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Application of voltammetric technique to the analysis of indanthrene dye in alkaline solution

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Abstract

The Indanthrene Olive Green B (C.I. Vat Green 3; C.I. 69500), VG3 dye, a vat dye bearing an anthraquinonoid group and a ketonic group, can be detected by differential pulse voltammetry in alkaline solution using glassy carbon electrode. On the adsorbed form the dyes are reduced into three cathodic steps at −0.54 V, −0.65 V and −0.93 V vs Ag/AgCl. The leuco form generated after previous electrolysis at controlled potential of −1 V can be detected by voltammetry due to its reoxidation peak at −0.08 V. An analytical method is proposed for determining the vat dye using modified glassy carbon electrode by electrochemical activation in alkaline medium. Linear relationship was observed between I_{p_a} vs concentration from 1×10^{-5} mol L^{-1} to 6.0×10^{-4} mol L^{-1}. The detection limit was calculated to be 9.3×10^{-6} mol L^{-1}.

Keywords: Indanthrene dyes; Voltammetric reduction; Dye determination; Vat dyes

1. Introduction

Vat dyes account for about 15% of total consumption of textile dyes. They are firmly established in the market and are mainly used for high fastness requirements, yielding colored fibers with excellent colorfastness, particularly to light, washing and chlorine bleaching [1,2]. Vat dyes are practically insoluble in water, but can be reduced in the presence of an alkali and a reducing agent to form a soluble dye known as the leuco dye. With very few exceptions, vat dyes fall into two clearly defined groups, indigoid and anthraquinonoid. Included in the former are indigo, thioindigo and their derivatives of anthraquinone, as well as heterocyclic quinones. Commonly, in the textile dyeing processes, the reduction of vat dyes is carried out by applying a powerful reducing agent such as sodium dithionite, but other alternatives are reported as sulphite, glucose, α-hydroxyketones, iron (II) triethanolamine complexes and other reducing systems based on sulphur containing substances [2,3]. The reduced dyestuff penetrates into the fiber and it is reoxidized on the fiber back to the insoluble form, which remains fixed in the fabric.

Despite the efficiency of the dyeing process, many attempts are being made to replace the environmentally unfavorable reducing reagents by ecologically more attractive alternative as that offered by electrochemical techniques. Roessler [3] presents an excellent review about all the direct and indirect reductions based on

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electrochemical methods employed to reduce vat dyes, especially indigo. Although interesting results have been obtained, the most limiting factor seems to be the poor contact between the dye particles and the electrode, which decreases the process efficiency [3–6]. Therefore, indirect electrochemical reduction processes have been more successful, where a soluble redox mediator has been tested as electron-carrier [7–16], but the optimization of the processes is still in progress.

In order to obtain reproducibly colored textiles, the concentration of dyestuff in the dye baths has to be well controlled during the time of dyeing. The available analytical techniques are mainly based on photometric methods that are limited due to low selectivity and low solubility or on redox-titration using hexacyanoferrate (III), which is complicated due to excess of reducing agent and other chemicals in the dye bath [17–19]. Although most of the vat dyes display reducible or oxidative groups, few analytical methods have been proposed in the literature [20] and they are focused particularly in the indigo.

Glassy carbon is the electrode material used extensively in electrochemistry for the analysis of electroactive substances and as the basis for surface modified electrodes. The electrochemical properties of this material can be improved by surface treatment [21]. Electrochemical activation of the glassy carbon electrode through oxidation and reduction of the electrode surface is a widely used method to change its characteristics, which can improve the selectivity and sensitivity of the electroanalytical method application [22–25]. For instance, the electrode can present a good performance for catalysis and/or applications as electrochemical detectors for significant types of analyte due to selective chemical or physical interaction between specific functional groups generated on its surface and selective species in solution.

In spite of the high sensitivity and selectivity of electroanalytical methods and the great importance of vat dyes and their reduced forms in the textile industry, few studies have been conducted on the application of this technique for their determination.

So, the aim of the present work is the development of an alternative analytical method for vat dyes with indanthrone as chromophore group by voltammetric techniques. For this work the Indanthrene Olive Green B (C.I. Vat Green 3; C.I. 69500), VG3 dye, was chosen as a model compound, as it is one of the vat dyes largely used in the textile industry. The structure of this dye is shown in Fig. 1. As with other VAT dyes its application onto the fibers also occurs in an alkaline sodium dithionite solution through a reduction reaction. In addition, the possibility of using an electroactivated glassy carbon electrode for its reduction was also studied with the aim to increase the sensitivity or selectivity of the proposed method for this dye.

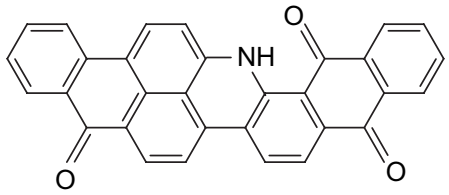

Fig. 1. Chemical structure of the Indanthrene Olive Green B (C.I. Vat Green 3; C.I. 69500).

2. Experimental

2.1. Apparatus and procedures

Cyclic voltammograms were obtained with an Eco Chimie Potentiostat/galvanostat PGSTAT30. A system of three electrodes (EG&G PARC) consisting of an Ag/AgCl (KCl saturated) as reference electrode, a platinum wire auxiliary and a glassy carbon electrode as working electrode were used. The glassy carbon electrode (3 mm diameter) was polished with alumina (0.3 μm, BUEHLER), washed and dried at room temperature before use. 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 VG3 dye (1×10^{-2} mol L^{-1}) were prepared from direct dissolution of the solid samples gently supplied from Dystar (Brazil). The samples were prepared daily and used as soon as possible. The studies were carried out in Britton–Robinson buffer (0.4 mol L^{-1} in each of acetic, phosphoric, and boric acids) adjusted to the required pH, using sodium hydroxide solution 0.2 mol L^{-1}.

Supporting electrolyte (10 mL) was placed in a voltammetric cell and the required volume of stock solution was added by micropipette. The solution was carefully purged with nitrogen for 60 min and the voltammetric curves were recorded under a nitrogen atmosphere on the surface. The general procedure for carrying out the voltammetric measurements was as follows. The dye sample was added and the solution was purged with nitrogen gas for 15 min again. The accumulation potential was then applied, whilst still stirring the solution under controlled time. After a 10 s quiescent period, with the stirring stopped, a potential scan was applied. Unless otherwise stated the following parameters were used: accumulation time 30 s, accumulation potential 0 V; pulse amplitude 50 mV and constant stirrer of speed 3.

2.2. Modified electrode preparation

Electrode modification was based on the following procedure described previously [22–25]. The glassy

carbon electrode surface was polished with 0.05 μm alumina suspension and rinsed with water. The electrode was immersed in 0.1 mol L^{-1} sodium bicarbonate and submitted to continuous potential cycling from −1.3 V to +1.6 V at scan rate of 50 mV s^{-1} for 5 min. Unless otherwise, the activated electrodes were rinsed and placed in a solution containing 1×10^{-3} mol L^{-1} of the VG3 dye in B–R buffer pH 8.0. The deposition was carried out during a controlled time of 5 min, before recording the voltammograms.

3. Results and discussion

3.1. Voltammetric behaviour of the Indanthrene Olive Green B

Linear voltammetric studies showed that solutions of 1×10^{-3} mol L^{-1} VG3 dye in sodium hydroxide 0.1 mol L^{-1} do not show electrochemical activity on glassy carbon or platinum electrode. Nevertheless, the dye can be reduced when accumulated on the glassy carbon electrode surface from stirred solutions. Fig. 2 exhibits the comparison of voltammetric response using differential pulse (Curve B) and linear scan voltammetry (Curve A) obtained for 1×10^{-3} mol L^{-1} VG3 dye in sodium hydroxide 0.1 mol L^{-1} pre-accumulated during 30 s at 0 V. A typical linear scan voltammogram (Fig. 2, Curve A) obtained for VG3 dye presents three reduction cathodic processes at −0.57 V, −0.67 V and −0.99 V, assigned as peaks I, II and III, respectively. All the peak currents increase when the accumulation time was increased from 0 to 30 min, clearly indicating that the dye adsorbs on the electrode surface, but the last one is always bigger and presents higher analytical potentiality. Differential pulse voltammograms (Fig. 2, Curve B) recorded for dye reduction is similar to that one by linear scan mode, with reduction peaks at −0.54 V, −0.65 V and −0.93 V, respectively, but the peak heights were found to be much greater than with linear scan voltammetry and it was chosen in the further measurements.

The effect of pH on the differential pulse voltammograms was investigated using transference of 0.1 mL of aliquots of VG3 dye (1×10^{-2} mol L^{-1}) dissolved in sodium hydroxide 0.1 mol L^{-1}–10 mL of B–R buffer adjusted to pH 2–12. The representative voltammetric curves obtained for pH values of 4, 6, 8, 10 and 12 after 30 s of pre-accumulation at 0 V are shown in Curves a–e, Fig. 3, respectively. As observed for reduction of other anthraquinone group also presented in other dyes [26–29] its reduction occurs at less negative potential in a single step but it is unfolded in two others at higher pH values, culminating in a well defined two peaks at pH ≥ 8. So, at acidic and neutral condition the anthraquinone group is reduced in one step of rapid two electron transfer in agreement with the following scheme [27]: $Q + e^- \rightarrow Q^{-\bullet}$; $Q^{-\bullet} + 2H^+ + e^- \rightarrow QH_2$ leading to formation of hydroquinone as final product. The occurrence of two peaks at alkaline conditions is attributed to the sequinone stabilization before formation of the corresponding hydroquinone, as shown in the following scheme [27]: $Q + e^- \rightarrow Q^{-\bullet}$; $Q^{-\bullet} + 2H^+ \rightarrow QH_2^{+\bullet}$; $QH_2^{+\bullet} + e^- \rightarrow QH_2$. The third peak (III) is presented in all pH values at more negative potential and could be attributed to the reduction of other ketonic group, following the scheme: $>C{=}O + 2e^- + H^+ \rightarrow >C{-}OH$ [26].

Fig. 4 shows the influence of pH on all peak potentials and peak currents obtained from these voltammograms. The graph of E_p vs pH exhibits a linear relationship at $2 \leq pH \leq 12$ for all peaks, but peaks I and III present a break at pH 4 and 6, respectively. The

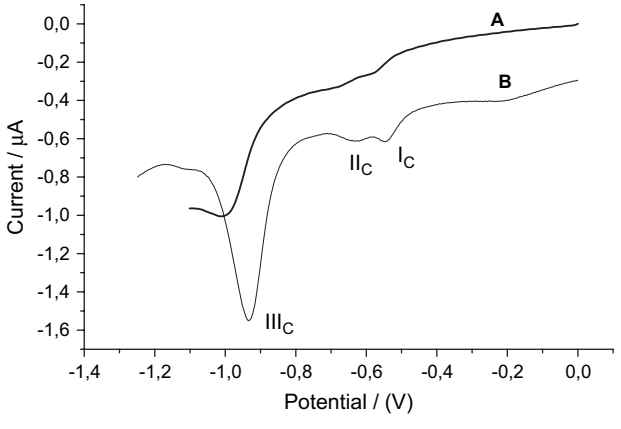

Fig. 2. Linear scan (A, $\nu = 50$ mV s^{-1}) and differential pulse (B, $\nu = 10$ mV s^{-1}) voltammograms of 1×10^{-3} mol L^{-1} VG3 dye in sodium hydroxide 0.1 mol L^{-1} pre-accumulated during 30 s at 0 V on glassy carbon electrode. Pulse amplitude = 50 mV.

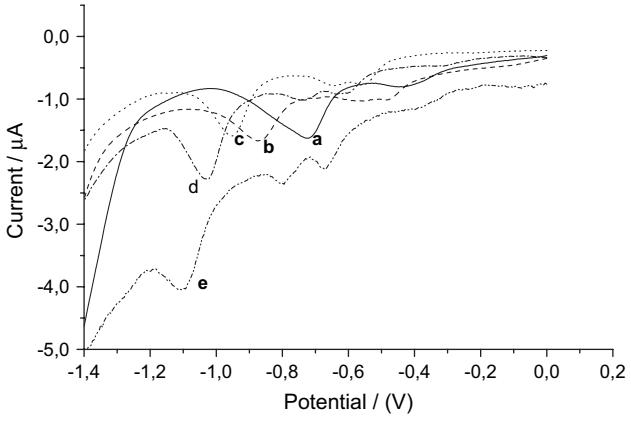

Fig. 3. Influence of pH on differential pulse voltammograms recorded for 1×10^{-3} mol L^{-1} VG3 dye pre-accumulated during 30 s at 0 V on glassy carbon electrode in B–R buffer at: (a) pH 4; (b) pH 6; (c) pH 8; (d) pH 10; and (e) pH 12. Pulse amplitude = 50 mV, scan rate = 10 mV s^{-1}.

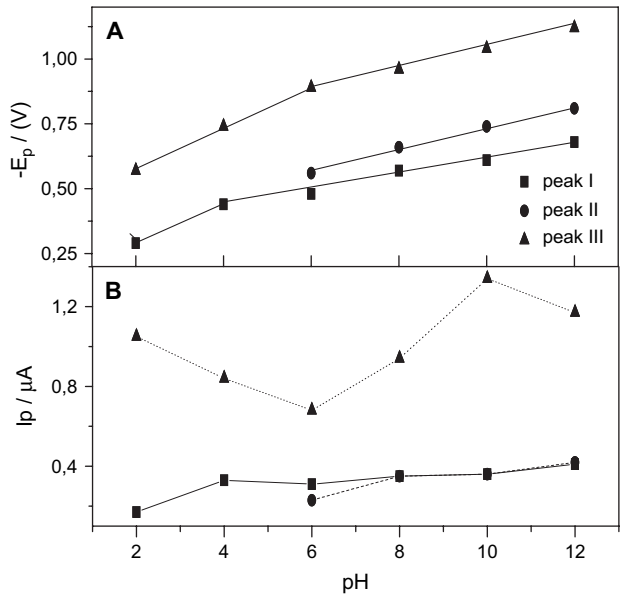

Fig. 4. Influence of pH on the peak potential (A) and peak current (B) obtained from voltammograms of reduction 1×10^{-3} mol L^{-1} VG3 dye on glassy carbon electrode previously accumulated during 30 s at 0 V.

slope of the curves changes from 73 mV to 33 mV for peak I and from 76 mV to 38 mV for peak III, indicating that both reduction processes are influenced by pre-protonation reactions [26]. These results are very similar as expected to a mechanism [26–29] consistent with an electrodic reaction where the anthraquinone group (Fig. 1) is reduced in the protonated form at pH $\leq$ 4. At higher pH values both protonated and unprotonated forms are being reduced and the process displays two reduction processes as verified in the reduction of other anthraquinone dyes [27–29]. A similar behaviour is observed for reduction of another carbonyl group in the dye molecule (Fig. 1) assigned as peak III. This reduction step also shows a linear relationship of E_p vs pH with a break at pH $\leq$ 6.0, indicating that also the reduction of the other reductive site in the VG3 dye is influenced by pre-protonation reactions [26].

The intensities of peaks I and II are always smaller than that verified to peak III in any pH investigated, as shown in Fig. 4. Although maximum currents for all the peaks are observed at acidic conditions pH 2, it was chosen pH 8 to monitor the VG3 dye, since the best discrimination between the three reduction steps is seen.

Taking into consideration the adsorption of VG3 dyes on the electrode surface could be used as an effective pre-concentration step prior to their voltammetric determination in aqueous solution, a systematic study of the various experimental parameters such as accumulation time, accumulation potential and pulse amplitude was investigated. The peak current increased with the pulse amplitude between 20 mV and 60 mV, following the equation: I_p (µA) = −1.284 + 0.0929ΔE(mV), r = 0.9971, n = 5. Above ΔE = 70 mV the peak current is practically constant. So, best potential amplitude was chosen as 50 mV.

The influence of accumulation potential on the peak currents was investigated using 5×10^{-4} mol L^{-1} of VG3 dye in B–R buffer pH 8.0 recording voltamograms from 0 V to −1.4 V after previous accumulation of 30 s at potential from +0.4 V to −1.0 V. As expected all the three peaks increased when accumulated at potential change from +0.4 V to −0.3 V, but the two first peaks are vanished from the voltamograms at more negative potential. Nevertheless, the third reduction peak decreases dramatically in intensity only when accumulated at potential higher than −0.8 V, proving that probably the reduction process of VG3 dye involves different groups in the molecule. So, a potential of 0 V was adopted as the optimum accumulation potential to pre-concentrate the vat dye investigated.

The dependence of peak current on the accumulation time (0–5 min) at 0 V was studied using dye concentration of 5.0×10^{-4} mol L^{-1} of VG3 dye in pH 8 (Fig. 5). The peak current corresponding to the third reduction step increases markedly with increasing accumulation time up to 3 min, when constant values are obtained. Comparatively, an inexpressive increase of the peaks I and II is seen, as shown in Fig. 5. This behaviour indicates that probably the adsorption of the dye occurs in an oriented way, where the accumulation and reduction of carbonyl group are more favoured than anthraquinone group reduction. For this reason, the third reduction peak was chosen as the best analytical potentiality.

The differential pulse voltammograms of anodic scan of the 5×10^{-4} mol L^{-1} of VG3 dye pre-electroreduced at −0.4 V and −1.0 V during 30 s are shown in Fig. 6. Reoxidation of the leuco form of VG3 on the electrode surface seems to occur in two steps. Firstly, if the VG3 dye is reduced at −0.4 V (Curve A, Fig. 6) the product

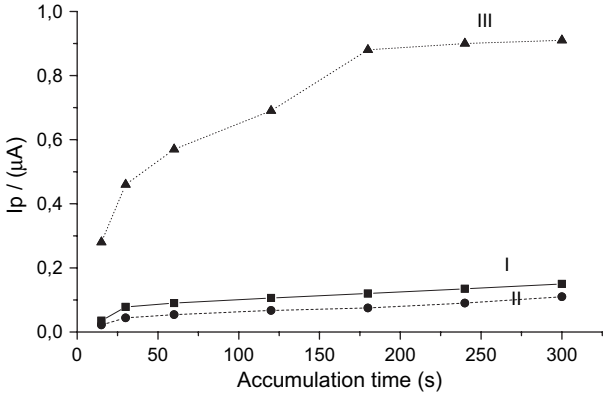

Fig. 5. Effect of accumulation time on the peak current obtained from differential pulse voltammograms of reduction 5.0×10^{-4} mol L^{-1} VG3 dye in B–R buffer pH 8, pre-accumulated at 0 V.

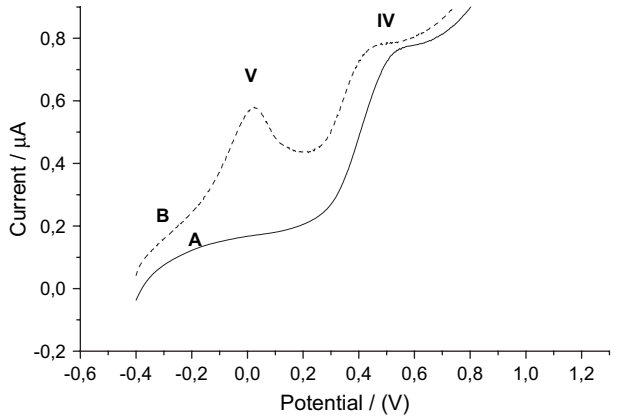

Fig. 6. Differential pulse voltammograms of 5×10^{-4} mol L^{-1} VG3 dye in sodium hydroxide 0.1 mol L^{-1} electroreduced at −0.4 V (A) and −1.0 V (B) during 30 s on glassy carbon electrode. Pulse amplitude = 50 mV.

generated is reoxidized at +0.56 V (peak IV). Nevertheless, when the same solution is reduced during 30 s at −1.0 V (Curve B, Fig. 6), an extra peak is observed in the reverse scan at −0.080 (peak V) clearly indicating that the product formed after the third reduction step is different from that formed after reduction at less negative scan.

Taking into consideration that the peak at −0.08 V (peak V, Fig. 6) could be attributed to the oxidation of the leuco specie generated under previous electrochemical reduction, the effect of reduction potential and time of electrolysis on this peak current was investigated. The peak current related to peak V increases when electrolysis is carried out at controlled potential from −0.6 V to −1.2 V during 30 s and reaches a plateau at higher potential. Using previous electrolysis at −1.0 V during controlled time from 10 s to 300 s, the peak current (peak V) increases linearly indicating that its peak intensity depends on the leuco form of VG3 dye formed by electrochemical reduction previously.

The influence of VG3 dye concentration on the current of the third reduction peak (III) and in its leuco form (peak V) followed by the reoxidation peak (Fig. 2 B) was analyzed with the aim of developing voltammetric methods of determining both redox forms of the VG3 dye. Analysis of the signals obtained for both was carried out in concentrations from 1.0×10^{-5} mol L^{-1} to 1.0×10^{-3} mol L^{-1} of VG3 dye in B−R buffer pH 8.0.

The peak currents corresponding to the peak III recorded from differential pulse voltammograms of VG3 dye pre-accumulated during 30 s at 0 V present a good linear correlation only in the range of 1.0×10^{-4} mol L^{-1}–7×10^{-4} mol L^{-1}. The regression line equations are I (µA) = 0.1597 + 7.481×10^{2} C (mol L^{-1}). A detection limit for VG3 dye using the reduction peak at −1 V is 5×10^{-5} mol L^{-1}. Above this concentration the peak height exhibits a change in slope and reaches a steady height due to strong adsorption of the compound produced after its reduction.

The height of the reoxidation peak (leuco VG3 dye) assigned as peak V (Fig. 6) also increases when the original dye concentration increases. If the dye is pre-reduced during 30 s at −1.0 V, the differential pulse voltammograms recorded from −1 V to 0 V present both reoxidation peaks attributed to the leuco form. Nevertheless, an irreproducible current is observed, probably because during the oxidation of the reduced form of the indanthrene, the reaction product, which is less soluble, most likely adheres to the electrode surface and blocks part of the surface area. So, even using a cleaning step between each measurement of the continuous recording of voltammetric measurement, the results cannot be used for the determination of the leuco form in solution. Further experiments are in progress to solve this problem.

The findings show that differential pulse voltammetry can offer a simple analytical method to determine indanthrene dyes in alkaline medium by monitoring the reduction of quinoid groups at −1.0 V and can be used only to detect its leuco form generated as product electroactive at −0.08 V.

3.2. Reduction of VG3 dye at modified glassy carbon electrode

As described previously [21,23–25], glassy carbon electrode pre-treated by electrochemical activation can have its surface modified by active groups formation, where quinones, imidazolic groups and enzymes could be electrodeposited. Therefore, the analytical potentiality of the activated glassy carbon electrode obtained as described in the experimental section [23–26], was investigated to improve the voltammetric signal due to anthraquinone reduction in the VG3 dye based on its interaction with the modified electrode, since its reduction curve is ill defined on bare glassy carbon electrode.

The glassy carbon electrode was activated by continuous potential cycles from −1.3 V to +1.6 V at a sweep of 50 mV s^{-1} (50 cycles) in sodium bicarbonate (0.1 mol L^{-1}) solution, carefully rinsed with water and immersed in the B−R buffer pH 8.00. The voltammetric curve does not exhibit any electroactive signal in the potential range from −0.8 V to +1.0 V. The activated electrode was then transferred to a cell containing 1×10^{-3} mol L^{-1} of VG3 dye in B−R buffer pH 8.0 solution. The comparison between differential pulse voltammograms obtained in the same solution using glassy carbon electrode before (Curve A) and after activation (Curve B) is shown in Fig. 7. A couple of peaks at −0.58 V and −0.67 V are observed at activated electrode attributed to reduction of anthraquinone

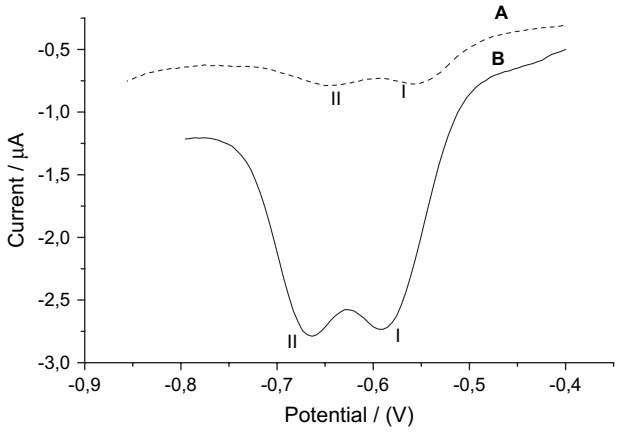

Fig. 7. Differential pulse voltammograms obtained for reduction of 1×10^{-3} mol L^{-1} VG3 dye on glassy carbon modified electrode in B–R buffer pH 8.0. $\nu = 10$ mV s^{-1} without (A) and with (B) previous electrochemical activation.

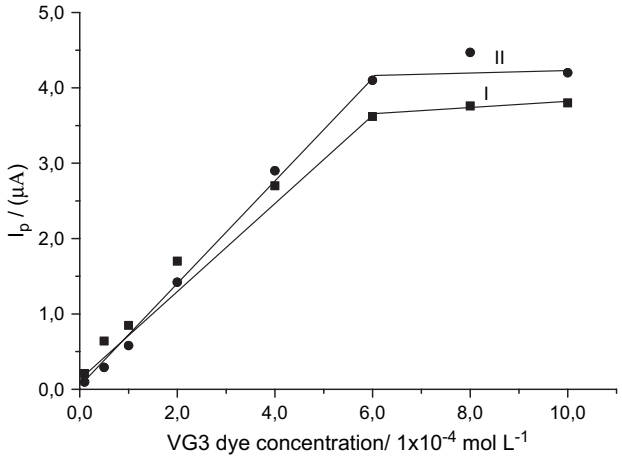

Fig. 8. Calibration curves for VG3 dye in B–R buffer pH 8.0, previously electrodeposited on modified glassy carbon electrode by electrochemical activation $\nu = 10$ mV s^{-1}. $\Delta E = 50$ mV. (I) Reduction peak at −0.58 V; (II) reduction peak at −0.67 V.

group in the VG3, which are slightly shifted to more negative potential in relation to the bare electrode but presents a current intensity at least 5 times higher. This behaviour indicates that probably at the activated electrode, VG3 dye is adsorbed on the electrode by interaction with antraquinone group. The accumulation time and accumulation potential investigated from 0 V to −0.4 V does not affect the peak intensity, suggesting that VG3 dye can be deposited on the activated electrode surface due to rapid interaction with groups generated on glassy carbon electrode previously electrochemically activated.

In order to assess the reproducibility of the electrode response, a series of 10 repetitive measurements were carried out using differential pulse voltammograms (at 10 mV s^{-1}) recorded for the activated electrode immersed in 1×10^{-3} mol L^{-1} VG3 dye solution in B–R buffer pH 8. The electrode response indicated mean current peak (peak I) of 4.24 ± 0.12 μA, where the coefficient variation calculated was 4.3%.

Under these experimental conditions, the calibration plots were tested immerging the coated electrode in VGA dye solution containing 1×10^{-5} mol L^{-1}–1×10^{-3} mol L^{-1}. The respective curves obtained for I_p vs dye concentration for both peaks I and II are shown in Fig. 8. Linear relationship was observed from 1×10^{-5} mol L^{-1} to 6.0×10^{-4} mol L^{-1}. Constant values of peak current were always obtained above concentration of 7×10^{-4} mol L^{-1}, as shown in Fig. 8, suggesting saturation of the electrode surface. The detection limit was calculated to be 9.3×10^{-6} mol L^{-1}.

4. Conclusion

Although the most of the studies involving vat dyes have demonstrated that they are present in an aqueous suspension and cannot be reduced electrochemically without redox mediator. These preliminary findings indicate that voltammetry can be an excellent alternative to follow its reduction when carbonyl groups in the indanthrene are present as chromophore in the vat dyes. These groups, which can be reduced when they are spontaneously adsorbed on the glassy carbon electrode or pre-concentrated on activated glassy carbon electrode.

This voltammetric study shows that using a pre-concentration step at controlled potential and controlled time it is possible to reduce vat green B dye adsorbed on the glassy carbon electrode. As other compounds containing anthraquinone dyes, they are reduced in two consecutive one electron transfer reaction leading anthraquinone to generate the corresponding hydroquinone from Refs. [27,29] in the potential range of −0.5 V to −0.7 V. The reduction system is followed by new step around −1.0 V, where the quinoid group (−C=O) is also reduced to the −C−OH (peak III). This last peak is higher and presents better analytical potentiality to monitor dye concentration, even in suspension. Nevertheless, better response is obtained for reduction of anthraquinone group at less negative potential (peaks I and II) when the vat green B dye is accumulated on the electrode surface modified by previous electrochemical activation. The modified electrode could be interfering in the orientation of the dye molecule on the electrode surface, which improves the sensitivity and selectivity for the vat green B determination on solid electrodes. Therefore, the proposed method needs to be optimized in the presence of other chemicals used in the dye bath and must be carried out by adapting the system to the given dyestuff. The ease and rapidity of the modified electrode preparation constitutes an interesting advantage over more sophisticated techniques used for this analysis. Work is continuing to produce more satisfactory

procedures as the use of the modified electrode in a flow system and/or screen printed electrode that could streamline the method with automatic solution transfer.

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