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Sequential use of Fenton and electro-Fenton process for the oxidation of an effluent-containing hypophosphite and phosphite

Anna Da Pozzo, Elisabetta Petrucci*

Department of Chemical Engineering Materials & Environment, Sapienza—University of Rome, via Eudossiana 18, 00184 Rome, Italy
Tel. +39 06 44585569, Fax: +39 06 4827453; email: elisabetta.petrucci@uniroma1.it

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ABSTRACT

The efficiency of both chemical and electrochemical Fenton processes to treat wastewater effluents from the manufacture of phosphorus-based flame retardants was investigated. Experimental tests were performed on solutions ranging from 600 to 2000 mg l^{-1} in terms of reduced phosphorus. Different concentrations and ratios of hydrogen peroxide and ferrous ions were tested, and the best conditions were found for both the processes. For the electrochemical treatment, where a gas diffusion cathode was adopted, the effect of carbon coating and current density was investigated, identifying the hydrophilic carbon coating, named Vulcan, as the best cathode material and the value of 100 A m^{-2} as the optimal current density. The results show that both the Fenton processes provide a powerful conversion to phosphate, with oxidation yields higher than 99%. However, a more cost-friendly sequential treatment, combining a preliminary chemical step to a final electro-oxidation, was proposed to reach a residual concentration of non-oxidized phosphorus less than 10 mg l^{-1}, in compliance with the Italian regulation limits for industrial wastewater disposal. A preliminary economic evaluation is provided.

Keywords: Fenton's oxidation; Electro-Fenton; Flame retardant; Real wastewater; Hypophosphite; Phosphite

1. Introduction

Flame retardants, with a worldwide market estimated at about one million tonnes per year, are the most important family of plastic additives, as they enhance the resistance to ignition and flame propagation. Due to the potential risk posed by the traditional halogenated flame retardants, commonly based on bromine, that, in case of fire, can release toxic and dense smokes, the use of innovative halogen-free compounds mainly based on phosphorus is rapidly growing [1–4].

Wastewaters from the manufacture industry contain an overall phosphorus load ranging from 600 to 2000 mg l^{-1}, mainly as hypophosphites, phosphites and phosphates, together with red-suspended phosphorus [5]. These salts are known to be highly soluble and their spontaneous oxidation to phosphates hardly occurs.

In the treatment of these effluents, strong oxidation agents are needed to transform all the phosphorus compounds into phosphates, thus reaching, after flocculation and precipitation, the bulk limit of 10 mg l^{-1} of residual phosphorus in compliance with the

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*Corresponding author.

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Italian regulation limits for industrial wastewater disposal [6].

Different treatments have been so far tested to remove reduced phosphorus via oxidation to phosphate: using a Pd/activated carbon catalyst [7], a combined UV light and hydrogen peroxide system [8], an heterogeneous catalysis using hydrogen peroxide and ferrous salts [9] or hydrogen peroxide and an iron oxide [10] and, eventually, with adsorption by hydrotalcite-like compounds [11].

Many of these methods are based on the oxidizing action of hydroxyl radical whose simplest generation is obtained under acidic conditions by adding hydrogen peroxide and ferrous iron, according to Fenton's reaction [12]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \tag{1}$$

The so-called electrochemical Fenton [13–19] offers an interesting alternative to the corresponding chemical process [20–24]. In this system, hydrogen peroxide is electrochemically generated, by a graphite cathode, via oxygen reduction:

$$O_2 + 2H_3O^{+} + 2e^{-} \rightarrow H_2O_2 + 2H_2O \tag{2}$$

The simultaneous cathodic regeneration of Fe^{2+} in acidic solution:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \tag{3}$$

allows a continuous supply of this reagent, thus making it possible to minimize the reagent consumption and the sludge production, reducing the overall operating costs.

Recently, a boron-doped diamond (BDD) anode was also tested in electrolyses of reduced phosphorus [5]. Compared with either the classical Fenton treatment or the electro-Fenton, anodic oxidation with BDD allowed faster oxidation to phosphate even at circumneutral pH without phosphite accumulation. However, the formation of soluble compounds, mainly dimers, was observed [25]. Their production, strongly dependent upon the operating conditions, caused the persistence of a residual phosphorus content in solution, thereby avoiding the achievement of the threshold required by law.

For this reason, Fenton-like treatments, where the hydroxyl radical formed in the bulk solution does not show any ability to polymerize phosphorus, have to be reconsidered.

In this paper, the traditional chemical Fenton is compared with the electrochemical process performed using a gas diffusion electrode (GDE) as the cathode. This electrode material enables high production of hydrogen peroxide in a large range of potentials even when fed with air [26–29]. Recent results suggest the electrosynthesis feasibility even in a quiet complex medium, such as marine water either in divided [30, 31] or in undivided reactor [32].

To reach the required residual amount of total phosphorus, reagent concentrations have been optimized for both treatments. Moreover, for the electrochemical oxidation, the effect of cathode material and current density has been tested.

With the aim of reducing reagents' dosage, sludge production and process time, a coupled treatment was thus proposed combining an initial chemical oxidation to an electrolytic final step.

A preliminary evaluation of the operating costs was also performed to compare the different treatments studied thus assessing their economic feasibility.

2. Materials and methods

2.1. Chemicals

The effluent investigated was provided by an Italian plant for the manufacture of phosphorus derivatives whose composition, depending on the single production, varied in the range reported in Table 1.

In the Fenton reaction, bivalent iron was added as solid heptahydrate iron sulphate ($FeSO_4{\cdot}7H_2O$) and hydrogen peroxide as 30 wt.% solution.

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

Table 1
Wastewater characteristics

pH	Conductivity mS cm^{-1}	$[P]_{hypoph.}$ 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	8–10	200–700	200–1,500	200–500	20–30	800–2,000	400–700

2.2. Analyses

pH was measured with a Crison GLP 421 pH-meter.

Hypophosphite, phosphite and phosphate were quantified by isocratic ion chromatography with suppressed conductometric detection using a Dionex 120 chromatograph equipped with an IONPAC AS12A anionic column.

The concentration of total residual phosphorus was confirmed by a UV–vis spectrophotometer according to standard methods [33]. The concentration of hydrogen peroxide and iron were determined reflectometrically by means of a Merck-specific analytical test based on a peroxidase and a Ferrospectral/2.2´ bipyridine reagent, respectively.

Filtration was done in a Buchner funnel with a 0.45-μm membrane filter under 0.05 Mpa vacuum. The filter cake was then weighed after drying at 105˚C for 2.5 h.

2.3. Chemical treatment procedure

Oxidation tests were performed at ambient temperature, under constant stirring (1,250 rpm), on 100 ml solution after adjustment to pH 2.8 with hydrochloridric acid. Experiments were carried out using three different wastewaters directly supplied by the plant, characterized by different initial phosphorus content. The treatment was carried out by stepwise addition of iron until disappearance of the previously dosed hydrogen peroxide that was entirely added at the beginning of the test. Phosphates were then 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).

2.4. Electrochemical treatment procedure

The electrolyses were performed in a two-compartment cell of 100 ml useful volume separated by a cationic-exchange membrane (Nafion® 324).

Although the use of a membrane involves additional costs, the adoption of a divided scheme is needed to limit hydrogen peroxide depletion via anodic decomposition and chemical reactions with the species anodically generated [30,32].

Moreover, the presence of the cationic membrane enables the continuous transfer of the protons generated in the anodic compartment by water oxidation, thus contributing to the maintenance of the acidic conditions required by Fenton's chemistry. In particular, the proton-conducting membrane adopted, in this study, is a perfluorosulfonic acid cation-exchange membrane with a polytetrafluoroethylene fibre reinforcement that provides chemical resistance, dimensional and thermal stability and notable durability.

A GDE with a geometric area of about 5 cm^2 was used as the cathode. The electrode presented a sandwich structure with a nickel net as the current collector between two carbon-PTFE layers (supplied by De Nora Tecnologie Elettrochimiche). Starting from two carbon materials, differentiated by their wettability, three different GDEs were prepared: with hydrophilic coating on both sides (Vulcan), hydrophobic coating on both sides Shawinigan acetylene black (SAB) and with Vulcan on the side in contact with the solution and SAB on the side in contact with gas (SAB-Vulcan).

Electrolyses were conducted after adjustment to pH 2.8 by means of sulphuric acid under air flow and galvanostatic conditions using an AMEL 2051 potentiostat. Experiments were performed on either real or synthetic solutions of 100 mg l^{-1} of initial phosphorus as sodium hypophosphite, as further specified in the text.

The solution was maintained at the constant rate of 1,250 rpm by means of a magnetic stirrer and maintained at 25˚C with a recirculating water bath.

Iron was added at the start of the electrolysis to reach the required concentration in the range 100–200 mg l^{-1}.

Sulphuric acid 0.1 M was used as supporting electrolyte in the anodic compartment where a platinum electrode was used as the anode.

2.5. Combined treatment

Sample solutions, after chemical Fenton oxidation and sludge separation, were subjected to electrolysis under the conditions specified in the text. An iron concentration of 150 mg l^{-1} was restored, if necessary, at the start of the electrolysis.

The oxidation efficiency was expressed according to the following formula where the hypophosphites were taken into account twice with respect to phosphites in order to consider the different oxidation states of the reduced phosphorus compounds thus making a proper yield assessment:

$$\eta\ (\%) = \left\{ 1 - \frac{\left(2[\mathrm{P}]_{\text{hypophosphites}} + [\mathrm{P}]_{\text{phosphites}}\right)_t}{\left(2[\mathrm{P}]_{\text{hypophosphites}} + [\mathrm{P}]_{\text{phosphites}}\right)_{t=0}} \right\} \times 100 \tag{4}$$

3. Results and discussion

3.1. Chemical treatment

Fenton chemical oxidation tests were carried out on wastewaters in a wide range of concentration. However, the conditions leading to the threshold value were optimized for solutions characterized by an initial phosphorus content ranging from 800 to 1,400 mg l^{-1} as hypophosphites and phosphites.

Owing to the complexity and the heterogeneity of the wastewaters tested, the dosage of Fenton's reagents has been carried out following the procedure specified in the experimental section without adopting fixed molar ratios. In particular, the selected H_2O_2 content was provided at the start of the run, while the iron salt was included in known amounts until disappearance of hydrogen peroxide whose concentration was constantly monitored by colorimetric determination.

Results shown in Table 2 indicate that a chemical Fenton treatment can oxidize the wastewater studied until the required threshold value. It is worth noting that hypophosphite oxidation with Fenton's reagent occurs via rapid formation of phosphite as intermediate species and subsequent slower conversion to phosphate. Thus, for high oxidation efficiencies, phosphites were the only species present in the solution, as confirmed by ion-chromatography quantification. As expected, an increase in the reagents' dosage led to an increase in the oxidation yield. In particular, to reach higher efficiencies, a larger dosage of iron than hydrogen peroxide was necessary. For example, as can be seen considering the solution characterized by a phosphorus content of 1,000 mg l–^{1}, to enhance the oxidation from 91.4 to 99.5% (corresponding to a residual concentration of phosphorus of 129 and 7.5 mg l^{-1}, respectively), an increase in hydrogen peroxide of 27% was required, while about a three times higher concentration of iron was needed. This result can be explained by considering that iron is depleted by the phosphates continuously produced during the oxidation, capable of forming very stable Fe-complex with a growing inhibition effect on the process [34]. The high consumption of iron, which was here added as sulphate, causes high operating costs, the production of a considerable amount of sludge and additionally might lead to exceeding the law limit even for sulphates, whose concentration in the real effluent is already remarkable.

3.2. Electrochemical treatment

Because of the high reagent consumption and the large amount of produced sludge, chemical Fenton cannot be considered suitable for the treatment of effluents characterized by high phosphorus content, such as those considered in the present work and the feasibility of an electro-Fenton treatment was thus tested.

Preliminary tests conducted under unoptimized conditions, on the real effluent containing 1,000 mg l^{-1} of reduced phosphorus as hypophosphites and phosphites, indicated that the attainment of the threshold value occurred after the passage of about 10,000

Table 2
Oxidation efficiency (η) in the chemical treatment: pH = 2.8, $T = 25.0 \pm 0.1$ ℃

Initial phosphorus concentration		Fenton reagent concentration		Final phosphorus concentration		
$[P]_{\text{hypoph.}}$ (mg l^{-1})	$[P]_{\text{phosphites}}$	H_2O_2 (mg l^{-1})	Fe(II)	$[P]_{\text{hypoph.}}$ (mg l^{-1})	$[P]_{\text{phosphites}}$	η (%)
400	400	1,000	400	0	151.2	87.4
		1,250	900	0	32.4	97.3
		1,500	1,500	0	4.8	99.6
500	500	1,000	300	62	318	70.5
		1,250	450	11	200	85.2
		1,500	600	0	129	91.4
		1,750	1,200	0	25.5	98.3
		1,900	1,600	0	7.5	99.5
660	680	500	200	369	802	23.0
		1,250	400	43	606	65.4
		1,500	800	0	496	75.2
		2,000	1,600	0	64	96.8
		2,250	2000	0	10	99.5

Table 3
Effect of GDE carbon coating on the oxidation yield of an electro-Fenton treatment conducted at $j = 100$ A m^{-2}. Catholyte: 100 ml of real effluent 1,000 mg l^{-1} P, $[Fe^{2+}] =$ 100 mg l^{-1}. pH = 2.8. $T = 25.0 \pm 0.1$℃. Anolyte: 100 ml $NaClO_4$ 0.01 M. Feeding gas: Air. $Q = 6{,}000$℃

Coating	SAB	Vulcan	SAB-Vulcan
η (%)	33.4	95.0	92.3

coulomb, corresponding to a treatment of more than two days if a current density of 100 A m^{-2} is adopted.

To improve the oxidation yield, different carbon coatings were tested. The first, named SAB-Vulcan, presented a hydrophobic carbon coating on the electrode side in contact with the feeding gas and a hydrophilic carbon coating on the side in contact with the solution, while the second and the third electrode, named Vulcan and SAB, presented on both the sides hydrophilic and hydrophobic coatings, respectively.

The results reported in Table 3 for a treatment conducted at 100 A m^{-2} with 100 mg l^{-1} of $FeSO_4$ and stopped after the passage of 6,000 coulomb of charge (corresponding to a 33 h treatment) indicate that the oxidation yield was significantly enhanced by the hydrophilic nature of the coating but without producing a significant reduction of the charge requested. The better performance is mainly justified by a higher capacity to generate hydrogen peroxide [35]. In particular, the Vulcan coating, because of its resistance to degradation, was found to be the optimal material and thus adopted in the following tests.

Fenton's reaction electrochemically driven, in spite of requiring a ferrous ions concentration of one order of magnitude lower than that needed in the corresponding chemically driven treatment, is time-consuming and it cannot be considered as a viable treatment for this kind of effluents while it would be better evaluated as a final stage after a chemical pretreatment.

To this aim, the oxidation of the real untreated effluent was considered unnecessary and further tests to optimize the main electrochemical parameters were conducted on synthetic solutions with lower phosphorus content (100 mg l^{-1} of initial phosphorus as sodium hypophosphites).

Fig. 1 shows the influence of the current density in the range 100–1,000 A m^{-2} on the oxidation yields. In this series of tests, the initial concentration of Fe^{2+} was 100 mg l^{-1}.

As expected, results show that an increase in the current density led to a considerable decrease in the oxidation yields as it favoured the water reduction with hydrogen release, which is the main reaction competing with the electrogeneration of hydrogen peroxide and reduction of ferric ions. For example, to achieve an oxidation value of 95%, the passage of about 1,600, 1950 and 4,800 coulomb was required when a current density of 100, 200 and 500 A m^{-2} was, respectively, applied. Under these conditions, a cell potential of 4.5, 8 and 12.5 V, respectively, was observed corresponding to an energetic consumption, for the treatment of 100 ml volume, of 0.002, 0.004 and 0.017 kWh, calculated according to the following equation:

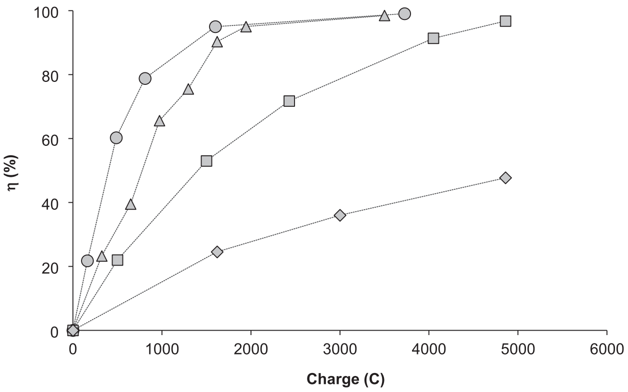

Fig. 1. Effect of current density on the oxidation yield of an electro-Fenton treatment of 100 ml of synthetic effluent containing 100 mg l^{-1} $P_{hypophosphite}$, conducted at $j =$ 100 A m^{-2} (●), $j = 200$ A m^{-2} (▲), $j = 500$ A m^{-2} (■), $j =$ 1,000 A m^{-2} (♦). [Fe2+] = 100 mg l^{-1}; pH = 2.8; $T = 25.0 \pm 0.1$℃. Anolyte: 100 ml $NaClO_4$ 0.01 M. Feeding gas: air.

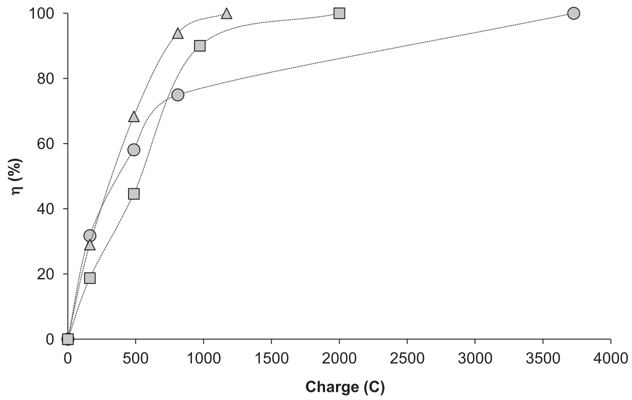

Fig. 2. Effect of ferrous ions concentration on the oxidation yield of an electro-Fenton treatment of 100 ml of synthetic effluent containing 100 mg l^{-1} $P_{hypophosphite}$ conducted at j = 100 A m^{-2}. $[Fe^{2+}]$: 100 mg l^{-1} (■), 150 mg l^{-1} (▲), 200 mg l^{-1} (●). pH = 2.8; $T = 25.0 \pm 0.1$℃. Anolyte: 100 ml $NaClO_4$ 0.01 M. Feeding gas: air.

$$\text{Energetic consumption (kWh)} = Q \times E_{\text{cell}} \times \frac{10^{-6}}{3.6} \qquad (5)$$

where Q is the charge and E_{cell} the cell potential.

The adoption of a current density of 1,000 A m^{-2} allowed to reach an oxidation value less than 50% after 5,000 coulomb. Additionally, at current densities higher than 500 A m^{-2}, the deposition of metallic iron on the cathodic surface was also observed with fast deterioration of the electrode surface. Since lower current density involved also lower cell potentials, with a subsequent lower energetic consumption, the optimal value of 100 A m^{-2} was adopted for the following tests.

Results reported in Fig. 2 refer to the influence of ferrous ions concentration, in the range 100–200 mg l^{-1}, on the reaction efficiency. As indicated, oxidation yields increase with increasing iron concentration, reaching a maximum at 150 mg l^{-1}, which was the optimal value adopted in the following tests. Beyond this value, a notable worsening in the process yield was observed because of the competition between ferrous ions in excess with hypophosphite.

3.3. Combined treatment

To avoid the huge reagent consumption of the chemical treatment and the high reaction time necessary for the electrochemical treatment, the possibility of a sequential combination of the two processes was evaluated. In the experiments, conducted on a real effluent containing 1,000 mg l^{-1} of reduced phosphorus as hypophosphites and phosphites, two combined treatments were tested, where a preliminary chemical Fenton was followed by a final electrochemical oxidation. The two sequences involved a preliminary chemical oxidation extended up to a 70% efficiency (treatment named "combined 1") and 85% efficiency (treatment named "combined 2"), obtained, as indicated in Table 2, by using 1,000 mg l^{-1} of H_2O_2 and 300 mg l^{-1} of Fe^{2+} and 1,250 mg l^{-1} of H_2O_2 and 450 mg l^{-1} of Fe^{2+}, respectively. The chemically pretreated solutions with a phosphorus content of 380 and 211 mg l^{-1}, respectively, mainly attributable to phosphites, undertook a final electrochemical Fenton step under the optimized operating conditions.

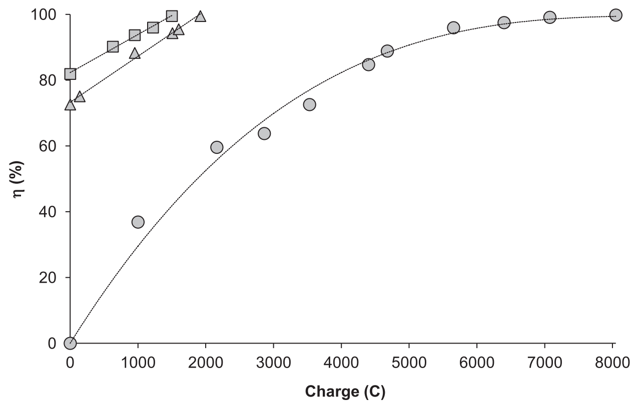

Fig. 3. Electro-Fenton yield of 100 ml of a real effluent containing 1,000 mg l^{-1} P treated entirely by electrochemical Fenton (●) or pre-treated by chemical Fenton with oxidation efficiency of 70% (▲), 85%(■). $j = 100$ A m^{-2}. $[Fe^{2+}] =$ 150 mg l^{-1}; pH = 2.8; $T = 25.0 \pm 0.1$°C. Anolyte: 100 ml $NaClO_4$ 0.01 M. Feeding gas: air.

In Fig. 3, the electrochemical steps of the two combined treatments are reported and compared with an electrochemical treatment conducted without preliminary chemical oxidation under the optimized conditions.

If compared to the chemical process, the combined treatments reached the limit value of residual phosphorus in solution with a reduction in the hydrogen peroxide consumption, respectively, of about 47% in the first treatment and of 34% in the second treatment and a reduction in the iron consumption of 81 and 72%, respectively. In comparison with the corresponding electrochemical test, the decrease in the charge consumption was, respectively, 81 and 76%, while the electrolysis time dropped from 44 to 11 and 8 h, respectively.

The results obtained indicate that the combined treatment represents an appealing compromise for the oxidation of this industrial effluent. The process proposed is illustrated in Fig. 4.

3.4. Economic evaluation

The choice of performing a combined treatment was also supported by a preliminary economic evaluation, based only on operating cost. Investment cost and amortization were at this stage intentionally neglected, since they greatly depend on the process scale, and the results obtained in bench scale cannot be considered significant. Results are illustrated in Table 4, where the three main entries were considered, that is, reagents, electricity consumption and sludge disposal. The cost evaluation associated with the reagents was done by taking into account: hydrogen peroxide (0.75 € kg^{-1} for a solution 30% w/w), ferrous sulphate (0.35 € kg^{-1}) and calcium hydroxide (0.25 € kg^{-1}), all at industrial grade. The values reported in Table 4 have been calculated by using the reagent concentration indicated in the text except for

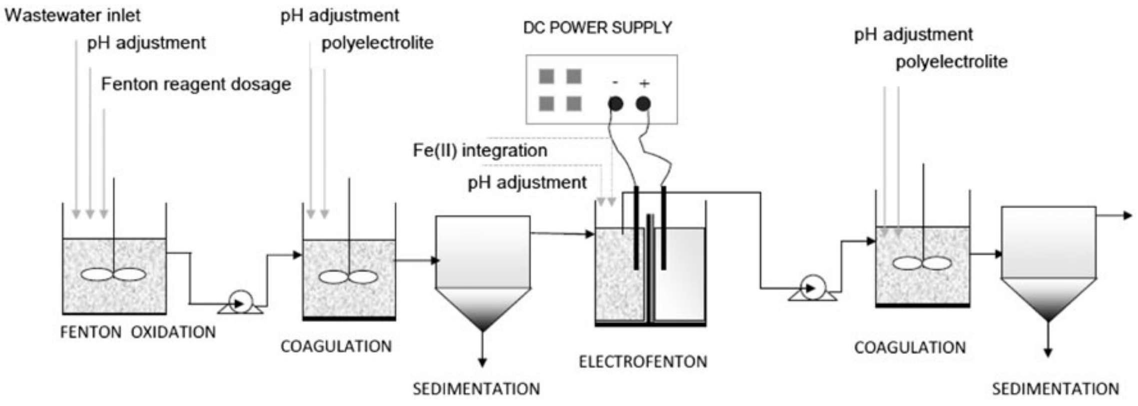

Fig. 4. Combined process scheme.

Table 4
Evaluation cost for the treatment of 1 m^3 of industrial effluent (1,000 mg l^{-1} P)

	Operating cost/€ m^{-3}			
	Chemical	Electrochemical	Combined 1	Combined 2
Reagents	5.58	0.26	2.64	3.10
Energy	–	11.67	2.92	2.19
Sludge	15.20	8.10	10.30	11.60
TOTAL	20.78	20.03	15.86	16.89

calcium hydroxide whose consumption was assumed of about 1 g l^{-1} in all the experiments tested.

The energy cost was assessed according to Eq. (5), considering an average cell potential of 3.5 V and a cost of 0.15 € kg^{-1}. It is worth noting that the charge values reported in the text refer to the treatment of 100 ml of solution.

In the overall estimate, the crucial entry is represented by sludge disposal whose amount mainly depends on the iron added and on the dewatering grade reached.

In particular, during the oxidation tests, the sludge produced after flocculation and precipitation was as follows: 152 g l^{-1} for the chemical treatment, 81 g l^{-1} for the electrochemical treatment and about 103 and 116 g l^{-1} for the two combined treatments. The value shown in Table 4 was calculated considering that in an industrial plant the sludge dewatering is normally performed using a filter press or a belt press with a 50% of dewatering power in the case of inorganic sludge and adopting a cost of 0.20 € kg^{-1} for the disposal of one kilogram of sludge.

The results obtained from this preliminary evaluation confirm the viability of the combined treatments. In particular, the first combined treatment, where the preliminary chemical oxidation reached a 70% efficiency, presents either the advantage of being cheaper or the environmental benefit of producing sludge with a lower iron contents.

Besides, as the cost associated with the electrochemical treatment is strictly related to cell potential, a significant save might be further obtained by adopting different cell geometry thus improving the fluid dynamic conditions.

4. Conclusions

The efficiency of both chemical and electrochemical Fenton processes was investigated to treat an industrial effluent from the manufacture of phosphorus derivatives. A two-step treatment including an initial Fenton treatment and a final electro-Fenton oxidation was proposed.

The following conclusions can be drawn from this study:

- both chemical and electrochemical Fenton processes allowed also separately to reach the limit value of 10 mg l^{-1} as total residual phosphorus provided for the law in force;
- in comparison with the chemical treatment alone, sequential combined treatments led to the same reaction efficiency with a notable save both in reagents and in sludge production;
- in comparison with the electrochemical treatment alone, sequential combined treatments involved a significant save in time and charge and therefore in electric energy; and
- the economic evaluation confirmed that the first combined treatment, where a milder preliminary chemical oxidation was performed, represents the optimal compromise for the oxidation of the industrial effluent studied.

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