *Energetic evaluation*

In Figure 10, where, for the sake of clarity, only the curves of hypophosphites and phosphates are shown, the most significant runs, performed under various

Table 2. Comparison between electrochemical and chemical Fenton $[H_2O_2]$ = 100 mg l^{-1}, $[Fe^{2+}]$ = 164 mg l^{-1}

	$[P]_{hypophosphite}$ /mg l^{-1}	$[P]_{phosphite}$ /mg l^{-1}	$[P]_{phosphate}$ /mg l^{-1}
Electrochemical Fenton^a iron as ferrous ion	41.5	54.9	3.6
Electrochemical Fenton^a iron as ferric ion	83.2	16.8	0
Chemical Fenton^a iron as ferrous ion	37.8	42.9	19.3

[a] Data are monitored after 10 min of treatment, initial H_2O_2 is externally added.

operating conditions, are reported as a function of the charge actually passed, that is considering the charge also spent on hydrogen peroxide production. For this reason the curves start at a charge value corresponding to the addition of iron; that is, when the indicated initial concentration of electrogenerated hydrogen peroxide was attained. This figure also shows a curve where the initial amount of required hydrogen peroxide was externally added just before the iron addition.

Figure 10 confirms that higher reaction rates were observed with increasing iron concentration when hydrogen peroxide was initially present, as demonstrated by the run conducted with $[H_2O_2]$ = 100 mg l^{-1} and $[Fe^{2+}]$ = 328 mg l^{-1}. However, the quantitative oxidation of the reducing agent was reached more rapidly by the run where a lower amount of iron ($[Fe^{2+}]$ = 164 mg l^{-1}) was added and 100 mg l^{-1} of hydrogen peroxide was externally provided, since, despite a slower reaction rate, it had the advantage of an earlier start.

A rather comparable performance was obtained in the run where 100 mg l^{-1} of ferrous ions were added at the start of the electrolysis: in this case, although the passage of a higher charge was required, a much lower reagent consumption was needed to obtain complete oxidation.

The results indicate that the electro-Fenton process can offer a broad range of different ways of conducting the same treatment whose choice, from time to time, is determined by considering the best compromise between energy saving and costs associated with the addition, removal and disposal of the reagent.

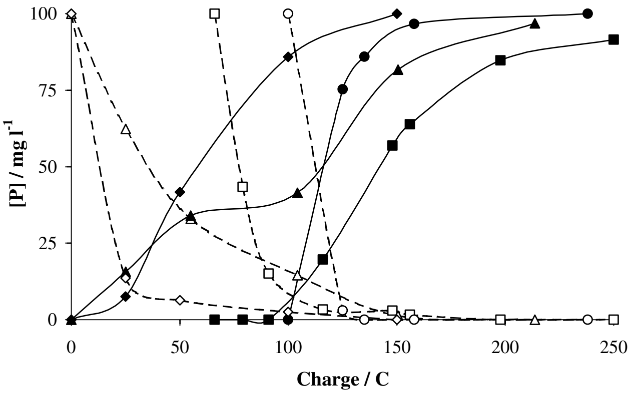

Fig. 10. Phosphorus oxidation vs total charge. $[H_2O_2]_{in=0}$ mg l^{-1}, $[Fe^{2+}]$ = 100 mg l^{-1} (*): hypophosphites (△), phosphates (▲); $[H_2O_2]_{in}$ = 50 mg l^{-1}, $[Fe^{2+}]$ = 150 mg l^{-1} (*): hypophosphites (□), phosphates (■); $[H_2O_2]_{in}$ = 100 mg l^{-1}, $[Fe^{2+}]$ = 328 mg l^{-1} (*): hypophosphites (○), phosphates (●); $[H_2O_2]_{in}$ = 100 mg l^{-1}, $[Fe^{2+}]$ = 164 mg l^{-1} (†): hypophosphites (◇), phosphates (◆). (*) Fe^{2+} added when the indicated H_2O_2 concentrations were reached. (†) H_2O_2 externally added at the start of the electrolysis.

4. Conclusions

The electro-Fenton process provided an efficient conversion of the phosphorous solution to phosphate. The results showed that, with respect to the stoichiometric value, a small overdosage of iron was required: this is justified by the fact that several side reactions contribute to its consumption.

A constant monitoring of iron and hydrogen peroxide throughout the reaction highlighted how more efficient reactions were obtained when lower concentrations of both reagents were present.

An external addition of hydrogen peroxide might offer an alternative to its preliminary electrogeneration, thus confirming the versatility of the electro-Fenton treatment, though the total costs need to be evaluated in an industrial process.

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