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Use of a composite electrode modified with magnetic particles for electroanalysis of azo dye removed from dyed hair strands

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ABSTRACT

The analysis of dyes in hair samples can provide useful information for forensic purposes. The present work describes a novel method for the extraction of dye from a hair sample and its determination using a composite electrode to pre-concentrate carboxyl-functionalyzed magnetic nanoparticles (CFMP) employed to collect the dye in solution, hence increasing the sensitivity of the analysis. The Basic Brown 16 dye, which is widely used in temporary hair dying, was chosen as a model compound. After 15 s of reaction between 1.5×10^{-5} mol L^{-1} of dye and 0.1 mg mL^{-1} of carboxyl-functionalyzed magnetic nanoparticles in phosphate buffer electrolyte at pH 7.0, the derivative dye was collected during 40 s at the graphite-epoxy composite electrode and then transferred to a new solution of phosphate buffer at pH 7.0. The dye presented a peak current at a potential of 0.42 V that was almost 400 times higher than without the preconcentration step, suggesting that the dye was pre-accumulated due to strong magnetic interaction with the composite electrode. Under optimized conditions, the analytical curve constructed using square wave voltammetry was linear for BB16 dye concentrations between 1.00×10^{-7} and 1.00×10^{-6} mol L^{-1}. The limits of detection and quantification were 1.01×10^{-8} and 2.37×10^{-8} mol L^{-1}, respectively. The proposed method was successfully applied in the determination of BB16 dye extracted from a dyed hair strand sample by alkaline digestion.

1. Introduction

The use of hair analysis is widely accepted in forensic toxicology [1–5]. Its application for detection of drugs of abuse is well documented, and several analytical methods can be employed to identify drug abusers [6–13]. Hair analysis can also provide important information about a person by determining the chemical makeup of the hair or by extracting DNA from the hair follicle [14–15], enabling determination of hair color, ethnic origin, presence of dye, and hairstyle, hence helping investigators to understand the basic features of a suspect. This kind of examination is typically conducted by comparing the sample with known hairs.

The literature reports several analytical methods for the determination of hair dyes in commercial formulations or in wastewater, using chromatographic [16–30] or electroanalytical methods [31–33]. However, although determination of synthetic colorants extracted from hair can be useful in many ways, the analyses require low detection limits and the literature is lacking in suitable techniques for this purpose.

The use of magnetic nanoparticles (MNPs) as modifiers in the construction of electrochemical sensors has been demonstrated to provide low levels of detection for different analytes [34–38]. Magnetic nanoparticles such as iron oxides have the special ability to move under the influence of an external magnetic field. Typically, these non-porous and highly stable superparamagnetic nanoparticles (such as magnetite) are composed of a set of superparamagnetic grains that can be magnetized in the presence of a magnetic field, with alignment of the poles in the direction of the external field. This mechanism can be used to preconcentrate analytes of interest that are incorporated in these nanoparticles. Preconcentration using magnetic nanoparticles has been shown to provide high sensitivity, compared to traditional methods [39], with increased signal/noise ratio, reduced response time, and increased stability.

The present work describes the use of magnetic nanoparticles coated with carboxyl groups as a tool for dye preconcentration. Prior to the detection step, the use of modified nanoparticles enables extraction and preconcentration of the analyte of interest present in a complex sample, hence increasing the sensitivity of the analytical method. The aim was to combine the high efficiency of preconcentration using magnetic nanoparticles and the selectivity of electrochemical sensors, in order to obtain a sensitive and selective analytical method for the determination of dye extracted from hair. The widely used Basic Brown 16 temporary

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hair dye [40] (chemical structure shown in the insert of Fig. 1) was used as a dye model.

2. Experimental

2.1. Reagents and equipment

All chemicals were analytical grade and were purchased from Merck. The Basic Brown 16 (BB16) hair dye (Arianor) was provided by LCW Dyes (São Paulo, Brazil). The magnetic nanoparticles modified with carboxylic groups (MyOne carboxylic acid) were obtained from Dynal Biotech ASA (Oslo, Norway).

All the electrochemical measurements were performed using an EcoChemie μAutolab-2 potentiostat coupled to a computer via a GPES interface. The system employed three electrodes: an Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode, a platinum wire auxiliary electrode, and a magnetic composite working electrode with an area of 0.04 cm^2. The working electrode was constructed using graphite powder and epoxy resin containing a magnet bar, as described previously [41].

Spectrophotometric measurements were carried out in the spectral range from 200 to 800 nm, using a Hewlett Packard Model 8453 spectrophotometer equipped with a 1.0 cm optical path length quartz cuvette (Hellma Analytics).

Analysis of Basic Brown 16 dye and products after extraction was performed by high performance liquid chromatography/mass spectrometry (LC-ESI-MS/MS), using an Agilent Technologies Model 1200 HPLC coupled to a Model 3200 QTRAP linear ion trap quadrupole mass spectrometer. Separation was achieved using either a Phenomenex Kinetex PFP column (150 × 4.6 mm; 5 μm) or an Agilent XDB C18 column (150 × 4.6 mm; 5 μm). Elution of the sample was performed in isocratic mode, using a mixed mobile phase of 0.1% formic acid in water (A) and acetonitrile (B), at a flow rate of 1 mL min^{-1}. The injection volume was 20 μL and the column temperature was 40 °C. The ion source was operated at 600 °C, with the following ionization conditions: IS = 5000 V; CUR = 20 psi; Gas_1 = 50 psi; Gas_2 = 50 psi.

2.2. Procedures

2.2.1. Electroanalytical behavior

The dye was captured by the magnetic carboxylate nanoparticles by mixing 1.5×10^{-5} mol L^{-1} dye solution with 0.1 mg mL^{-1} of the nanoparticles in phosphate electrolyte (pH 7) during 40 s. The pre-cleaned magnetic composite electrode was then immersed in this solution and the nanoparticles were pre-concentrated on the surface of the electrode during a specified time. After the pre-concentration, the electrode was transferred to the electrochemical cell containing B-R buffer (pH 7), and electrochemical measurements were performed with recording of both cyclic and square wave voltammograms.

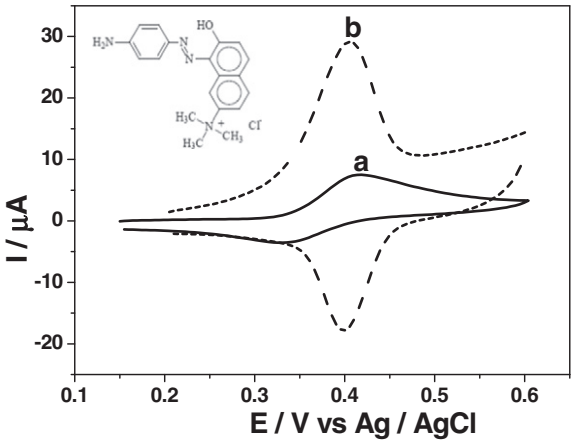

Fig. 1. Cyclic voltammograms obtained for oxidation of 3.0×10^{-5} mol L^{-1} BB16 dye at the magnetic graphite composite electrode, before (a) and after (b) 40 s of preconcentration in pH 7 phosphate buffer containing 0.1 mg mL^{-1} of carboxyl-functionalyzed magnetic nanoparticles (CFMP). $\nu = 100$ mV s^{-1}. Insert: Chemical structure of Basic Brown 16 dye.

2.2.2. Dye extraction from dyed hair samples

Human hair was dyed with BB16 as recommended in the commercial formulation instructions (LCW Dyes). The hair dyeing process was divided into 4 stages: (a) preparation of the dye; (b) application of the product to the hair and leaving to act for 40 min; (c) rinsing the hair with water until complete removal of the unfixed dye; (d) rinsing, shampooing, and conditioning of the dyed hair. The wash water was collected in 2 L glass bottles, and after a further four stages of rinsing, samples were stored in vials in a freezer at −5 °C. The final stage was performed five times, with washing of the hair at predetermined times on different days. In each case, the untreated water was collected for chromatographic analysis, as described by APHA [42], using suitably washed glass flasks [43]. The samples were protected from light during transportation and were stored under refrigeration.

Afterwards, 1 g of previously dried hair was weighed out and incubated [44] in 2 mol L^{-1} NaOH solution for 24 h at 37 °C. Following completion of the alkaline digestion of the dyed hair, the sample was neutralized with sulfuric acid. Aliquots of this solution were diluted in phosphate buffer (pH 7) and submitted to electroanalysis using the proposed method (Section 2.2.1), without any further treatment. The same solution was also analyzed by mass spectrometry.

3. Results and discussion

3.1. Voltammetric behavior of the dye Basic Brown 16 dye

Fig. 1 compares the cyclic voltammograms obtained for oxidation of 3.0×10^{-5} mol L^{-1} BB16 at the composite electrode before (curve a) and after (curve b) 40 s of preconcentration in phosphate buffer (pH 7.0) containing 0.1 mg mL^{-1} of carboxyl-functionalyzed magnetic nanoparticles (CFMP). The current was four times higher in the presence of CFMP, indicating the accumulation of CFMP with dye on the electrode surface. Values of $I_{PC}/I_{PA} = 0.91$ and E_{PA}-$E_{PC} = 8$ mV were obtained for the modified electrode at 100 mV s^{-1}, while the direct oxidation of BB16 dye showed values of $I_{PC}/I_{PA} = 0.51$ and E_{PA}-$E_{PC} = 61$ mV. This behavior indicated that the BB16 dye was oxidized at the composite electrode, involving the transfer of approximately one electron (0.97) [45]. After preconcentration on the electrode, the oxidation of adsorbed BB16 associated with CFMP was confirmed by E_{PA}-E_{PC} close to zero. In addition, the oxidation process involving BB16 dye in its derivatized form was more reversible than without modification, with the original dye remaining on the electrode surface. The signal was recovered when the electrode was washed successively with acetone and water.

In order to confirm the reaction between BB16 and the CFMP nanoparticles, UV–Vis spectra were recorded after 40 s of reaction using 3.0×10^{-5} mol L^{-1} BB16 and 0.1 mg mL^{-1} carboxyl-functionalyzed magnetic nanoparticles, in pH 7 phosphate buffer (Fig. 2x). In order to confirm the presence of magnetic nanoparticles, comparison was made with nanoparticles modified with tosyl groups. Although the spectrum for BB16 dye was similar to that obtained using the tosyl-modified nanoparticles (Fig. 2x), there was a 60% decrease in absorbance after reaction with the carboxylic group, indicating that the dye interacted with CFMP. This phenomenon can be explained by the electrostatic interaction from carboxylate on the nanoparticles (pka = 4.74) and the secondary amine group in the Basic Brown 16 dye that is positively charged (chemical structure in Fig. 1). Fig. 2y compares the infrared spectra recorded from 4000 to 400 cm^{-1} for the magnetic nanoparticle modified by carboxylate group before (curve a) and after reaction with the Basic Brown 16 dye (b) and for the pure Basic Brown 16 dye (c). It is possible to notice that the two sharp absorption bands at 3318 and 3190 cm^{-1} attributed to the stretch N—H present as

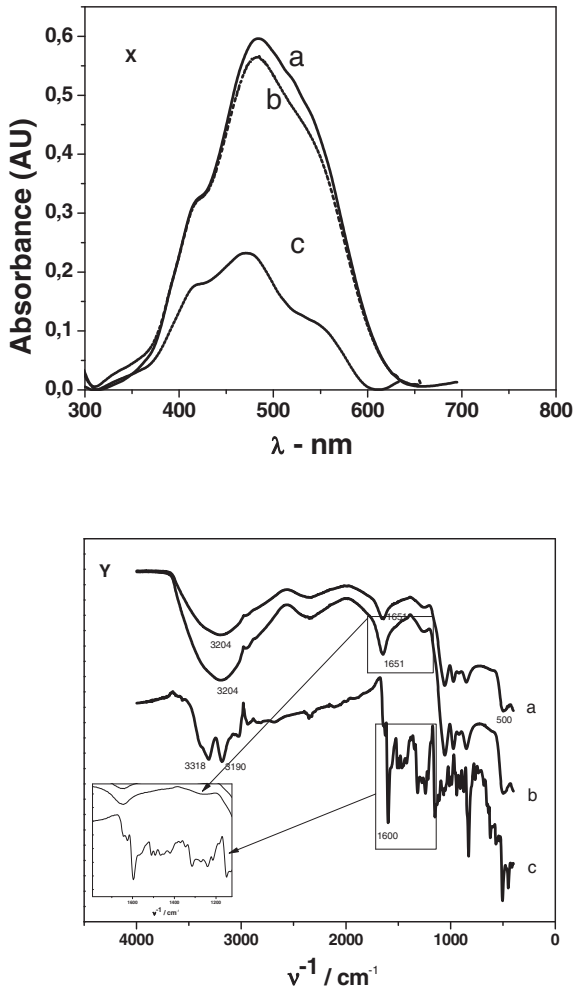

Fig. 2. Comparison of (X) UV–Vis spectra obtained for 1.5×10^{-5} mol L^{-1} BB16 dye in pH 7 phosphate buffer, before (a) and after 40 s reaction with 0.1 mg mL^{-1} carboxyl-functionalyzed magnetic nanoparticles (c) and tosyl-modified magnetic nanoparticles (b). (Y) Infrared spectra in the range 4000–400 cm^{-1}, corresponding to the magnetic nanoparticle with the Basic Brown 16 dye (a), magnetic nanoparticle (b) and Basic Brown 16 dye (c).

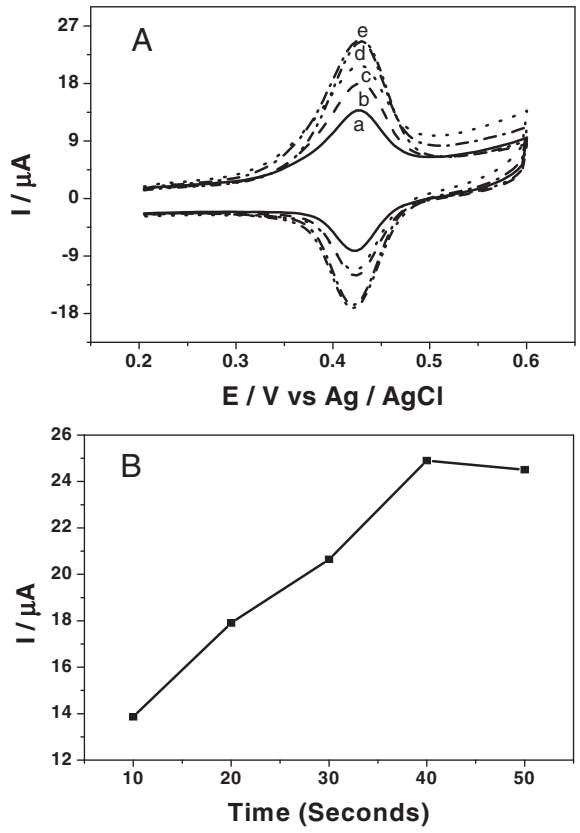

Fig. 3. Cyclic voltammograms (**A**) recorded for oxidation of 5×10^{-5} mol L^{-1} dye $+0.10$ mg mL^{-1} CFMP in pH 7 phosphate buffer, using preaccumulation for (a) 10 s, (b) 20 s, (c) 30 s, (d) 40 s, and (e) 50 s, followed by transfer of the electrode to a new solution containing pH 7 phosphate buffer alone. (B) Effect of accumulation time of BB16 + CFMP at the magnetic graphite composite electrode in pH 7 phosphate buffer. $\nu = 0.05$ V s^{-1}.

secondary amine in the Basic Brown 16 are substituted for a broad and intense band at 3204 cm^{-1} attributed to the absorption of axial deformation OH in the carboxylic acids. In addition, the intense absorption band at 1600 cm^{-1} corresponding to the symmetrical angular deformation in the N—H plane of the dye is substituted for defined band at 1651 cm^{-1}, which comes from the asymmetric axial deformation of carboxylate ion in the magnetic nanoparticles, confirming that the interaction between dye and modified nanoparticles occurs due strong interaction between carboxylate ion at CFMP and the amine group in the BB16 dye.

The influence of nanoparticle concentration on the collection of BB16 dye was investigated by measuring the anodic peak current obtained for 5×10^{-5} mol L^{-1} of dye in pH 7 phosphate buffer containing 0.05–0.20 mg mL^{-1} of CFMP. The peak current increased for CFMP concentrations from 0 to 0.08 mg mL^{-1}, with maximum preconcentration obtained from 0.10 to 0.20 mg mL^{-1}. Further studies were carried out using 0.10 mg mL^{-1} CFMP.

Fig. 3 illustrates the influence of reaction time (0–50 s) on the preconcentration of BB16 dye. The experiments were carried out recording cyclic voltammograms for electrodes immersed in a solution containing 5×10^{-5} mol L^{-1} of dye in pH 7 phosphate buffer with 0.10 mg mL^{-1} of CFMP. After preaccumulation for a specified time, the electrode was transferred to a new solution consisting only of pH 7 phosphate buffer. The pair of peaks corresponding to BB16 oxidation/reduction increased for times from 10 to 40 s (Fig. 3B), indicating that the dye + CFMP was accumulated on the electrode surface. Maximum peak intensity was observed after 40 s, suggesting saturation of dye + CFMP deposited on the magnetic composite electrode. Further studies were carried out using 40 s exposures to the solution containing dye + CFMP, followed by transfer to a fresh electrolyte solution.

Cyclic voltammograms recorded from 10 to 100 mV s^{-1} for 1.5×10^{-5} mol L^{-1} BB16 in pH 7 phosphate buffer, after pre-concentration for 40 s, showed progressively larger anodic and cathodic peaks (not shown). A linear relationship was obtained between the anodic peak current and the scan rate, described by the equation: I (μA) = $5.5 + 0.36$ mV s^{-1} ($r = 0.9987$, $n = 7$). This behavior indicated that oxidation of the dye at the magnetic electrode was controlled by adsorption [46]. It was also noted that for scan rates of between 10 and 50 mV s^{-1}, the values obtained were $I_{PA}/I_{PC} = 1$ and E_{PA}-$E_{PC} = 0$ mV. This behavior is typical of a reversible process involving the adsorption of oxidized and reduced forms on an electrode surface [46].

The effect of pH on the anodic peak current and peak potential obtained from the cyclic voltammograms acquired at 50 mV s^{-1} was investigated for 4×10^{-5} mol L^{-1} BB16 in phosphate buffer (pH 3–9), in the absence and presence of magnetic nanoparticles. The peak potential shifted to less positive potentials with increasing pH, following a linear relationship: Ep (V) = 0.70–0.050 pH (Fig. 4, curve A). In addition, there was a gradual increase in current from pH >3.0 up to pH 7.0 (Fig. 4, curve B), with the values remaining constant at higher pH. This behavior confirmed that the dye + CFMP was preconcentrated at the composite electrode due to magnetic interaction, reaching a maximum at pH 7. The slope of −50 mV pH^{-1} obtained from ΔE/ΔpH suggested

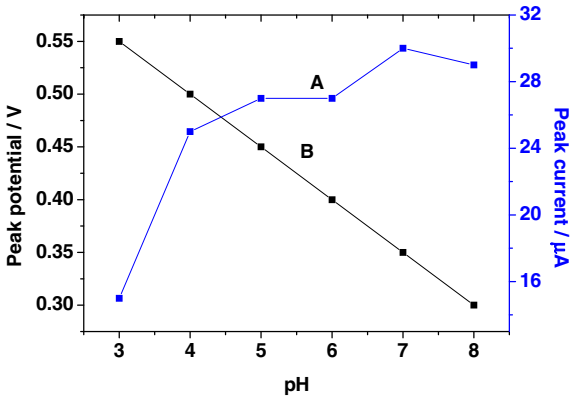

Fig. 4. Influence of pH on anodic peak current (A) and anodic peak potential (B), obtained from cyclic voltammograms recorded for oxidation of 4×10^{-5} mol L^{-1} BB16 + CFMP in phosphate buffer.

that a one electron/one proton transfer mechanism occurred in this pH range. Considering that the process involved the transfer of one electron, according to the equation $\Delta E/\Delta pH = (59.1\ mV/n)^{*}mH^{+}$ ($n = 1$), and using the slope obtained, it appeared that the number of protons (mH^{+}) transferred was one [47–48]. These results indicated that the hydroxyl group close to the azo group in the BB16 dye (see Fig. 1 insert) was oxidized to the quinone radical at around +0.40 V, after previous interaction with the CFMP on the magnetic electrode [47]. Therefore, pH 7 was selected in the subsequent analyses.

In order to achieve detection of BB16 dye at low levels, the use of square wave voltammetry (SWV) was evaluated, with monitoring of the oxidation of 4.0×10^{-5} mol L^{-1} of BB16 dye in phosphate buffer solution (pH 7.0) after accumulation for 40 s (Fig. 5). A peak increase of approximately 400% was obtained, relative to linear scanning voltammetry, so these conditions were used for quantification of the dye. The peak current obtained was dependent on various instrumental parameters of the SWV technique, such as square wave amplitude, square wave frequency, and step height. The experimental parameters evaluated were frequency, f (from 10 to 300 Hz), scan increment, ΔEs (from 1 to 15 mV), and pulse amplitude, Esw (from 10 to 150 mV). The optimum voltammetric signal was obtained for a frequency of 30 Hz, pulse amplitude of 50 mV, and ΔEs of 2 mV, which provided better voltammogram definition as well as higher peak currents.

Fig. 6 illustrates square wave voltammograms recorded for between 1.0×10^{-7} and 9.0×10^{-7} mol L^{-1} BB16 dye derivatized with

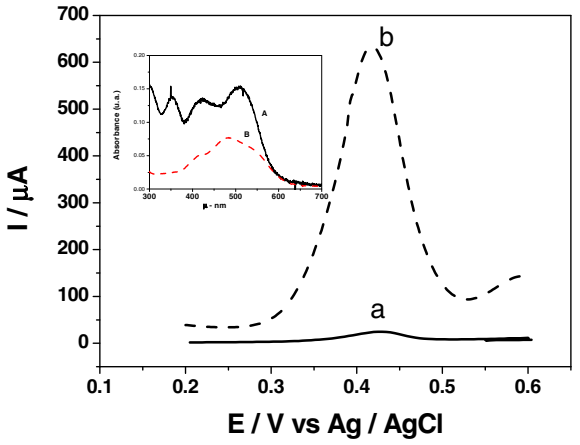

Fig. 5. Linear scanning voltammograms (a) and square wave voltammograms (b) obtained for 4.0×10^{-5} mol L^{-1} BB16 in pH 7 phosphate buffer after accumulation for 15 s at the magnetic graphite composite electrode. Insert: UV–Vis spectra for 5×10^{-5} mol L^{-1} BB16 in 2 mol L^{-1} NaOH (30 min) (curve A), and after neutralizing and adjusting to pH 7 (curve B).

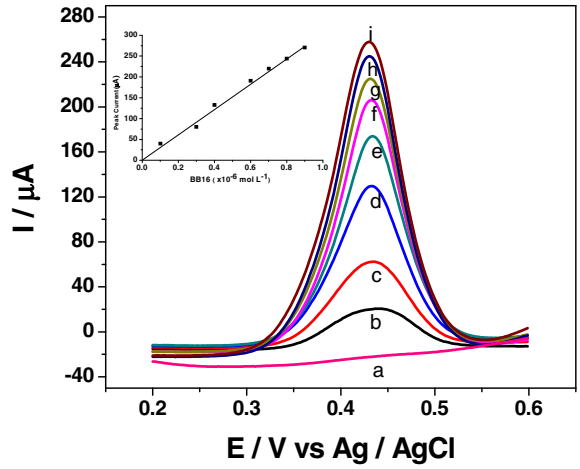

Fig. 6. Square wave voltammograms recorded for 1.0×10^{-7} (b), 2×10^{-7} (c), 4×10^{-7} (d), 5×10^{-7} (e), 6×10^{-7} (f), 7×10^{-7} (g), 8×10^{-7} (h), and 9×10^{-7} mol L^{-1} (i) of BB16 dye derivatized with 0.1 mg mL^{-1} CFMP in pH 7 phosphate buffer, using preconcentration for 40 s at the composite electrode. (a) Voltammogram for pH 7 phosphate buffer; f = 30 s^{-1}; a = 50 mV; ΔEs = 2 mV. Insert: analytical curve.

0.1 mg mL^{-1} CFMP, using 40 s preconcentration at the composite electrode. The linear range was described by the equation: $-Ipc\ (\mu A) = -1.230 + 183.6^{*}C_{BB16}\ (\mu mol\ L^{-1})$ ($r = 0.996$, $n = 7$). The limits of detection and determination were 1.01×10^{-8} and 2.37×10^{-8} mol L^{-1}, respectively. The repeatability of the proposed sensor, evaluated in terms of the relative standard deviation, was 3.79% for ten SWV experiments, indicating that the technique provided satisfactory reproducibility.

The proposed method based on BB16 + CFMP was applied using tap water samples spiked with 7.5×10^{-7} mol L^{-1} BB16 and 0.10 mg mL^{-1} CFMP. Recoveries were performed in triplicate using the standard additions method, with 40 s of pre-reaction and transfer of the electrode to a solution containing 10 mL of pH 7 phosphate buffer. For all the samples, the recovery values were in the range 99.1–102.4%.

In order to verify the selectivity of the proposed method the interference of Basic Red 51 dye (BR51), a common temporary hair dye usually commercialized in a formulation containing BB16 dye. In a solution containing 5.0×10^{-7} mol L^{-1} BB51 dye was added BB16 dye in the

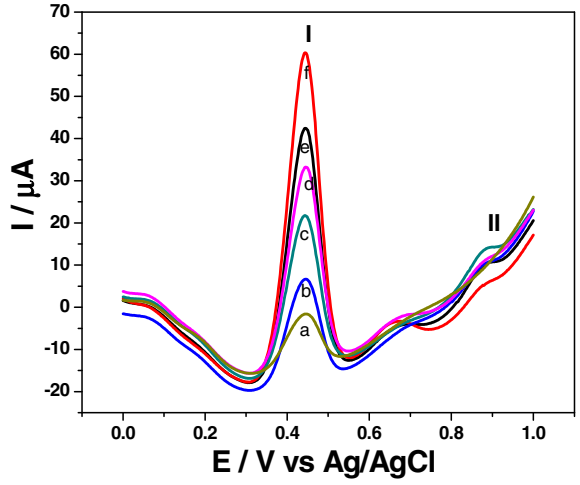

Fig. 7. Square wave voltammograms obtained for oxidation of 5.0×10^{-7} Basic Red 51 in the presence of Basic Brown 16 dye (Peak I) at concentrations of (a) 5.0×10^{-7}, (b) 7.5×10^{-7}, (c) 1.0×10^{-6}, (d) 1.25×10^{-6}, (e) 1.5×10^{-6} and (f) 1.75×10^{-6} mol L^{-1} at composite electrode in phosphate buffer solution (pH 7) using metal nanoparticles CFMP.

concentration range from 5.0×10^{-7} to 2.0×10^{-6} mol L^{-1}. Fig. 7 shows the square wave voltammograms recorded after preconcentration of 15 s. Although BR51 presented a small peak at −0.87 V, there is no effect on the peak current of BB16 dye at 0.45 V, which increases successively with the addition of BB16 dye while the current peak attributed to dye BR51 remains constant. A linear relationship was obtained following the equation: $I\ /\ (\mu A) = -2.33 \times 10^{-6} + 49.68 \times 10^{-6}$ [BB16]/mol L^{-1}; $r = 0.9882$ and $n = 5$. The results indicated that the voltammetric sensor can be used to analyze the BB16 dye even in the presence of BR51 dye, bearing azo groups in the molecule.

3.2. Analytical application of the proposed method

3.2.1. Analysis of wastewater from dyed hair

The applicability of the proposed method was tested using water from the washing of hair previously dyed with BB16. Portions (1 g) of hair dyed with BB16 according to the instructions of the commercial formulation were washed with water that was collected and analyzed to determine the stability of the dye (not shown). Aliquots (1 mL) of the washing water were analyzed using the proposed method. The use of square wave voltammetry resulted in well-defined peaks and an excellent linear relationship after standard additions of BB16 in the concentration range from 1.08×10^{-7} to 1.34×10^{-6} mol L^{-1}. The results showed that 0.045 mg of the dye was leached from 1 g of dyed hair during the first washing, corresponding to a loss of 1.26% of the dye used to color the hair.

3.2.2. Analysis of the dye extracted from hair

Finally, the proposed method was tested in the analysis of dye extracted from dyed hair strands, following the methodology described in the Experimental section. Portions (1 g) of dyed hair were washed, dried, and subjected to alkaline digestion, as described previously. Different methodologies were tested for the removal of the dye from the hair strands, and the best performance was achieved using alkaline digestion [44]. The techniques were evaluated by recording UV–Vis spectra and mass spectra for the dye, before and after treatment with 2 mol L^{-1} NaOH.

The insert of Fig. 5 shows a comparison of the UV–Vis spectra for 5×10^{-5} mol L^{-1} BB16 in 2 mol L^{-1} NaOH (30 min) (curve A), and after neutralizing and adjusting to pH 7 (curve B). A typical UV–Vis spectrum was obtained for BB16 dye at pH 7.0, showing main bands with maximum absorption wavelengths at 495 and 425 nm, attributed to the azo group of BB16[45]. For the dye in alkaline medium, the UV–Vis spectrum showed four bands, at 509, 416, 353, and 249 nm, due to temporary hydrolysis (curve B, insert of Fig. 5). However, the UV–Vis spectra were recovered when the alkaline solution was once again neutralized to pH 7, and were very similar to the spectrum obtained previously (Fig. 2, curve A). These results showed that in alkaline solution, the dye did not undergo any irreversible changes in its chemical structure, and that the process could be used during the extraction phase in an alkaline medium.

Further LC-ESI-MS/MS measurements of BB16 were carried out before and after treatment with alkaline solution. Fig. 8 presents the chromatograms obtained for the dye in water containing 0.1% of formic acid and acetonitrile, using the selected reaction monitoring (SRM) transitions and the optimized MS parameters. The original dye (curve 2, Fig. 8) showed a well-defined peak at a retention time of 5.80 min, attributed to the $[M + H]^+$ ion with $m/z = 321$. The fragmentation of this ion produced the expected product ions with higher abundance. Curve 1 (Fig. 7) shows the LC-MS-MS chromatogram for BB16 submitted to treatment with NaOH for 120 min. A peak ($m/z = 321$) was observed at a retention time of 5.80 min, indicating that treatment of the dye with sodium hydroxide did not cause any modification of its chemical structure. Hence, the developed procedure was adopted for extraction of the dye from hair followed by analysis using the electroanalytical method.

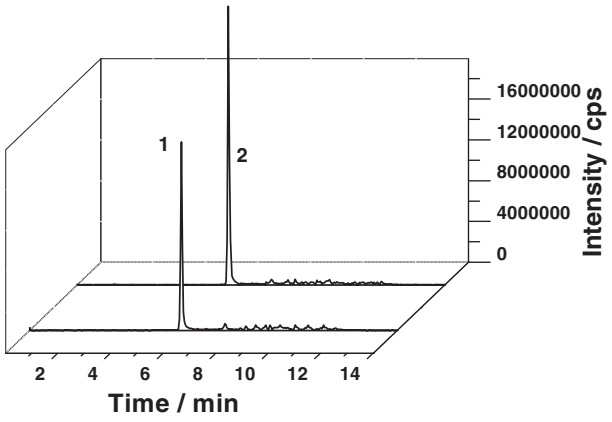

Fig. 8. LC-MS-MS chromatograms obtained for BB16, before (2) and after (1) 120 min in sodium hydroxide followed by neutralization to pH 7.0.

Square wave voltammograms were obtained for 50 μL aliquots of extract (described in the experimental section) transferred directly to 1 mL of pH 7 phosphate buffer containing 0.1 mg mL^{-1} of magnetic nanoparticles. After pre-accumulation for 40 s, the composite electrode was transferred to 10.0 mL of pH 7 phosphate buffer containing 0.1 mg mL^{-1} of magnetic nanoparticles. Square wave voltammograms were then obtained using standard additions of BB16 at concentrations from 7.5×10^{-7} to 1.5×10^{-6} mol L^{-1}, without any pretreatment. An excellent linear relationship was obtained, and the results indicated that 0.017 mg of the dye was present, corresponding to 3.51 mg of dye per 1 g of hair.

4. Conclusions

A simple and reliable electroanalytical method is proposed based on the interaction of carboxyl-functionalyzed magnetic nanoparticles (CFMP) with Basic Brown 16 dye, followed by preaccumulation on a graphite-epoxy composite electrode. The derivatized dye presented a well-defined peak attributed to hydroxyl oxidation. Square wave voltammetry was used to construct an analytical curve for BB16 concentrations from 1.0×10^{-7} to 1.0×10^{-6} mol L^{-1} after reaction in the presence of 0.1 mg mL^{-1} of CFMP and further preconcentration for 40 s at the composite electrode. The azo dye was extracted from dyed hair strands using 2 mol L^{-1} sodium hydroxide, without any irreversible changes in its chemical structure, as shown by UV–Vis spectra and LC-MS/MS measurements. The proposed method is inexpensive and environmentally friendly, and enables the detection of BB16 dye at low levels in dyed hair extracts.

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