Hydrogen peroxide monitoring in photo-Fenton reactions by using a metal hexacyanoferrate modified electrode

Maiara Oliveira Salles, Thiago R.L.C. Paixão and Mauro Bertotti*

Instituto de Química - Universidade de São Paulo, São Paulo - SP - Brazil 05508-900
fax number: 5511-3815-5579
*E-mail: mbertott@iq.usp.br

A sensitive sensor for the determination of hydrogen peroxide was fabricated based on the enhanced response of the analyte at glassy carbon surfaces modified by a film of Co(II) hexacyanoferrate. Increased chemical stability of the film was gained by incorporation of ruthenium (III) ions. Following the optimization of the experimental conditions for the film deposition, the RuCoHCF modified electrode presented excellent analytical properties toward hydrogen peroxide with a low limit of detection (2.8 μmol L^{-1}), a large dynamic concentration range (10 – 500 μmol L^{-1}) and a very short response time ($t_{100\%}$ = 6.3 s for 0.02 mmol L^{-1} hydrogen peroxide). The usefulness of the proposed RuCoHCF electrochemical sensor was confirmed by monitoring the consumption of hydrogen peroxide during photodegradation reactions of an azo dye compound (Remazol Black B) present in wastewater samples.

1. INTRODUCTION

Many metals are able to promote oxygen transfer reactions which improve the oxidizing power of hydrogen peroxide. The most common used metal is iron, highly reactive hydroxyl radical being produced in the presence or absence of UV radiation from the reaction between hydrogen peroxide and iron (II). The reactivity of the generated species was first observed in 1894 and the so-called Fenton's reagent has been continuously used for the treatment of wastewater, contaminated soils and sludge.

During the Fenton's reaction some experimental parameters should be adjusted to promote an efficient reaction between pollutants and hydroxyl radicals. For instance, at pH values lower than 3 or higher than 6 the reaction is not favored because of the decomposition of hydrogen peroxide or Fe(III) precipitation. Furthermore, high concentrations of hydrogen peroxide are preferred in order to guarantee the complete conversion of the organic material and a steady reduction in COD (chemical

oxygen demand). Accordingly, the determination of the residual peroxide is a crucial parameter in the photodegradation process.

Hydrogen peroxide determination has been performed by using spectrophotometry [1-3], fluorimetry [4,6], fluorescence [7], chemiluminescence [8-11] and electrochemical methods [12-15] and some of them were directed to the analysis of hydrogen peroxide during photodegradation reactions [1,2]. Electroanalytical sensors are preferable under certain circumstances which involve applications such as field measurements performed in inaccessible places or with very low sample volumes or to provide on-line analytical information in chemical systems where the concentration of the target species varies in real time [16-19].

Direct electroanalytical determinations of hydrogen peroxide are difficult because quite positive potentials are required for the oxidation of the analyte at bare electrodic surfaces [20]. Consequently, hydrogen peroxide analysis does not seem to be realistic in a complex sample from environmental chemical systems. Accordingly, measurement of hydrogen peroxide by using electrochemical devices has exploited the advantages of the modification of the electrodic surface with films that confer to the sensor special features such as better sensitivity and selectivity. Among these films those based on the deposition of metal-hexacyanoferrate [14, 21-25] are the most used, even though there are in literature examples of other materials such as molybdenum oxides containing platinum microparticles [26].

The use of metal-hexacyanoferrates complexes in electroanalytical chemistry has been explored by several research groups because these compounds can be electrochemically immobilized onto bare electrode surfaces in a simple and controlled way. For instance, Lin and Jan [14] have reported the fabrication of a Co(II) hexacyanoferrate glassy carbon modified electrode and its use in a FIA amperometric procedure to the determination of hydrogen peroxide. In the present work we show our efforts to incorporate ruthenium centers in a Co(II) hexacyanoferrate film. The fabricated modified electrode possesses increased chemically stability and has been employed to determine hydrogen peroxide in wastewater samples previously treated with Fenton's reagent.

2. EXPERIMENTAL DETAILS

2.1 Chemicals

All the reagents were used without previous purification and the solutions were prepared dissolving the solid reagents or diluting acid solutions into deionized water. H_2O_2, H_2SO_4, KI, $(NH_4)_6Mo_7O_{24}.4H_2O$, $CoCl_2$, $K_3[Fe(CN)_6]$ and $FeSO_4.7H_2O$ were obtained from Merck (Darmstadt, Germany), KCl was purchased from Synth (São Paulo, Brazil) and $RuCl_3$ from Alfa Aesar (Massachusetts, USA). The solutions of $CoCl_2$ and $K_3[Fe(CN)_6]$ were freshly prepared and the H_2O_2 solutions were prepared by dilution to the required concentration and stored in a refrigerator (5^oC).

2.2 Instrumentation

A bipotentiostat from Autolab PGSTAT30 (Eco Chime) connected to a microcomputer was used in all electrochemical experiments. Voltammetry was performed in a three-electrode cell by using a Ag/AgCl sat. reference electrode, a platinum wire as auxiliary electrode and a glassy carbon

electrode. Rotating disc voltammetric experiments were carried out with a rotating system from Pine Instrument Company (AFMSRX model).

2.3 Modification of the electrode surface

The optimized procedure for the fabrication of the ruthenium-modified cobalt hexacyanoferrate (RuCoHCF) modified electrode used in the peroxide determinations involved three main steps, i.e., cleaning of the glassy carbon electrode, deposition of the Co(II) hexacyanoferrate (CoHCF) film and further incorporation of Ru(III) ions. Cleaning of the electrode surface was performed by using alumina powder, 1 μm (Massachutes, USA), rinsing with deionized water and subsequent sonication for 5 minutes in deionized water. The electrodeposition of the CoHCF film onto the glassy carbon surface was carried out by maintaining the potential of the working electrode at 0.1 V in a solution containing 0.5 mol L^{-1} KCl, 30 mmol L^{-1} K$_3$[Fe(CN)$_6$] and 30 mmol L^{-1} CoCl$_2$ (pH = 3) at 4000 rpm. The incorporation of Ru(III) into the CoHCF film was accomplished by cycling consecutively the potential of the CoHCF modified electrode in a 0.5 mol L^{-1} KCl + 2 mmol L^{-1} RuCl$_3$ solution (pH = 3) (50 potential cycles from 0.0 to 0.9 V).

2.4 Amperometric determination of hydrogen peroxide in real samples

Four wastewater samples containing an organic azo dye compound (Remazol Black B) were submitted to a photodegradation process and the remaining hydrogen peroxide was analyzed by using the RuCoHCF modified electrode in the amperometric mode. The initial concentration values were 0.028 mol L^{-1} Remazol Black B, 0.14 mol L^{-1} Fe(II) and the H$_2$O$_2$ concentration was set at two levels: 0.28 (H) and 0.14 mol L-1 (P). Samples from each of these two solutions were collected at two different times (0 and 10 minutes) from a reactor containing 300 mL of the wastewater, Fe(II) and hydrogen peroxide with a 10 mL syringe and stored in a amber flask at 5°C to stop the Fenton reaction. Aliquots of the samples (100 μL) were injected in 20 mL of supporting electrolyte solution for hydrogen peroxide measurements.

3. RESULTS AND DISCUSSION

3.1. Cobalt hexacyanoferrate film studies

Figure 1, curve (- • -), shows a voltammogram recorded with a bare glassy carbon electrode in supporting electrolyte solution containing hydrogen peroxide. The absence of a faradaic process demonstrates that hydrogen peroxide is electroinactive at the selected potential range. A typical voltammogram obtained with the CoHCF film is shown in curve (—), two cathodic and one anodic peaks being noticed at 0.12V, 0.46V and 0.60V respectively. This profile is quite similar to the one reported in literature and the voltammetric waves correspond to electron-transfer processes associated with the metallic centers [14]. By recording a new voltammogram with the modified electrode in a solution containing hydrogen peroxide, a significant current increase is observed in the potential range around 0 V and this electrodic process may be attributed to the electrocatalytic reduction of hydrogen peroxide.
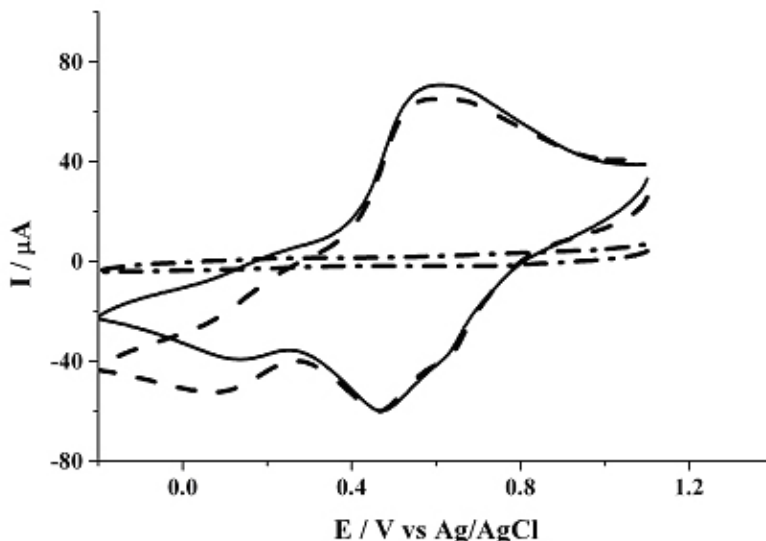
Figure 1: Cyclic voltammograms recorded with a CoHCF modified electrode before (—) and after (- - -) addition of hydrogen peroxide (final concentration = 3.0 mmol L^{-1}) to the supporting electrolyte (0.5 mol L^{-1} KCl). Line - • - represents the cyclic voltammogram recorded with a bare glassy carbon electrode in the solution containing hydrogen peroxide. Scan Rate = 50 mV s^{-1}.
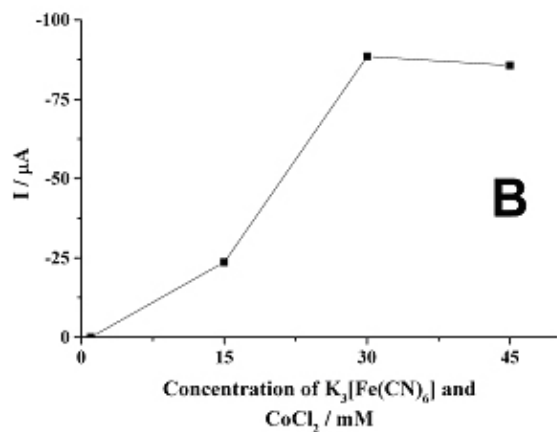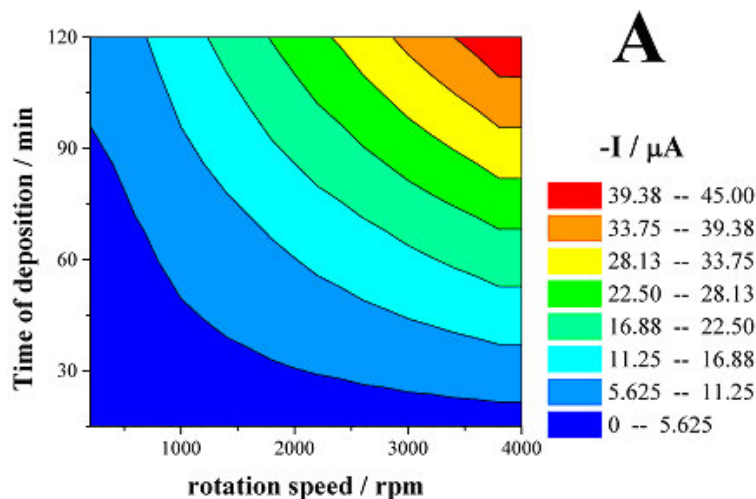

Figure 2: Cathodic peak values measured at 0.05 V in voltammograms (scan rate: 50 mV s^{-1}) recorded with CoHCF modified electrodes in a 0.5 mol L^{-1} KCl solution (pH = 3) containing 1.47 mmol L^{-1} hydrogen peroxide. Panel A shows the influence of the rotation rate and electrodeposition time (for a 15 mmol L^{-1} $K_3[Fe(CN)_6]$ + 15 mmol L^{-1} $CoCl_2$ + 0.5 mol L^{-1} KCl solution) and data in panel B represent the current dependence on the concentration of $K_3[Fe(CN)_6]$ and $CoCl_2$ (experiments carried out at 4000 rpm and 1 hour electrodeposition time).

As an attempt to enhance the signal response of the CoHCF film towards the cathodic reduction of hydrogen peroxide, further investigations were carried out to optimize the experimental conditions related to the electrodeposition process. As suggested in literature [14], the modification of the electrode surface was accomplished by applying a constant potential (E = 0.1 V) to the glassy carbon electrode immersed in a solution containing both Co(II) and $Fe(CN)_6^{3-}$ ions. Three main parameters were studied: concentrations of $CoCl_2$ and $K_3Fe(CN)_6$, time of electrodeposition and mass transport rate. Figure 2 shows the results of such experiments and it is clearly seen that better results, measured as the response of the prepared CoHCF modified electrodes to hydrogen peroxide, were obtained for thicker films. As a conclusion of this study, the optimized electrodeposition of the CoHCF film was carried out in a supporting electrolyte solution containing 0.5 mol L^{-1} KCl, 30 mmol L^{-1} $K_3[Fe(CN)_6]$ and 30 mmol L^{-1} $CoCl_2$ (pH = 3), rotated at 4000 rpm during 2 hours. At these experimental conditions, films with $\Gamma = 8.7 \times 10^{-9}$ mol cm^{-2} were obtained (charge under the Fe^{II}/Fe^{III} process at 0.60 V).

3.2 Cobalt hexacyanoferrate film modified with ruthenium(III) studies

Cataldi et.al. [27] have reported that CoHCF films are not stable and that for some metal-hexacyanoferrate modified electrodes a significant loss of electrochemical activity is noticed. This can be confirmed by looking at data shown in Table 1, where current peak values measured at 0.05V in consecutive potential scans are shown as a function of time.

Table 1: Peak values measured at 0.05 V in voltammograms (scan rate: 50 mV s^{-1}) recorded with CoHCF modified electrode in a 0.5 mol L^{-1} KCl solution (pH = 3)

Time / h	I / μA
0	70.7
1	67.3
2	65.7
3	64.3
4	62.8
5	61.7
6	60.7

After 6 hours the current peak drops up to 86% of its initial value, which in terms of an electrochemical sensor to be used continuously is not appropriate. On the other hand, when ruthenium ions are incorporated into the CoHCF film an expressive increase in stability was observed, as shows the voltammograms in Figure 3A. The better performance of the sensor regarding its chemical stability after insertion of ruthenium (III) has been attributed to the formation of mixed-valent dinuclear Ru-Fe oxo-bridges [27-32]. Hence, a more insoluble material is immobilized onto the electrode surface with a consequent increased chemical and electrochemical stability.

Figure 3B also shows the results of optimization studies on the amount of ruthenium (III) incorporated into the CoHCF film in terms of both the concentration of the Ru(III) solution and the time of electrodeposition (number of potential cycles). It seems that Ru(III) solutions more

concentrated than 2 mmol L^{-1} are not adequate as the response for hydrogen peroxide decreases. On the other hand, a sharp current enhancement is noticed as the number of potential cycles increases up to 50 cycles.
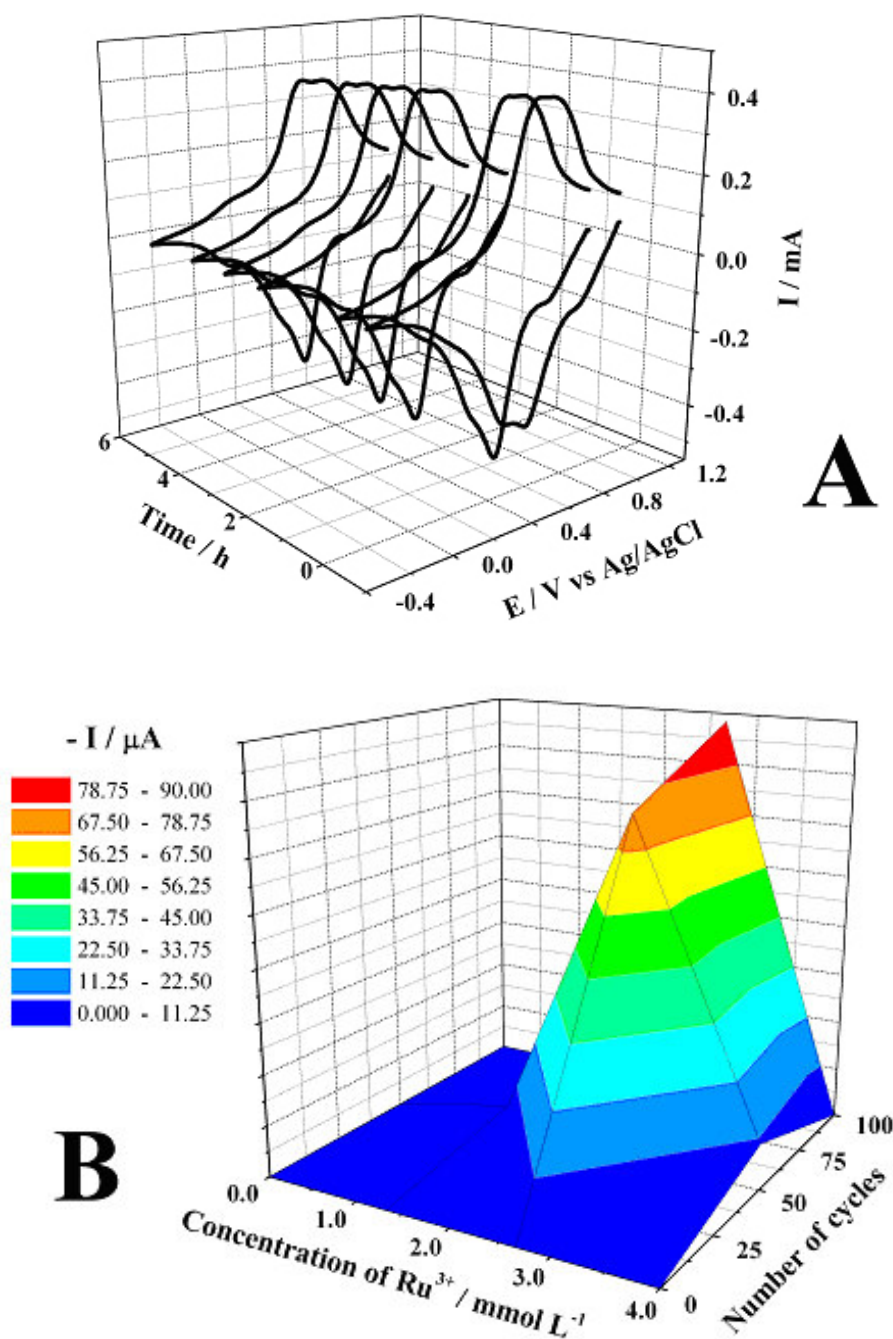

Figure 3: Consecutive voltammograms recorded with a RuCoHCF in 0.5 mol L^{-1} KCl solution (pH = 3) (A). A 3D plot of peak current values measured with RuCoHCF modified electrodes in a 0.5 mol L^{-1} KCl solution (pH = 3) containing 0.50 mmol L^{-1} hydrogen peroxide as a function of the experimental conditions employed in the film preparation (number of potential cycles and concentration of RuCl$_3$) is presented in panel B. CoHCF films prepared as stated in the Experimental Section.

The analytical applicability of the developed RuCoHCF sensor was investigated by amperometry in experiments performed at 0.05 V. Hydrogen peroxide aliquots were added to the supporting electrolyte under convection to reach steady state current conditions. Figures 4A and 4B show both the fast sensor response ($t_{100\%}$ = 6.3 s for 0.02 mmol L^{-1} hydrogen peroxide) and the good linear correlation between current and hydrogen peroxide concentration. The repeatability was evaluated by 3 replicate injections of 0.02 mmol L^{-1} hydrogen peroxide solution, the standard deviation being determined as 4.0%. A plot of current as a function of hydrogen peroxide concentration in the 10 – 500 µmol L^{-1} concentration range yielded a straight line ((I / µA) = –0.69 – 49.1 (C / mmol L^{-1})) with r^2 = 0.998. Detection (3SD) and quantification (10SD) limits were calculated as 2.8 and 9.4 µmol L^{-1}, respectively.
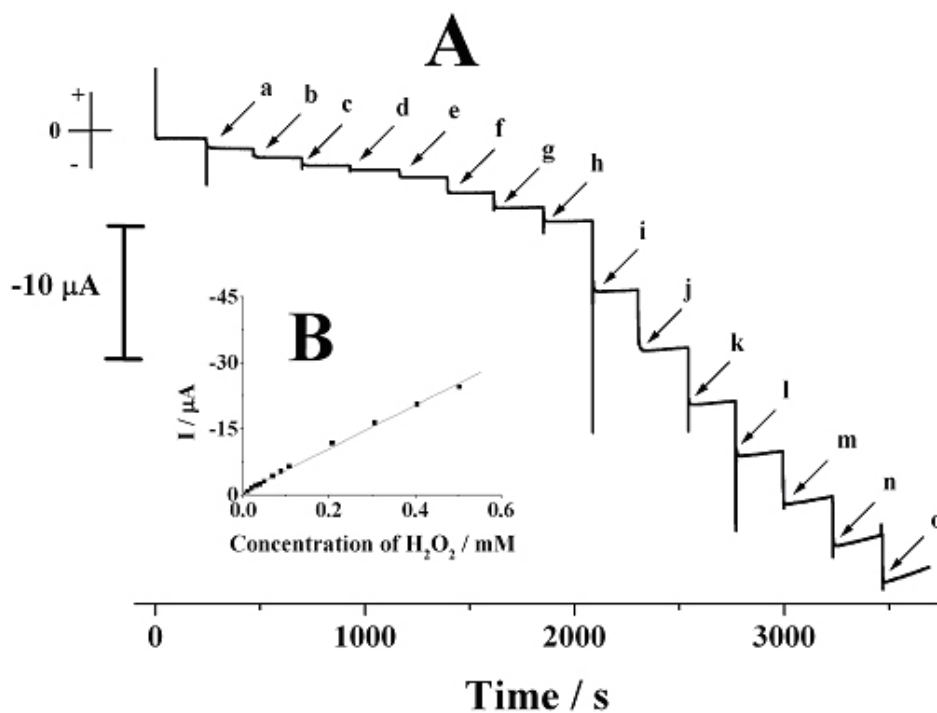

Figure 4: Current responses (A) monitored as a function of time with a RuCoHCF modified electrode immersed in 0.5 mol L^{-1} KCl supporting electrolyte during repetitive injections of hydrogen peroxide to give the following final concentrations: 10 (a), 20 (b), 30 (c), 40 (d), 49 (e), 69 (f), 88 (g), 107 (h), 207 (i), 306 (j), 405 (k), 503 (l), 601 (m), 698 (n) and 795 (o) µmol L^{-1}. The inset (B) shows the calibration curve. E = 0.05V. Rotation rate: 1000 rpm.

3.3. Studies with dye wastewater treated with Fenton's reagent

Color removal has become one the most important aspects in the dye wastewater treatment because of the association between residual color and toxicity of discharged effluents. Fenton-like reactions have been increasingly used by the industry in the reduction of azo dye levels from wastewater and, as already stated, the on-line control of the peroxide concentration in the reactor is very important. Accordingly, the usefulness of the RuCoHCF film to measure hydrogen peroxide in wastewater treated by photodegradation was investigated by performing amperometric experiments. By analyzing data

shown in Figure 5, where current values are measured for wastewater samples containing Fenton´s reagent at different experimental conditions, three main points should be addressed.
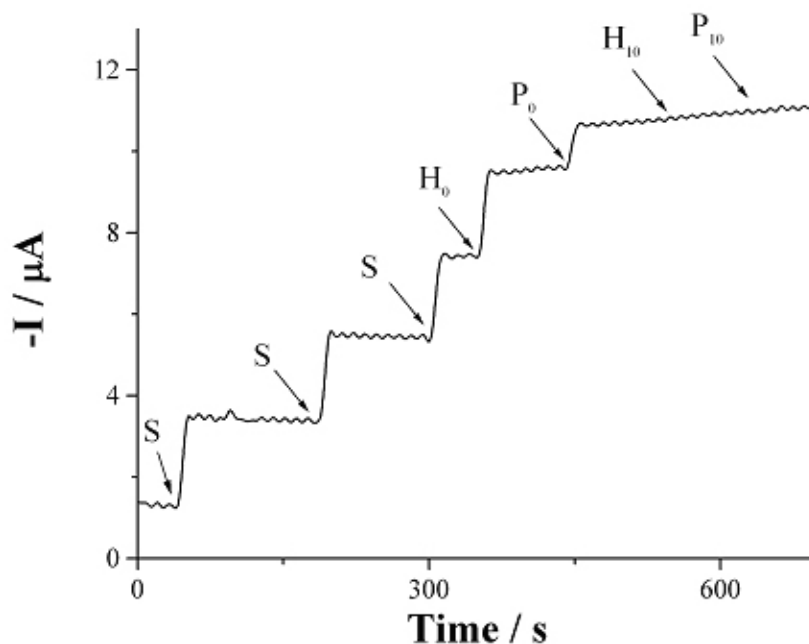

Figure 5: Current responses monitored as a function of time with a RuCoHCF modified electrode immersed in a 0.5 mol L^{-1} KCl supporting electrolyte solution during repetitive injections (100 µL) of hydrogen peroxide standard solution (final concentration = 20 µmol L^{-1}) (S) and different wastewater samples (H_x and P_x). The subscription represents the time (in minutes) after which the photo-Fenton reaction was interrupted. E = 0.05V. Rotation rate: 1000 rpm.

Firstly, higher current signals are obtained for samples containing hydrogen peroxide at an initial higher level (H). Secondly, the remarkable current decrease noticed as the Fenton´s reaction proceeds is an indication of the hydrogen peroxide consumption. Finally, the initial levels of hydrogen peroxide were reduced to almost zero after a 10-minute time for both solutions (H and P).

4. CONCLUSIONS

The cathodic reduction of hydrogen peroxide is facilitated at surfaces covered by CoHCF films and the stability is enhanced by incorporating ruthenium (III) into the film. At optimized conditions, a linear relationship between current response and concentration is maintained over a relatively large hydrogen peroxide concentration range, assuring the use of this modified electrode as an amperometric sensor. The RuCoHCF modified electrode was found to work properly in the determination of the hydrogen peroxide in wastewater samples submitted to photodegradation reaction, avoiding cumbersome processes that make difficult fast and practical analysis. Hence, the proposed sensor may be adapted for continuous routine sensing of hydrogen peroxide in Fenton´s reaction processes,

providing a reliable approach for on-line monitoring. Accordingly, further studies will be directed to evaluate the long-term response in flow systems, especially in solutions containing hydrogen peroxide at higher concentrations. Also, the influence of interfering species in the sensor response will also be subject of investigation but it should be observed, however, that at the RuCoHCF working potential (0.05 V) no influence of typical electroactive species is expected.

References

1. R.F.P. Nogueira, M.C. Oliveira, W.C. Paterlini, *Talanta*, 66 (2005) 86.
2. I. Arslan, I.A. Balcioğlu, D.W. Bahnemann, *Dyes Pigm.*, 47 (2000) 207.
3. B.C. Madsen, M.S. Kromis, *Anal. Chem.*, 56 (1984) 2850.
4. T.R. Holm, G.K. George, M.J. Barcelona, *Anal. Chem.*, 59 (1987) 582.
5. J.H. Lee, I.N. Tang, J. B. Weinstein-Lloyd, *Anal. Chem.*, 62 (1990) 2381.
6. H. Hwang, P.K. Dasgupta, *Anal. Chim. Acta*, 170 (1985) 347.
7. A. Gomes, E. Fernandes, J.L.F.C. Lima, *J. Biochem. Biophys. Methods*, 65 (2005) 45.
8. W. Quin, Z. Zhang, B. Li, S. Liu, *Anal. Chim. Acta*, 372 (1998) 357.
9. H. Hoshino, W.L. Hinze, *Anal. Chem.*, 59 (1987) 496.
10. K. Hool, T.A. Nieman, *Anal. Chem.*, 59 (1987) 869.
11. K. Hool, T.A. Neiman, *Anal. Chem.*, 60 (1988) 834.
12. I.G.R Gutz, D. Klockow, *Fresenius Z. Anal. Chem.*, 335 (1989) 919.
13. M. Somasundrum, K. Kirtikara, M. Tanticharoen, *Anal. Chim. Acta*, 319 (1996) 59.
14. M. S. Lin, B. I. Jan, *Electroanalysis*, 9 (1997) 340.
15. F. Ricci, G. Palleschi, *Biosens. Bioelectron.*, 21 (2005) 389.
16. E. Bakker, M. Telting-Diaz, *Anal. Chem.*, 74 (2002) 2781.
17. N.R. Stradiotto, H. Yamanaka, M.V.B. Zanoni, *J. Braz. Chem. Soc.*, 14 (2003) 159.
18. E. Bakker, *Anal. Chem.*, 76 (2004) 3285.
19. J.R. Stetter, W.R. Penrose, S. Yao, *J. Electrochem. Soc.*, 150 (2003) S11.
20. G.G. Guilbault, G.J. Lubrano, *Anal. Chim. Acta*, 64 (1973) 439.
21. P.A. Fiorito, V.R. Gonçales, E.A. Ponzio, S.I.C. de Torresi, *Chem. Commun.*, 3 (2005) 366.
22. S.M.S. Kumar, K.C. Pillali, *Electrochem. Commun.*, 8 (2006) 621.
23. C.G. Tsiafoulis, P.N. Trikalitis, M.I. Prodromidis, *Electrochem. Commun.*, 7 (2005) 1398.
24. J. Lin, D.M. Zhou, S.B. Hocevar, E.T. McAdams, B. Ogorevc, X.J. Zhang, *Front. Biosci.*, 10 (2005) 483.
25. R. Pauliukaite, M. Florescu, C. M. A. Brett, *J. Solid State Electrochem.*, 9 (2005) 354.
26. L. Kosminsky, R. C. Matos, M. H. Tabacniks, M. Bertotti, *Electroanalysis*, 15 (2003) 733.
27. T.R.I. Cataldi, G.E. De Benedetto, A. Bianchini, *J. Electroanal. Chem.*, 471 (1999) 42.
28. T.R.I. Cataldi, G.E. De Benedetto, *J. Electroanal. Chem.*, 458 (1998) 149.
29. M.H. Pournaghi-Azar Æ R. Sabzi, *J. Solid State Electrochem.*, 6 (2002) 553.
30. G.E. De Benedetto, M.R. Guascito, R. Ciriello, T.R.I. Cataldi, *Anal. Chim. Acta*, 410 (2000) 143.
31. V.A. Pedrosa, M. Bertotti, *Int. J. Electrochem. Sci.*, 2 (2007) 113.
32. T.R.L.C. Paixão, M. Bertotti, *Electrochim. Acta*, 52 (2007) 2181.