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Electrochemical reduction and determination of Cibacron Blue F3GA at poly-L-lysine modified glassy carbon electrode

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Abstract

The oxidation of a reactive dye, Cibacron Blue F3GA, CB, (C.I. 61211), widely used in the textile industries to color natural fibers, was studied by electrochemical techniques. The oxidation on glassy carbon electrode occurs in two steps at $2.0 < pH < 10$ involving one electron transfer each to the amine group leading to the imide derivative. Stable films of poly-L-lysine (PLL) in the presence of glutaraldehyde (GA) 97.5%:2.5% on glassy carbon electrode can be used to detect low levels of dye using its oxidation peak at +0.75 V by voltammetry. Linear calibration graphs were obtained for the CB reactive dye, from 1.0×10^{-6} to 1.0×10^{-5} mol L^{-1} in B–R buffer, pH 2.0, using a pre-concentration off-line during 10 min. The detection limit (3σ/slope) was calculated to be 4.5×10^{-8} mol L^{-1}. Films of PLL can readily be applied for the determination of CB dye bearing aminoanthraquinone as chromophore and chlorotriazinyl as reactive group at concentrations at least 100 times lesser than using a glassy carbon electrode without modification. The method described was applied for the determination of CB dye in tap water and raw water collected from the municipal treatment plant with a recovery of 89.2% ± 5.4 and 88.0% ± 6.5, respectively.

Keywords: Poly-L-lysine; Cibacron Blue; Reactive dyes; Dye determination; Modified electrode

1. Introduction

Since its introduction, triazine-based dye ligands have been considered as one of the important alternatives to natural counterparts for specific affinity chromatography [1–4]. They are able to bind most types of proteins in some cases in a remarkably specific manner. Dye ligands are commercially available, inexpensive and can easily be immobilized, especially on matrices bearing hydroxyl or amino groups. As an example, Cibacron Blue F3GA (Fig. 1) a kind of reactive dye are commercially important in the dyeing of cellulose fibers [5–7] and have also been coupled to a variety of supports applied to dye–ligand chromatography [1,8,9].

As synthetic dyes, Cibacron Blue F3GA (C.I. 61211) is extensively used in the textile industry due to their characteristic of fixation in the fibers. In addition to the triazine groups acting as reactive group the CB dye presents an anthraquinone group as chromophore (Fig. 1), dyeing textile fibers through covalent bonds [7]. The major environmental problem associated with the use of these reactive dyes is due to their inefficient fixation to the fibers. Therefore, significant losses (12–20% of the annual dye production) occur during the manufacture and processing with dyes being discharged as effluents into publicly owned water treatment plants.

A corresponding increase in the use of this type of reactive dye has highlighted the need to develop rapid and reliable analytical methods for evaluating unfixed

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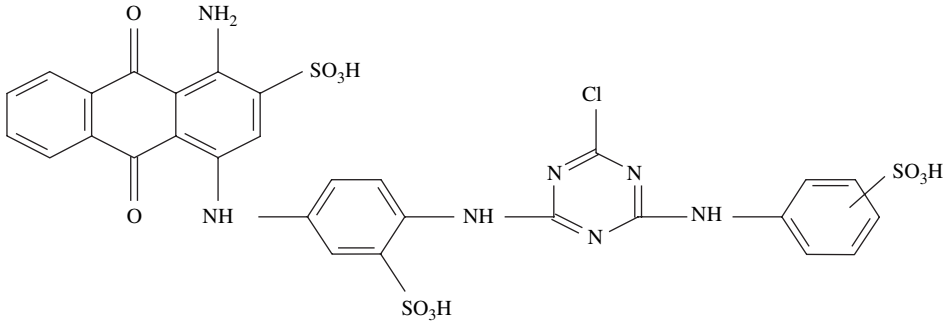

Fig. 1. Molecular structure of Cibacron Blue F3GA (CB) reactive dye.

dyes with sufficient sensitivity to quantify it in water samples obtained from various sampling points. The analytical methods frequently mentioned in the literature [7–20] for determining dye concentration are developed mainly to follow its incorporation on support material. For these purposes, UV–vis spectrophotometry [7,10] and chromatographic methods [11–18] have been described in the literature. In previous studies [19–21] it was demonstrated that differential pulse polarographic methods [19] and cathodic stripping voltammetry [20,21] could be successfully used to determine Cibacron Blue F3GA (CB) in aqueous solution. The methods based on spectrophotometric determination are complicated by: Lambert–Beer deviation due to dye molecule association, low sensitivity and poor resolution for mixture of dyes and its contaminants. Although HPLC methods are reported as sensitive and very suitable for organic compounds analysis, it is limited by high polarity and high reactivity leading to irreversible impregnation of chromatographic columns, use of strong buffer solutions and solid-phase extractions that requires expensive reagents and complicated handling procedure. Although CB dye presents the anthraquinone group as chromophore, which is electrochemically active in all the methods described in the literature that are based on mercury electrodes, which present all the problems inherent of the technique and are limited due to adsorption complication.

The modification of glassy carbon, screen printed carbon, platinum and gold electrodes with films of poly-L-lysine (PLL) has been investigated by several authors [22–31]. PLL is a synthetic polyamino acid with NH_2 groups in the side chain, which are protonated up to pH 10.5. In addition, poly-L-lysine has been used in the literature [25–28], as a model reaction to investigate more complex interactions, since the polypeptide skeleton of poly-L-lysine is more similar to the protein site of more complex biological molecules than other amines or aminoacids. Taking into consideration that it can be used to prepare electrodes modified with thin films of PLL, which have ion-exchange properties, has provided a new approach in electroanalytical chemistry. The most important properties observed are those of facilitating electron transfer, decreasing overpotentials significantly, and pre-concentrating anionic compounds [22–30]. Recently, the present authors have shown that the light cross-linking of PLL by means of glutaraldehyde (97.5% PLL/2.5% (m/v) produces stronger adhesion to the electrode surface, without affecting significantly the high anion exchange capacity of the PLL [31].

The aim of the present work was to investigate the possibility of using the known anion exchange properties and presence of available amino groups in PLL films to test interaction and accumulation with Cibacron Blue dye. The electrochemical behavior of CB on glassy carbon electrode with and without modification by PLL/glutaraldehyde (PLL/GA) films was investigated and an alternative method for dye determination in tap water is proposed.

2. Experimental

Voltammetric measurements were made with a Potentiostat/Galvanostat AUTOLAB PGSTAT 30. A three-electrode system was utilized, where a glassy carbon disc electrode (0.2 mm of diameter) was used as working electrode, a platinum wire as auxiliary electrode and an Ag/AgCl (3 mol L^{-1}) electrode was used as the reference electrode. All pH measurements were made using a Metrohm E500 pH meter with a Metrohm EA 121 glass electrode, which had been calibrated previously. Supporting electrolytes and stock solutions were prepared using demineralized water obtained from a Milli-Q system (Millipore).

Stock solutions of Cibacron Blue F3GA (CB) (1×10^{-2} mol L^{-1}) were prepared from solid samples obtained from Aldrich. The studies were carried out in Britton–Robinson buffer (0.4 mol L^{-1} each of acetic, phosphoric, and boric acids) adjusted to the required pH using 0.2 mol L^{-1} sodium hydroxide solution. Hydrolysis reactions were carried out by treating the dye at an appropriate concentration in aqueous sodium hydroxide solution (pH 12) by heating at a controlled temperature

of 80 °C in an ultra-thermostatic bath (Nova Técnica, Brazil).

2.1. Working electrode preparation

The glassy carbon electrode (2 mm diameter) was polished with alumina (0.3 μm, BUEHLER), and then washed and dried at room temperature. Solutions of the product of the reaction between PLL and glutaraldehyde were prepared using PLL (1% w/v) and glutaraldehyde (0.05% w/v) solutions. The reaction appeared to be complete in 10 min [31]. Ten microlitres aliquot of the glutaraldehyde solution was placed on the polished electrode surface: the tip of the pipette was used to spread the solution evenly over the whole surface and subsequent aliquot of PLL solution was added. After mixing directly on the electrode surface, it was then placed in a drying oven at 80 °C for 2 min. After this drying procedure the electrode was rinsed thoroughly with water and was then immersed in a solution of B–R buffer, pH 2.0. The performance of the modified electrode was tested by two procedures. In the first approach, the voltammograms were recorded after transference of the modified electrode to a solution containing CB. After sufficient time had elapsed (10 min) to accumulate the dye off-line, the electrode was washed and transferred to the electrochemical cell containing the blank buffer in order to record the cyclic voltammograms. In the second procedure the modified electrode was immersed directly in a solution containing the analyte, which was then accumulated under controlled time before recording voltammograms.

For determination of the dye in tap or raw water (collected from the lake of municipal treatment plant station – Araraquara, Brazil), the following procedure was adopted. The modified electrode was immersed in 10.00 mL of tap water, buffered at pH 2.0, spiked to 1.0×10^{-5} mol L^{-1} CB dye. After 10 min of pre-accumulation under stirring, the loaded electrode was gently washed and transferred to a blank solution of B–R buffer, pH 2.0, where linear voltammograms were recorded followed by standard addition method.

3. Results and discussion

3.1. Electrochemical oxidation of CB dye on glassy carbon electrode

Cyclic voltammetric studies showed that CB dye is oxidized on glassy carbon electrode in two steps in all pH range 2–12. Typical oxidation curves obtained for 1.0×10^{-3} mol L^{-1} CB in 0.01 mol L^{-1} B–R buffer at pH 2.0 and pH 10 are shown in Fig. 2, respectively. With increasing the pH, the first anodic peak current (I_{pa}) decreases at $2 \leq pH \leq 5$, is constant at $6 \leq pH \leq 9$ and decrease again at $pH > 10$, as shown Fig. 3A. The peak potential is shifting towards less positive potential at similar interval (Fig. 3B) following two linear segments with a break at $pH \leq 5$ (slope of 56.5 mV) and $pH \geq 10$ (slope of 57.5 mV), indicating that at acidic condition proton reaction of the amine group is involved in the process [31] and probably at alkaline medium there is occurrence of hydrolysis reaction. The second oxidation step (II_a) occurs at more positive potential, around 380 mV, and presents similar intensities when compared with the first oxidation peak. Fig. 3 (A and B) also shows the influence of the pH on the peak potential and peak current of the second oxidation step (II_a). The graph of peak II_a shows an independent relationship between pH and potential (Fig. 3), but the process was accompanied by a lowering of peak height, from $pH \leq 4$ and above $pH \leq 10$ with constant values in this interval.

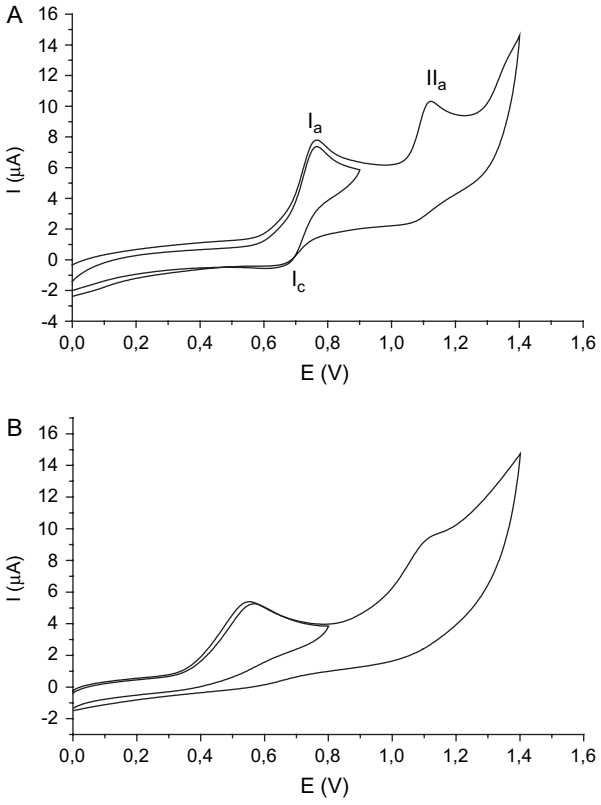

Fig. 2. Cyclic voltammograms of 1.0×10^{-3} mol L^{-1} of CB dye on glassy carbon electrode in (A) B–R buffer, pH 2.0, and (B) B–R buffer, pH 10. Scan rate 20 mV s^{-1}.

The first peak presents a cathodic peak in the reverse scan, which is only observed in acidic solution of $pH < 5.0$, as shown in Fig. 2A. The $E_{pa} - E_{pc}$ values are around 70 mV and the ratio of the cathodic-to-anodic peak heights, recorded in the reverse scan for this couple increased with the scan rate (ν) from 0.49 (10 mV s^{-1}) to 0.77 (500 mV s^{-1}), indicating that the anion radical generated after first electron transfer could be consumed by a slow subsequent chemical reaction [31]. This

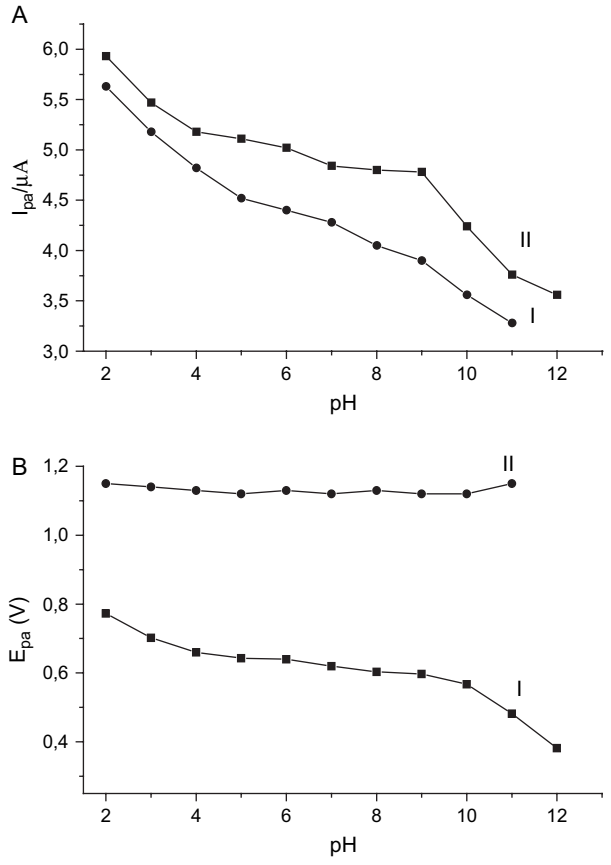

Fig. 3. (A) Graphs of I_p vs pH and (B) E_p vs pH for 1×10^{-3} mol L^{-1} of CB dye in B–R buffer, using values obtained from first (I) and second (II) oxidation steps. Scan rate 20 mV s^{-1}.

reaction is probably rapid at neutral and alkaline conditions, since it is observed in the absence of this reduction peak in all scan rates investigated, as shown in Fig. 2B.

The second oxidation step (II_a) is completely suppressed at pH 12. The effect of scan rate (ν) on both the peaks' potential and the cathodic peaks was also studied in the range 0.01–500 mV s^{-1} for pH 2 and 10. At both pH values, the first cathodic peak presents a shifting of potential to more negative values with an increase in scan rate. Linear relationship between peak current (I_{pc}) and $\nu^{1/2}$ was obtained at pH 2.0 [I_{pa} (μA) = $0.330 + 0.900\ \nu^{1/2}$ (mV $s^{-1})^{1/2}$] and at pH 10 [(I_{pa} (μA) = $-0.020 + 0.900\ \nu^{1/2}$ (mV $s^{-1})^{1/2}$)] indicating that the process is diffusion controlled [32]. The second oxidation step process is also controlled by diffusion, as shown by the linear relationship between I_{pa} and $\nu^{1/2}$, obtained at pH 2 or 10, following the equations [(I_{pa} (μA) = $0.11 + 0.980\ \nu^{1/2}$ (mV $s^{-1})^{1/2}$)] and [(I_{pa} (μA) = $-0.13 + 0.900\ \nu^{1/2}$ (mV $s^{-1})^{1/2}$)], respectively.

Potential controlled electrolysis was carried out using 1.0×10^{-4} mol L^{-1} of CB dye solution at glassy carbon electrode as anode. The variation in current with time was followed during the 60 min of electrolysis for CB dye at pH 2.0 and the number of electrons consumed in the total oxidation is exhibited in Table 1. The log I decreases linearly with time, and the n values obtained indicate that the global dye oxidation involves around one electron at +0.90 V and two electrons when electrolyzed at +1.2 V.

In agreement with the literature [33], it is possible to conclude that the electrochemical oxidation of RB4 dye in aqueous solution involves the amino group adjacent to the anthraquinone group of the imide derivative. Taking into account the values of $n_e- = 1.06$ obtained from electrolysis, it is possible to estimate the number of protons (mH^+) involved in the reaction by the equation ($\Delta E_p/\Delta pH = 59\ mH^+/n_{e-}$) as 1.01 (one proton).

So, it is possible to suggest that at acidic condition (pH ≤ 5) the amino group is oxidized to protonated form ($R{-}NH_2 + H^+ \rightarrow R{-}NH_3^+$), forming a cation radical after one proton and one electron transfer ($R{-}NH_3^+ + e^- \rightarrow R{-}NH_3^{+\bullet}$). The second oxidation step occurs at more positive potential and also involves subsequent oxidation after new electron transfer and di-cation radical formation ($R{-}NH_3^{+\bullet} + e^- \rightarrow R{=}NH + 2H_3O^+$). Nevertheless, as verified previously for Reactive Blue 4 dye [33], the imide generated after subsequent chemical reaction do not promote significant change in the quinone group as chromophore group. The process is similar at neutral and alkaline condition, except for oxidation of an amine group at non-protonated form, following an overall scheme: $R{-}NH_2 + e^- \rightarrow R{-}NH_2^{+\bullet}$; $R{-}NH_2^{+\bullet} + 1e^- \rightarrow R{=}NH + H_3O^+$.

To optimize the voltammetric technique as an analytical method for determining CB dye via oxidation on glassy carbon electrode a calibration curve was tested monitoring the first reduction step of CB dye in B–R buffer, pH 2.0, 4.0, 7.0 and 10.0. The anodic peak current was linearly dependent on the CB dye concentration in the range of 1.0×10^{-4}–1.0×10^{-3} mol L^{-1}, following equations shown in Table 2. The relative standard deviation calculated for 5×10^{-4} mol L^{-1} CB dye is around 4.0% using 5 repetitions and a determination limit of around 10^{-5} mol L^{-1} was obtained. These results indicate that glassy carbon electrode can be used for CB dye determination with simplicity, low cost and good accuracy but the method is not useful for low concentration of CB dye. For this reason, the use of modified electrode was investigated.

Table 1
Coulometric results obtained by controlled potential electrolysis of the dye Cibacron Blue F3GA in B–R buffer, pH 2, on glassy carbon electrode

E (V)	t (s)	Q (C)	n	SD
+0.900	3600	0.410	1.06	±0.10
+1.200	3600	0.760	1.97	±0.40

n = Average values of 3 determinations.

Table 2
Results obtained for voltammetric oxidation of Cibacron Blue F3GA in B–R buffer on glassy carbon electrode

pH	Calibration line (mmol L^{-1})	Regression coefficient	C_l (mol L^{-1})	RSD (%)
2.0	I_p (μA) = $4.4 \times 10^{-8} + 0.00856C$	0.994	2.4×10^{-5}	2.52
4.0	I_p (μA) = $3.6 \times 10^{-8} + 0.00604C$	0.999	1.7×10^{-5}	2.91
7.0	I_p (μA) = $-4.0 \times 10^{-8} + 0.00500C$	0.991	2.0×10^{-5}	4.37
10.0	I_p (μA) = $-3.0 \times 10^{-8} + 0.00800C$	0.994	3.7×10^{-5}	2.52

Scan rate 20 mV s^{-1}. RSD = relative standard deviations; C = concentration in mol L^{-1}; C_l = limit detection (3σ/slope).

3.2. Oxidation of Cibacron Blue F3GA on PLL/GA modified electrodes

Typical cyclic voltammograms obtained for the oxidation of 5×10^{-6} mol L^{-1} CB in B–R buffer, pH 2, on bare and modified electrodes of PLL (97.5%)/GA (2.5%) are shown in Fig. 4. The curve obtained for oxidation of CB dye presents one anodic peak (I_{pa}) at +0.75 V with the corresponding cathodic peak at +0.64 V (curve 2), for which there is no signal at a bare glassy carbon electrode at this concentration (curve 1). The relationship I_{pa}/I_{pc} for voltammograms obtained for oxidation of CB on the film generated an anion radical more than at bare electrode.

In order to characterize the retention capability of CB dye on the PLL/GA coating the electrode modified by PLL (50%)/GA (50%) films was loaded after 10 min of immersion in 7.5×10^{-6} mol L^{-1} of CB dye in B–R buffer, pH 2, and then, after gentle washing of the electrode with water, it was transferred into a B–R buffer solution, pH 2.0, where cyclic voltammograms were produced with identical characteristics of that shown in Fig. 5. The typical CB redox couple response was observed, showing that the dye is maintained at the PLL:GA film. Constant values of current of 0.75 ± 0.22 μA were obtained over 10 repetitions, with a coefficient of variation of 7.8%. This reproducibility shows clearly that PLL:GA promotes the adherence of CB in the film onto the electrode surface. Washing step with electrolytes such as 0.01 mol^{-1} KCl and 0.1 mol L^{-1} KNO_3 was also tested, but there is no significant improvement when compared with demineralized water. So, between measurements the regeneration was obtained with water washing step.

The scan rate dependence of the cyclic voltammetric peak currents was evaluated using a modified electrode loaded with CB from a 5×10^{-6} mol L^{-1} solution for 10 min of pre-concentration. The electrode was then transferred to fresh supporting electrolyte (pH 2.0). Scan rates in the range 0.01–1.0 V s^{-1} gave a straight line for the plot of the peak current vs scan rate (ν) as shown by the equation: I_{pa} (μA) = $-0.1277 + 2.06 \times 10^{-2}\,\nu$ (mV s^{-1}), $R = 0.9948$ ($N = 10$). This indicates that CB dye is being oxidized in adsorbed form on the electrode surface and there is insignificant leaching of dye from the films.

The influence of accumulation time on the electrode response was investigated by immersing the electrode in 1×10^{-5} mol L^{-1} CB solution for 1–100 min and then removing it to the voltammetric cell containing B–R buffer, pH 2.0. In each study voltammograms were recorded after washing and re-equilibration for 10 s. The typical cyclic voltammograms are shown in Fig. 6. As can be seen, the peak currents are significantly larger for

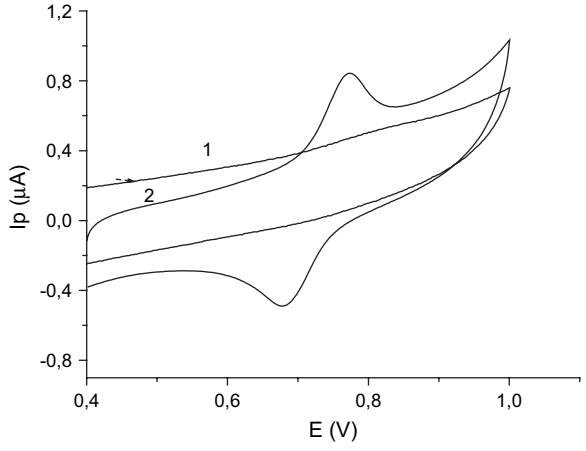

Fig. 4. Cyclic voltammograms obtained for the oxidation of 5×10^{-6} mol L^{-1} CB in B–R buffer, pH 2, on bare and modified electrodes of PLL (97.5%)/GA (2.5%). Scan rate 20 mV s^{-1}.

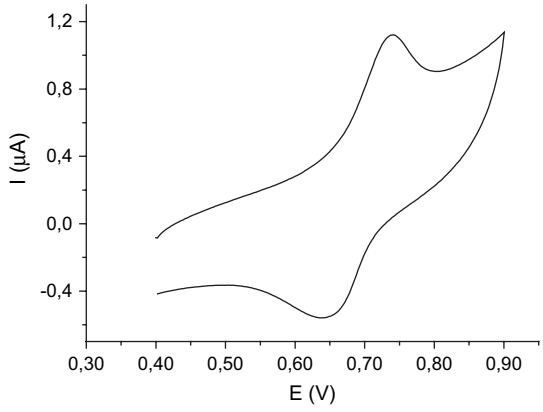

Fig. 5. Cyclic voltammograms obtained for oxidation of CB dye incorporated on films of PLL:GA on glassy carbon electrode surface in B–R buffer, pH 2.0, after previous immersion in 7.5×10^{-6} mol L^{-1} of CB in B–R buffer, pH 2, during 10 min, followed by the step of washing and subsequent transference to a blank buffer.

longer accumulation times and the voltammograms reach a steady state after 100 min. Graph of I_p vs time of immersion is linear, following the equation: I_p (μA) = $-0.028 + 0.021\,t$ (t = min), $R = 0.998$. The current increases linearly up to 100 min, showing that the analyte is slowly taken up by the film on the electrode surface and reaches saturation effect at longer accumulation time. In addition, Fig. 6 shows that the cyclic voltammograms obtained after 30 min of accumulation present larger peaks and a slight modification in the cathodic peak in the reverse scan. So, immersion time of 10 min was adopted in the further experiments. The effect of time for dye concentration at 1.0×10^{-3} mol L^{-1} has shown that current increases from 0.5 to 8 min, which surface saturation at time superior to 10 min of pre-concentration.

The effect of pH on the incorporation of CB dye on the modified electrode with PLL/GA was investigated from pH 2 to 12. The oxidation peak was monitored after transference of the modified electrode loaded during 10 min of immersion in 1×10^{-4} mol L^{-1} CB solution to a blank solution of B–R buffer, pH 2.0. The peak current (I_{pa}) and peak potential (E_{pa}) dependence on pH is shown in curves I and II of Fig. 7, respectively. The currents are higher at pH $\leq$ 8, but the film is retaining the dye even at pH $\geq$ 9, where measurable peaks are recorded. The peak potential is almost independent of pH changing. Taking into consideration that the PLL can present positive charged amino groups ($pK_a = 10.44$) [31], and that Cibacron Blue is a free anion in all the pH range investigated due to the presence of sulfone groups, the strong affinity that PLL coating exhibited for the CB dye seems to be attributed to preponderant electrostatic interaction. Nevertheless, the incorporation of CB on the PLL film even at pH 12 demonstrates that other type of interaction could be occurring, as that predicted via covalent bond, between R–Cl (chlorotriazine groups in the dye) and NH_2–R (poly-L-lysine film).

It is known from the literature [5–7] that triazinyl reactive dyes are usually recommended for fixation to natural fibers via covalent bond using batchwise conditions under alkaline conditions at a temperature of 80 °C. Under these conditions, complete reaction of the electrophilic group present in any remaining reactive dye with a hydroxyl ion would be expected to occur after some time. Nevertheless, competitive hydrolysis reaction takes part too, inactivating the triazinyl reactive group due to the chemical reaction in alkaline solution. So, CB reactive dye was submitted to hydrolysis reaction and compared with the original one.

In order to test the interaction between triazinyl group and amine group from poly-L-lysine, spectrophotometric curves were recorded for CB reactive dye's original and hydrolysed form in the absence and presence of poly-L-lysine. The UV–vis spectra for both experimental conditions are shown in Fig. 8. To obtain solution of fully hydrolysed dye, standard solution of the CB dye in 0.1 M of sodium hydroxide was heated under controlled temperature of 80 °C for 5 h. The solution was allowed to cool to room temperature and the pH was adjusted to pH 7.0 by the addition of 0.1 mol L^{-1} hydrochloric acid. Aliquots of this solution were removed, redone in B–R buffer, pH 2.0, and submitted to UV–vis spectrophotometric analysis in the absence and presence of PLL (Fig. 8).

Fig. 8X presents typical absorption spectra of CB in original form at pH 2. There are three bands at 620, 375 and 294 nm attributed to the anthraquinone groups [7] and other aromatic rings in the dye molecule. In the presence of PLL the peak at $\lambda_{max} = 620$ nm is slightly decreased in height and promotes a shift to longer

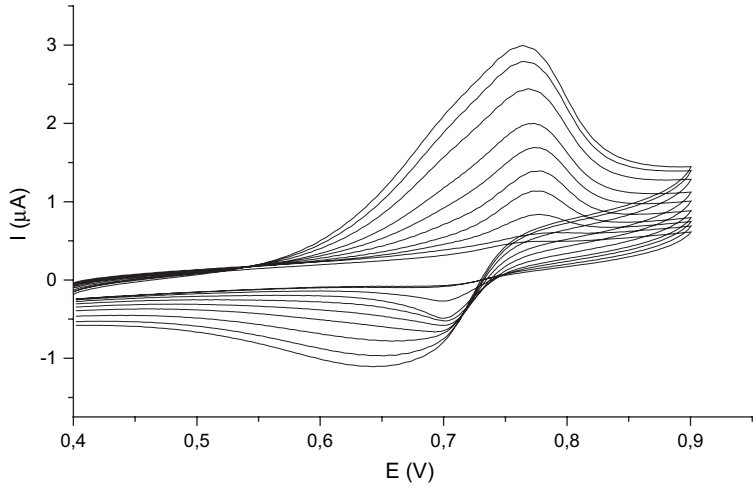

Fig. 6. Influence of accumulation time on pre-concentration of 1.0×10^{-5} mol L^{-1} CB dye on glassy carbon electrode modified by PLL/GA films, pH 2.0 during: (1) 10, (2) 20, (3) 30, (4) 40, (5) 50, (6) 60, (7) 70, (8) 80, (9) 90, (10) 100 min and scan in B–R (pH 2.0). $\nu = 20$ mV s^{-1}.

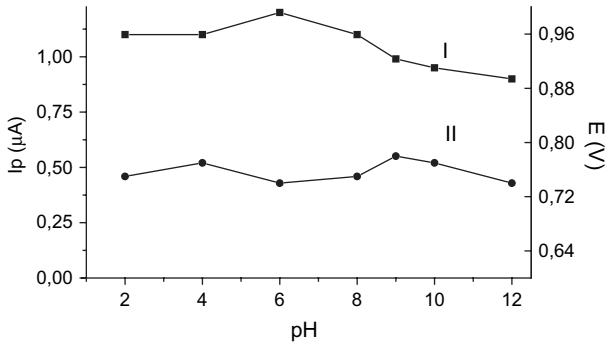

Fig. 7. Graphs of I_p vs pH (I) and E_p vs pH (II) obtained for oxidation of CB dye previously incorporated on films of PLL:GA in B–R buffer, pH 2.0. Accumulation time = 10 min, scan rate 20 mV s^{-1}.

wavelengths. Fig. 8Y do not show any modification in the spectra of the hydrolysed dye in the presence of PLL. This behavior indicates that after nucleophilic substitution of R–Cl by R–OH, the triazine ring loose interaction with amino group of PLL. So, it is possible to conclude that the accumulation of CB dye on the modified electrode surface with PLL via two types of interactions: electrostatic attraction with sulfones group and protonated amino group of the PLL and covalent bond due chlorotriazine group and the aminoacid group also present in the PLL film. After analysis of these parameters, pH 2.0 was chosen as the appropriate pH value for the determination of CB dye on modified electrode with PLL films by voltammetric techniques.

3.2.1. Determination of CB dye at the PLL electrode

The dependence of the PLL/GA coated glassy carbon electrode response on CB dye concentration was investigated, immersing the modified electrode for 10 min directly in a cell containing CB in B–R buffer, pH 2.0. Linear scan voltammograms were recorded and the respective calibration graphs obtained are linear from 1.0×10^{-6} to 1.0×10^{-5} mol L^{-1} following the equation: I_{pa} (μA) = $0.00273 + 9.803 \times 10^{4}$ C (C = mol L^{-1}), $R = 0.994$; ($N = 11$). The detection limit (3σ/slope) was calculated to be 4.5×10^{-8} mol L^{-1}. Thus films of PLL can readily be applied for the determination of CB dye bearing aminoanthraquinone as chromophore and chlorotriazinyl as reactive group at concentrations at least 100 times lesser than using a glassy carbon electrode without modification.

The method described was applied for the determination of CB dye in tap water and raw water collected from the municipal treatment plant. The modified electrode after immersion in 10.00 mL of tap water or raw water, buffered at pH 2.0, spiked to 10×10^{-6} mol L^{-1} of CB dye during 10 min, was washed and transferred to a blank solution of B–R buffer, pH 2.0. The corresponding voltammetric curves obtained have shown the characteristic peaks at +0.76 V, which increased after each standard additions of 20.0 μL of 1.00×10^{-3} mol L^{-1} solutions of the dye following the equations: I_{pa} (μA) = $0.442 + 9.88 \times 10^{4}$ C (C = mmol L^{-1}), $R = 0.998$, $N = 5$ and I_p (μA) = $0.421 + 8.32 \times 10^{4}$ C (C = mol L^{-1}), $R = 0.999$, $N = 5$. A recovery of 89.2 ± 5.4% and 88.0 ± 6.5%, respectively was obtained. The transference of the loaded electrode with the reactive dye to a new blank solution minimizes the matrices interference, indicating that voltammetric method based on modified electrode with PLL:GA could be an alternative method to detect the dye at relatively low concentration in sample of tap water or untreated water.

4. Conclusion

The electrochemical oxidation of Cibacron Blue F3GA dye in aqueous solution on glassy carbon electrode involves the amino group adjacent to the anthraquinone group of the imide derivative after two defined steps. The first oxidation step promotes the generation of a cation radical after one proton and one electron transfer, which is more stable at acidic

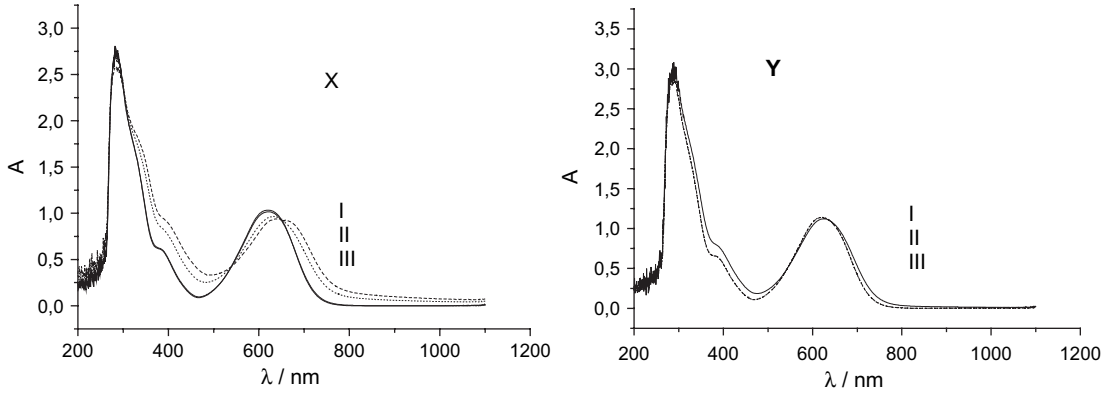

Fig. 8. UV–vis spectra obtained for 7.5×10^{-5} mol L^{-1} CB dye before (X) and after hydrolysis reaction (Y) in B–R buffer, pH 2, without (I) and with the presence of: (II) 10 μL of PLL 1% and (III) 40 μL of PLL 1%.

condition pH < 5. The second oxidation step occurs at more positive potential after one electron transfer and formation of respective imide due to subsequent chemical reaction. Our findings indicate that the first oxidation step can be used for determining dye at any pH range from 2.0 to 10.0 up to a concentration limit of 1×10^{-5} mol L^{-1}. Glassy carbon electrode modified by films of PLL:GA has been shown to be able to determine the reactive dye at very low levels (4.5×10^{-8} mol L^{-1}), well below those achievable spectrophotometrically. This voltammetric study shows that a PLL modified electrode can be used to determine CB dye in raw and tap water, and can also give valuable information with respect to dye poly-aminoacid interactions. The electrode modification improves the sensitivity and selectivity of the dye determination on solid electrodes. The ease and rapidity of electrode preparation constitutes an interesting advantage over more sophisticated techniques used for dye analysis such as chromatography.

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