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In memoriam prof. dr. Ioan A. Silberg

REMOVAL OF NITRODERIVATES FROM SYNTHETIC WASTEWATERS BY ELECTROCHEMICAL REDUCTION

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ABSTRACT. The electrochemical reduction of 4-nitrophenol (4-NP) and 2,6-dinitrophenol (2,6-DNP) in different conditions (0.2N H_2SO_4 and 0.1 M NaCl aqueous solution) were studied in this work. In the case of 4-NP the cathodic materials were nickel and graphite, and the electrochemical reduction processes were performed in two different reactors (two compartment reactor type filter-press, and undivided electrochemical reactor, both with electrolyte recirculation). In the case of 2,6-DNP the cathode was made from graphite using two compartment reactor with electrolyte recirculation. The experimental processes were pursued by different methods: cyclic voltammetry (BAS100), and spectrophotometry in UV-Visible (Unicam Helyos B and DR/2000 HACH); λ_{max} = 318 nm for 4-nitrophenol and λ_{max} = 440 nm for 2,6-DNP. The experimental determinations demonstrated practically 65-99% removal yield for the both nitro derivatives, depending on the experimental conditions. The best result have been obtained, in the case of 4-NP, in undivided electrochemical reactor with graphite electrode (90% of 4-NP removal), and in the case of 2,6-DNP the final removal was of 99% in two compartment reactor with graphite cathode.

Keywords*: 4-nitrophenol; 2,6-nitrophenol; electrochemical reduction; voltammetry.*

INTRODUCTION

Phenolic compounds including nitrophenol are widely used in pharmaceutical, petrochemical, and other chemical manufacturing processes. Nitrophenols are considered as hazardous wastes and priority toxic pollutants by the U.S. Environmental Protection Agency [1]. The E.U. adopted Council Directive 67/544/EEC, classifying nitrophenols as toxic and dangerous for the environment. Due to its harmful effects, wastewaters containing phenolic compounds must be treated before being discharged to receiving water bodies. The secondary biological treatment processes are commonly used for domestic and industrial wastewaters, but they cannot treat phenolic

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wastewaters at high concentrations successfully. Moreover, widely used organophosphorus pesticides yield nitrophenols as the initial and major degradation product [2].Therefore, new treatment technologies are still constantly researched and developed. Research efforts include biological degradation, chemical oxidation, solvent extraction, electrochemical treatment, and adsorption [3]. It is therefore important to assess the fate of these compounds in the environment and develop effective methods to remove them from water. The electrochemical treatment of waste water can be an interesting alternative to the chemical treatment for water containing toxic or non-biodegradable compounds.

Nitroaromatic compounds undergo reductive transformation to aromatic amines. The reduction of nitroaromatics occurred through a series of electron-transfer reactions and protonations, with nitroso compounds and hydroxylamines as highly reactive intermediates. In the case of polynitroaromatic compounds, the location of the first nitro group reduced is influenced by regioselectivity [4].

The electrochemical reductions of nitrophenols were studied in aprotic solvents, such as DMF (N.N-dimethylformamide) [5], and DMSO (dimethylsulphoxide) [6, 7], but they have mainly been studied in protic solvents [8]. Even in so-called “aprotic” solvents, the radical anion of 4-NP is unstable, due to the acidic nature of the parent molecule, giving rise to a self protonation reaction, which is a very rapid step [9]. In literature is proposed a reaction mechanism for the reduction of 4-NP in DMSO, which give the nitrosophenol as the final product, which in this environment is thought to undergo further follow-up chemistry to yield 4-aminophenol (a 6 electrons transfer reaction) [6].

The dinitrophenols have been determinated by cyclic voltammetry and differential pulse voltammetry on the base of an irreversible reduction peak [11]. The first peak height was correlated with the pulse amplitude (correlation coeficient of 0.997) and there was also an increase of the peak potential with the pulse amplitude [12], in agreement with a practically irreversible behaviour.

The aim of this paper is to reduce the concentration of some nitrophenols like as: 4-nitrophenol (4-NP), 2,6-dinitrophenol (2,6-DNP) from synthetic wastewaters, in the concentration range 10^{-5} - 10^{-2}M, on nickel and graphite cathodes.

RESULTS AND DISCUSSIONS

Voltammmperometric behaviour of 4-NP and 2,6-DNP

4-NP (Fig.1.a.) and 2,6-DNP (Fig.1.b.) present classical voltammperometric behavior characteristic for nitro derivatives. Due to the different reactivity of the two nitro groups, in the case of 2,6-DNP, two well separated ($\Delta Є$ = 300 mV) reduction peaks have been obtained (Fig.1b).

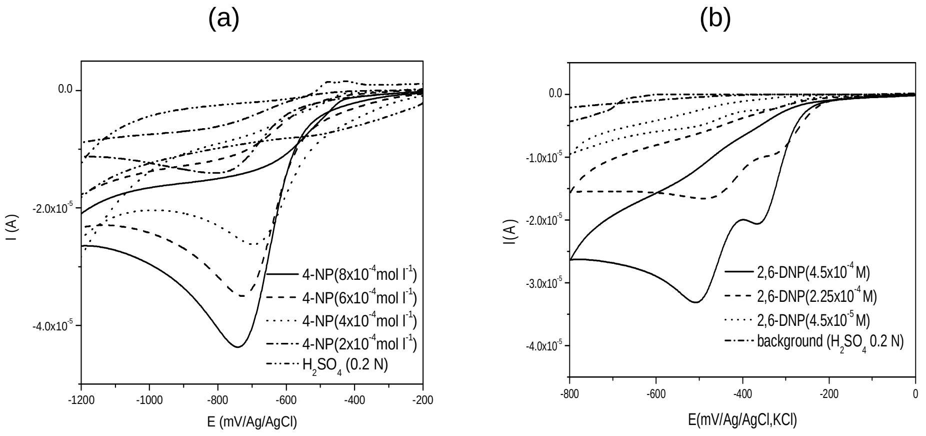
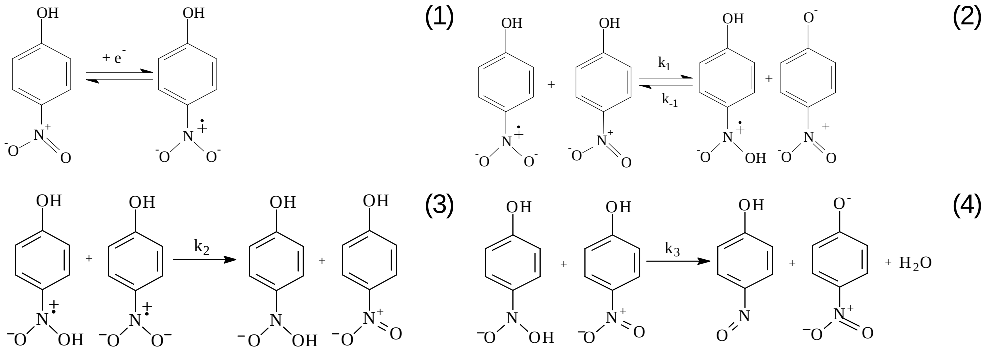


Figure 1. Cyclic voltammograms for: (**a**) 4-NP solutions at different concentrations, in 0.2N H_2SO_4; **(b)** 2,6-DNP solutions at different concentrations, in 0.2N H_2SO_4; WE: GC; RE: Ag/AgCl,KCl; CE: Pt; v : 50mV s^{-1}; s: 10 μA V^{-1}.

The radical anions of nitrophenols are unstable due to a fast self protonation reaction [10]. As it was expected, in protic medium the formation of radical anions during the first monoelectronic charge transfer is not easy to mark out, both for 4-NP and 2,6-DNP.



Scheme 1. Reaction scheme proposed for the reduction of 4-NP [10].

The 4e⁻ reduction of nitro group to the corresponding hydroxylamine, Fig.1, is the representative intermediary step in the electroreduction to amines, reaction 5.

$$\mathrm{Ar{-}NO_2} \xrightarrow{4\,e^-,\,4\,H^+} \mathrm{Ar{-}NHOH} \xrightarrow{2\,e^-,\,2\,H^+} \mathrm{Ar{-}NH_2} \qquad (5)$$

We can see from the examples in figure 2, that the reduction of 4-NP on glassy carbon takes place easier (E = - 0.5 V/Ag/AgCl,KCl) comparing to Ni electrode (E = - 0.88 V/Ag/AgCl,KCl). On Ni the potential is displaced to more negative values, but the involved current is more important, probably because the competitive reduction with electrochemically generated active hydrogen is also possible [13].

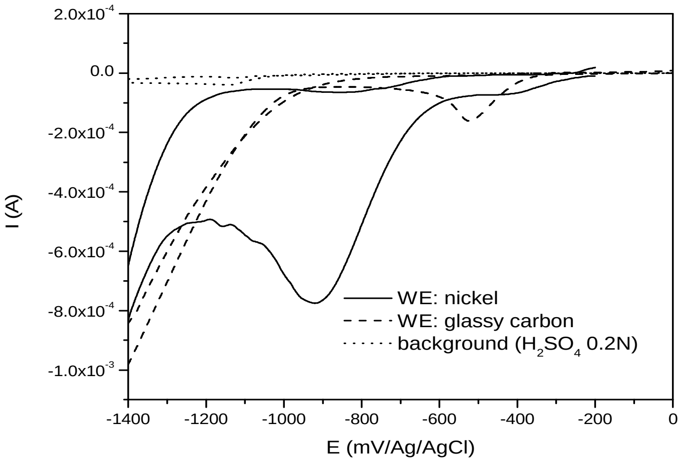


Figure 2. Cyclic voltammograms for a (10^{-2} M) 4-NP solution in 0.2N H_2SO_4 WE: GC and Ni; RE: Ag/AgCl,KCl; CE: Pt; v : 50mV s^{-1}; s: 100 µA V^{-1}.

The reduction potential strongly depends on pH, both for 4-NP and 2,6-DNP. The first peak potential, Ep_1 for 2,6-DNP, shows two linear regions with different slopes, corresponding to an acid behavior specific to nitrophenols values (pKa = 4-5), figure 3.a.

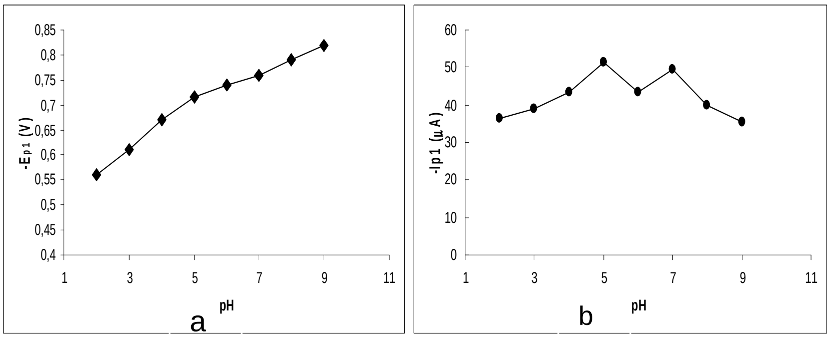


Figure 3. The variation of: **(a)** the first reduction peak potential (E_{p1}); **(b)** current intensity, with the pH, for a 4.5 x 10^{-4} M 2,6-DNP solution in Britton-Robinson buffer at different pH values WE: GC; RE: Ag/AgCl,KCl; CE: Pt; v : 50mV s^{-1}; s: 10 µA V^{-1}.

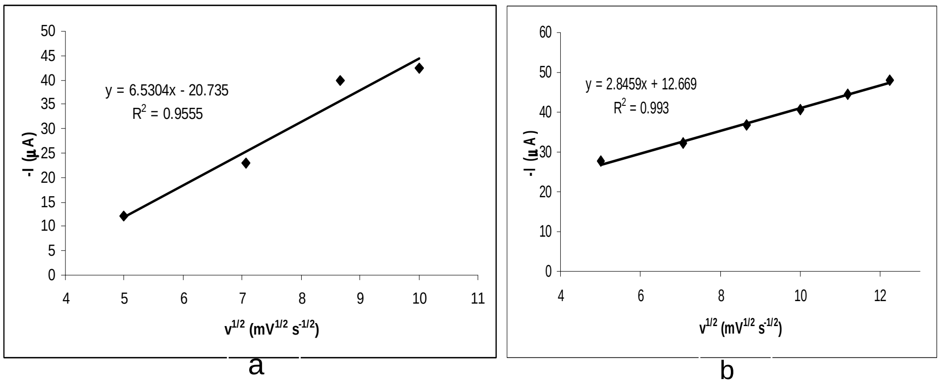
The reduction current at –350mV/Ag/AgCl,KCl corresponding to the first electrochemicaly active nitro group, reaches the maximum value at pH= 5-7, figure 3b. The same behaviour is also presented in literature for other dinitrophenols [14].

The variation of the peak intensity with the scan rate was studied. An approximately linear relationship was found between the reduction peak intensity and the square root of the scan rate, both for 4-NP (Fig.4a) and for 2, 6-DNP (Fig.4b). The peak potentials were found to move slightly more negative when the scan rate increased in agreement with the irreversible behavior of these substances.

Electrochemical reduction of 4-nitrophenol in electrochemical two compartment micro flow cel (A)

In figure 5 is presented the variation of the reduction peak current for the electrochemical reduction process for 4-NP solution, in electrochemical two compartment micro flow cell (A).

The reduction peak decreases during the electrochemical reduction of 10^{-3} M 4-NP, with 94% in 90 minutes of galvanostatic electrolyse (i = 20 mA cm^{-2}), (theoretical calculated time is 75 minutes, so it was used 120% of theoretical necessary time); the electrochemical reduction yield is 80%, Fig. 5.



a

b

Figure 4. The variation of current with the square root of the scan rate for: **(a)** 10^{-3} M 4-NP and **(b)** 4.5 x 10^{-4} M 2, 6-DNP solutions in in 0.2N H_2SO_4; WE: GC; RE: Ag/AgCl,KCl; CE: Pt; v : 50mV s^{-1}; s: 10 μA V^{-1}.

The removal of 4-NF is quite total after 75 minutes of electrolysis.

During electrolysis the solution becomes shining brown from colourless, probably due to the forming of some colorated condensation products. This phenomenon was mentionned in other works [15, 16], and is in good agreement with the characteristic of 4-aminophenol, which was reported to be the most possible intermediate accumulated from the reduction of 4-NP.

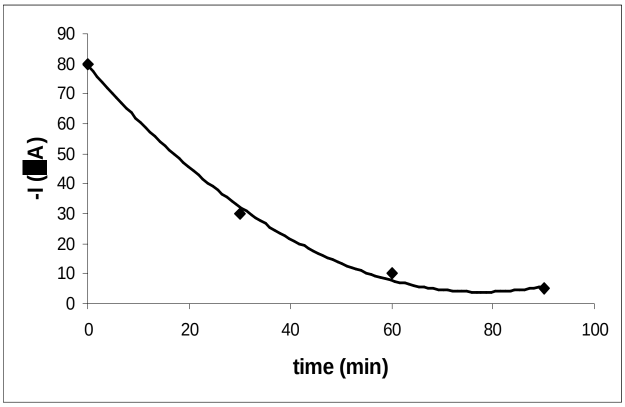


Figure 5. The variation of the reduction peak intensity at – 0.9 V/Ag/AgCl,KCl, for 10^{-3} M 4-NP in 0.2 N H_2SO_4, on Ni (experimental set-up A); i:20 mA cm^{-2}; WE: nickel; RE: Ag/AgCl,KCl; CE: Pt.

For future experiments it is wanted that the electrochemical reduction obtained products to be identified.

Electrochemical reduction of 4-nitrophenol in electrochemical mono-compartmented reactor with electrolyte recirculation (B)

In figure 6. it can be seen that, in case of electrochemical reduction of 10^{-2} M 4-NP in mono-compartmented reactor (B), the reduction peak intensity, which appears at approximate –0.9 V/Ag/AgCl,KCl, diminishes with approximately 90% comparative tot he initial value in 120 minutes, (theoretical calculated time is 100 minutes), so the electrochemical reduction yield is good enough.

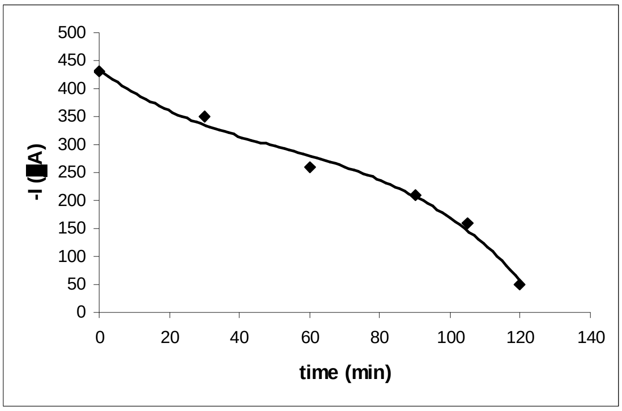


Figure 6. The variation of the reduction peak intensity during electrochemical reduction process for 10^{-2} M 4-NP in 0.2 N H_2SO_4, on graphite cathode (experimental set-up B); i: 20 mA cm^{-2}.

The decrease of the reduction current corresponding to reaction (5) during electrolysis can be used to appreciate the electrochemical removal of 4-NP and 2,6-NP because, for both, quasi-linear variation with the concentration for large concentration range (from 10^{-5} to 10^{-2}M) was found (relations 6 and 7):

$$I_{red} = 0.5395 \cdot C_{4\text{-}NP};\ R^2 = 0.9506 \qquad (6)$$

$$I_{red.1} = 0.6448 \cdot C_{2,6\text{-}DNP} + 0.4525;\ R^2 = 0.9953 \qquad (7)$$

The removal on nitrophenols during electroreduction was demonstrated also by spectrophotometric determinations in UV-Visible, as the second method of determination.

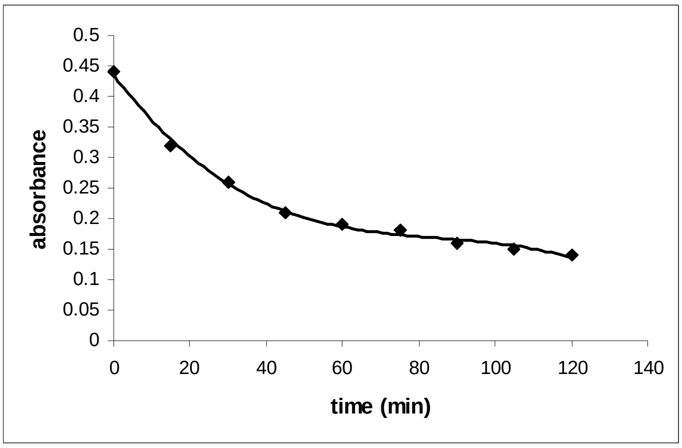


Figure 7. Spectrophotometric control of electrochemical reduction process for 10^{-2} M 4-NP in 0.2 N H_2SO_4 on graphite cathode (B); λ_{max} = 318 nm; log Є = 3.87.

The calibration curve for the 4-NP in 0.2N H_2SO_4 is: $A = 0.0923 \cdot C_{4\text{-}NP}$; $R^2 = 0.9839$; where: A is the absorbance of the 4-NP solution; $C_{4\text{-}NP}$ represent the concentration of 4-NP.

In figure7. it can be seen that, in case of electrochemical reduction of 10^{-2} M 4-NP on graphite cathode (experimental set-up B), the absorbance diminishes with approximately 70% comparative tot he initial value in 120 minutes. For the same experimental conditions, using the voltammperometric determination, figure 6, the decrease of the current was about 90%. This difference is probably due to the dyeing of the solution from colourless to brown, during the electrolyse, problably due to the chemical reactions of the electrogenerated species [15,16].

*Electrochemical reduction of diluted solution (*4.5 x 10^{-5} M) *of 2,6-dinitrophenol*

The electrochemical two compartmented reactor (experimental set-up C) has been used. As catholyte it was used 400 ml solution of 4.5 x 10^{-5} M of 2,6-DNP in aqueous solution of 0.1N NaCl, and as anolyte it was used 300 ml aqueous solution of 0.1N NaCl.

The absorbance of 2,6-DNP solution, figure 8, diminishes with approximately 75% in the first 15 minutes, comparative tot he initial value, (theoretical calculated time is 20 minutes) and the discouloration is continuing (99% after 100 minutes).

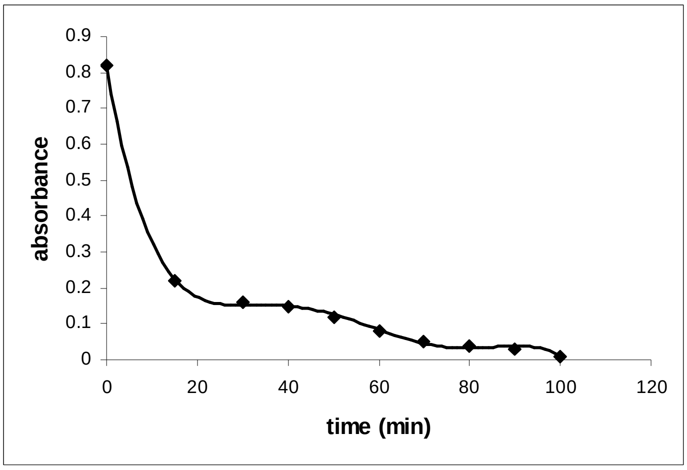


Figure 8. Spectrophotometric control of electrochemical reduction process for 4.5 x 10^{-5}M 2,6-DNP in (0.1N) NaCl, on graphite cathode (experimental set-up C). λ_{max} = 440 nm; log Є = 3.58.

The summarized average results (two determinations for every case) are presented in Table1.

Table 1.

Synoptic presentation of experimental determinations.

Experimental set-up	Treated nitrophenol	Cathodic material	Initial concentration (mol l^{-1})	Flow rate of recirculation (l min^{-1})	Nitrophenol removal (%)
A	4-NP	nickel	10^{-3}	3.3x 10^{-3}	94.2
B	4-NP	graphite	10^{-2}	1.2	90.6
C	2,6-DNP	graphite	4.5 x 10^{-5}	1.4	99.0
	2,6-DNP	nickel	4.5 x 10^{-5}	1.4	98.8

CONCLUSIONS

Electrochemical removal of 4-NP and 2,6-DNP have been performed in different reactors, with different hydrodynamic conditions and using different type of electrodic material, with the aim to optimize the process.

The best results (99% removal) have been obtained in diluted solutions (10^{-5} mol l^{-1}). The nature of electrodes seems to be not very important but the high masse transfer (flow rate about 1 l min^{-1}), favorised the nitrophenols removal.

As perspectives, it is envisaged to perform some new electrochemical reduction experiments on 4-NP with the aim to settle the mechanism of electrodic processes, to optimize the experimental conditions for electrochemical reduction of 4-NP, to separate and to determine the products, and to extend the study on others mono and dinitrophenols.

EXPERIMENTAL SECTION

Reagents and solution preparation

4-NP with purity greater than 98% (Merk, Germany), and 2,6-DNP with purity greater than 95% (calculated based on dry substance), moistened with 20% H_2O (ALDRICH, Swizerland) were used to prepare the solutions, with desirable concentration, for the experiments in this study. Distilled water, in the case of 4-NP, and double distilled milliq water, in the case of 2,6-DNP, were used to prepare the aqueous solutions. For electrochemical determinations, the solutions were prepared using Britton – Robinson buffer (1:1:1 mixture of 0.04 M boric acid, phosphoric acid and acetic acid; the pH was adjusted to the right pH with 0.1 M NaOH and 0.2 N H_2SO_4.

Apparatus

The electrochemical experiments were carried out using three different experimental set-up. In the case of 4-NP the experiments were performed in an electrochemical filter press cell commercialised by Electrocell AB (Sweden) as the microflow cell equipped with an DSA-O_2 anode (20 cm^2 area), an nickel cathode (20 cm^2 area). Both compartments of the electrochemical cell are separated by a NAFION 350 millipore membrane. The electrochemical cell was inserted into a hydraulic circuit which comprises a GILSON MINIPULS 3 peristaltic pump forcing the circulation of the electrolyte in the compartments of the filter press cell, with flow rates in the range 1×10^{-6} to 3.3×10^{-3} l min^{-1}. The experimental setup (A) comprises two glass tanks containing anolyte and catholyte. The second experimental set-up (B) consist in a mono-compartment electrochemical reactor (with a capacity of 1500 cm^3) equipped with a pump, which assure the electrolyte recirculation, with flow rate of 1.2 l min^{-1}, two stainless steel anodes (212.3 cm^2 area), and an graphite cathode (185.7 cm^2 area). In the case of 2,6-DNP the experimental set-up (C) consist in a glass made electrochemical reactor, equipped with an Ti/Pt-Ir anode and a graphite cathode, both of 100 cm^2, a NAFION 117 millipore membrane, and a WATSON MARLOW Mod.313 F/D peristaltic pump with two heads, operating under conditions of full recycle, with flow rates in the range 0.09 to 1.4 l min^{-1}. In all experiments, the reactors were operated under galvanostatic conditions. Electrolysis efficiency was followed by regularly sampling the electrolyte and analysing the concentration of residual reagents, by voltammetric and spectrophotommetric measurements.

Voltammetric measurements were made using a potentiostat-galvanostat system – BAS 100B (Bioanalytical Systems, USA) with the specific software BAS 100W and a classic three electrode electrochemical cell. The electrochemical cell is comprised of a cell bottom of 20 mL capacity and a plastic cell top. The experimental design consist of a platinum plate auxiliary electrode, an Ag/AgCl,KCl reference electrode; the working electrodes were glassy carbon and nickel (2 mm diameter), inserted through the cell top into the cell.

Spectrophotometric determinations were made using a Unicam Helyos B spectrophotometer with the specific software VISION 32, and a quartz vat of 2 ml, with optical route of 1 cm, and a Direct Reading Spectrophotometer type DR/2000 HACH with a glass vat of 25 ml, and with optical route of 2 cm.

The pH measurements for the solutions were made with a pH-meter Basic 20 from Crison.

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