Preparation of activated carbon from date stones as a catalyst to the reactivity of hydroquinone: Application in skin whitening cosmetics samples

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In this study, the authors report the use of the date stones as a raw material for the production of activated carbon (AC) using the physical activation. The as prepared activated carbon were first characterized using X-ray diffraction (XRD), Fourier Transform Infra-Red (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM/EDX) and chemical methods, and then used as modifier agents for the carbon paste electrode (CPE) to study the electrochemical behavior of the hydroquinone (HQ). This electrochemical study was carried out using the cyclic voltammetry, the chronoamperometry and the differential pulse voltammetry (DPV). The Box-Behnken experimental design (BBD) of the response surface methodology was employed to investigate the effect of different parameters of the AC preparation on the peak potential of the hydroquinone.

The transfer coefficient a, the apparent electron transfer rate constant k, and the electro–catalytic activity K for the redox reaction of the hydroquinone at the surface of the AC-CPE were determined using electrochemical approaches. Differential voltammetric measurements of the hydroquinone at the modified electrode exhibited the linear range of 5.0 × 10⁻⁸ mol L⁻¹ to 1.0 × 10⁻⁵ mol L⁻¹ with a low detection limit of 3.6 × 10⁻⁸ mol L⁻¹. Finally, this method was applied for the determination of HQ in skin whitening cosmetics samples.

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1. Introduction

Creams for skin lighting or bleaching are increasingly popular, despite their use has reached epidemic levels in many countries of the world, particularly those in Africa. With some estimates putting, most African women want to keep their skin toned and beautiful by indulging in skin care products that bleach the skin [1]. Most of these bleaching cosmetics are generally mixtures of chemical compounds, some being derived from natural sources, many being synthetic such as hydroquinone [2]. Hydroquinone (HQ, 1,4-Benzenediol) is the most conventional skin whitening agent. However, exposures to hydroquinone have a side effect, causing skin irritation and sensitization, nail discoloration and hyperpigmentation [3]. The USFDA standards allow a maximum of 2–5% of hydroquinone in skin care products [4]. Despite the side effects of hydroquinone, skin lightening creams containing these harmful chemicals are still found in the market and are sold to the public. However, these creams are not legally labeled and circulated without permission. Therefore, this condition requires strict control and sensitive methods for the determination of the hydroquinone content.

At present, several methods have been commonly employed to determine HQ, such as chromatography, spectrophotometry and electrochemical methods [6–8]. The electrochemical methods are the most favorable techniques in detecting organic micropollutants because of their low cost, high sensitivity, rapid response and easy
sample-pretreatment procedures [9]. However, if a conventional electrode is used as the electrochemical detector, it is difficult to detect HQ due to its high overpotential and the poor detection selectivity [10]. Since then, many efforts have been devoted to developing functional materials with electrocatalytic properties as modifiers of the surface of these electrodes which leads to achieving sensitive and selective detection of HQ.

In this context, several materials have been used to develop different modifying electrochemical sensor strategies to determine the HQ in electrochemical methods. These materials include boron-doped diamond [11], functionalized SBA-15 mesoporous silica [12], carbon nanotubes [13], gold nanoparticles on carbon nanotubes [14], and biosensors [15].

Recently, prodigious research efforts have been made to overcome the cost of the modified electrode by using non-noble electrode. Carbon has more advantages than metal oxides due to the high speciﬁc surface area, high stability in acidic and basic media, large pore volume, thermal stability, better electronic conductivity and mechanical strength [16]. Indeed, many efforts have been done for fabricating activated carbons with high surface area and low cost from agricultural wastes [17]. Thus, we are interested in using AC from date stone as the electrode by using non-noble electrode.

In this context, several materials have been used to develop different modifying electrochemical sensor strategies to determine the HQ in electrochemical methods. These materials include boron-doped diamond [11], functionalized SBA-15 mesoporous silica [12], carbon nanotubes [13], gold nanoparticles on carbon nanotubes [14], and biosensors [15].

Activated carbon modified carbon paste electrodes (AC-CPE) were prepared according to the method reported in the literature [19]. Briefly, the carbon paste mixture was prepared by hand mixing the graphite powder with an appropriate amount of activated carbons to form a well homogenized mixture. The cyclic voltammetry and differential pulse voltammetry (DPV) were recorded in a suitable potential range under various conditions. The voltammetry procedure involves three experimental steps consisting of the optimization of parameters, the determination of detection limits and the optimization of the hydroquinone concentration in whitening cream samples. The optimization of parameters was carried out in a solution of 1.0 × 10^{-4} \text{mol L}^{-1} with the HQ dissolved in 1.0 × 10^{-1} \text{mol L}^{-1} phosphate buffer as the supporting electrolyte. The determination of the detection limits performed in an electrolytic solution with the varying HQ concentration. For the analytical application, the whitening cream samples were dissolved in the phosphate buffer solution with pH = 2. The determination of the hydroquinone concentrations in the whitening sample was done by the standard addition technique.

2.2. Electrochemical procedure

Activated carbon modified carbon paste electrodes (AC-CPE) were prepared according to the method reported in the literature [19]. Briefly, the carbon paste mixture was prepared by hand mixing the graphite powder with an appropriate amount of activated carbons to form a well homogenized mixture. The cyclic voltammetry and differential pulse voltammetry (DPV) were recorded in a suitable potential range under various conditions. The voltammetry procedure involves three experimental steps consisting of the optimization of parameters, the determination of detection limits and the optimization of the hydroquinone concentration in whitening cream samples. The optimization of parameters was carried out in a solution of 1.0 × 10^{-4} \text{mol L}^{-1} with the HQ dissolved in 1.0 × 10^{-1} \text{mol L}^{-1} phosphate buffer as the supporting electrolyte. The determination of the detection limits performed in an electrolytic solution with the varying HQ concentration. For the analytical application, the whitening cream samples were dissolved in the phosphate buffer solution with pH = 2. The determination of the hydroquinone concentrations in the whitening sample was done by the standard addition technique.

2.3. Response surface methodology

In order to develop electrocatalytic response of HQ, a number of factors influencing the process of preparation of activated carbon such as the activation temperature (A), carbonization time (B) and activation time (C) were considered. However, the study of each individual factor is quite tedious and time consuming. The Box-Behnken experimental design (BBD) minimizes the above difficulties by optimizing all the affecting parameters collectively at a time [20]. The three factors used in each variable were determined, where their respective domains were chosen on the basis of the literature data and preliminary experiments [21] (Table S1). The experiments were performed according to a three level design; –1, 0, +1 with N experiments (N = 2n (n = 1) + n0 (where n is the number of factors and n0 is the number of central points)). The BBD model consisted of 15 experimental points, including 12 factorial points and 3 central points, which were carried out in a random order [20]. The mathematical model associated with this design can be written as the following equation (Eq. (1)).

\[ Y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{123}ABC + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 \]  

where, Y is the response of interest (iodine number \( I_2 (Y_2) \), methylene blue index \( MB (Y_3) \) and the difference between the two peak potentials \( \Delta E = E_{pa} - E_{pc} \), with \( E_{pa} \) and \( E_{pc} \) are the anodic and cathodic potentials of HQ, respectively, \( Y_3 \)). The results were analyzed using the Design Expert 8.0.7.1 Trial software.

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3. Results and discussion

3.1. Characterization of the raw material

The proximate and ultimate analysis for the characterization of the date stones were studied (Table S2). The analysis findings show that tested samples are rich in carbon, hydrogen and oxygen contents (43.81, 6.41 and 46.9%, respectively). On the contrary, the relative contents of nitrogen and sulfur are low (0.15–0.19%). In comparison with the biomass, these materials have the typical composition. It is obvious from the table that the relatively high amount of volatile contents (73.46%) belongs to the high amount of the organic content, and the relatively low amount of ash arises from the low inorganic content. This shows that the biomass could be considered suitable for the pyrolysis, the gasification or the combustion processes [22]. Moreover, the knowledge of the ratios of H/C and O/C is more important for thermochemical conversion processes. In most cases, biomasses are of higher O/C and H/C ratios than the fossil fuels. The high values of the atomic H/C ratio (1.64) in date stones agree with the high volatile content found by the proximate analysis (73.46%). The values obtained for these parameters are relatively similar to those reported for date stones in the literature [23]. Higher heating value (HHV) was found at 18.7 kJ kg⁻¹. These values are in the same order of magnitude as the results obtained for sawdust, olive solid waste, oil palm fruit bunches, wood pellets and wood chips [24].

3.2. Electrochemical behavior of hydroquinone

The electrochemical behavior of hydroquinone was firstly studied on the surface of a CPE using the cyclic voltammetry (CV) in a 1.0 × 10⁻³ mol L⁻¹ phosphate buffer solution (pH = 7.0) containing 1.0 × 10⁻³ mol L⁻¹ (HQ) at a scan rate of 50 m s⁻¹. The response of cyclic voltammograms showed that the oxidation and reduction peaks appeared at 366.70 and 498.98 mV, indicating an accelerated electron transfer at AC-CPE. The peak potential difference (ΔE), which can indicate the reversibility behavior of the reaction, is very large (161.28 mV) at the unmodified carbon paste electrode, inferring that the electron transfer reaction is slow. In order to increase the reversibility of HQ, activated carbon was inserted into the carbon paste as a modifier. However, three factors influencing the process of preparation of activated carbon were studied.

3.3. Experimental results and statistical analysis

The codified and actual values of the three important factors together with the response values and observed results were determined (Table S3). The repetition of the experiments at the center point was used to estimate the variance of the experimental error. The quadratic model was selected for the responses of ΔE, as suggested by the software. The final empirical regression models in terms of the coded factors after neglecting the statistically insignificant effects for ΔE are described in the following equation (Eq. (2)).

\[
Y_3 = 222.132 - 67.936625A + 30.812125B - 67.62875A^2 + 40.75925AB + 16.1175AC + 5.775BC + 42.320625A^2 + 42.498125B^2 + 93.924875C^2
\]

The normal probability plot of the residuals is shown in Fig. 1a. From the figure, we can see that the data points for ΔE are close to the straight line, which shows that the developed regression models are appropriate to explain the variations in the experimental data.

In order to determine the main effects and the most important interactions influencing on ΔE, the analysis of variance (ANOVA) was calculated within a 95% confidence domain after the reduction of insignificant terms (Table S4). Based on the lack of fit values, calculated F-values and a very low Prob. > F values (<0.0001) for the response, we observed the good fitness and high significance of the regression models. Therefore, in the studied system, the AB interaction term was insignificant to the response. In addition, the linear effects of A (i.e. the activation temperature) and C (i.e. the carbonization time) show high and positive values, indicating a favorable or synergistic effect of these terms on the peak potential of HQ in the studied region of experiment. However, the AC and BC interaction terms, B and all the quadratic terms have significant and antagonistic effects on the responses, implying that the increase of these terms beyond the designed boundaries tends to decrease the difference between the anodic and the cathodic peaks of HQ (ΔE).

The three-dimensional (3D) response surface plots of the predictive quadratic model for ΔE are shown in Fig. 1b–d. It can be seen from Fig. 1b that the peak separation potential of HQ decreases with the increase of the activation temperature and the activation time. A smaller value of ΔE was obtained at the activation temperature of 800 °C and the activation time of 120 min. ΔE decreases when the activation temperature is increased despite whatever the carbonization time does (Fig. 1c). Also, if the carbonization time and the activation time increase, the ΔE decrease (Fig. 1d). The smaller value of separation potential of HQ was obtained with an activation time of 120 min and a carbonization time of 80 min.

The Design-Expert software was applied for the analysis. The predicted optimal results for AC were obtained by using the activation temperature of 800 °C, the activation time of 120 min and the carbonization time of 80 min. In these adjusted optimum conditions, the predicted uptakes of AC for ΔE were found to be 255.19 mV. To confirm the predicted results, three AC samples were prepared under the aforementioned optimum conditions. The average experimental value obtained was 256.03 ± 5.28. The characterization of optimal activated carbon was presented in the previous paper [19].

3.4. The electrocatalytic effect of activated carbon on the electroactivity of HQ

3.4.1. Cyclic voltammetric studies

Fig. 1e shows cyclic voltammograms (CVs) of the optimized activated carbon modified carbon paste electrode (i.e. AC-CPE) compared with the unmodified electrode (i.e. CPE). The CVs for HQ at AC-CPE show an oxidation peak at 223.1 mV and a reduction peak −32 mV with a redox peak separation of 255.19 mV. The redox peak separation for HQ at AC-CPE is smaller than that at CPE (498.98 mV), indicating an accelerated electron transfer at AC-CPE. The AC material shows an abundant porosity, and a large specific surface area, and thus ensuring a large electrochemically active surface, the fast mass transport and the rapid electron transfer. However, the value of the redox peak separation for HQ decreases when increasing the value of I₂ and MB adsorption (Table S3). Additionally, the CV of the HQ at the AC-CPE shows the presence of a second oxidation feature at −16 mV, which corresponds to the electro-adsorption of the ion H⁺, similar to that described in the literature [25,26]. This demonstrates the high adsorption capacity of activated carbons compared with carbon paste electrode.

For achieving the best shifting of the peak potential of hydroquinone, the amount of activated carbon was optimized in the phosphate buffer containing 1.0 × 10⁻³ mol L⁻¹ HQ using the cyclic voltammetry (see Fig. 1f). As it can be observed, there is a slight shift of ΔE to more negative values as the amount of activated carbon increases from 0 to 2% in the carbon paste electrode. Beyond
this field. $\Delta E$ increases which is probably due to the decrease of the conductivity of the modified electrode. Hence, 2% of AC ratio by weight was used throughout this work.

In order to understand the electron-transfer mechanism of the hydroquinone oxidation and reduction reaction, useful information can usually be acquired from the relationship between the peak current and the scan rate. Therefore, the electrochemical behavior of HQ at different scan rates in the range 10–400 mV s⁻¹ was also studied at a fixed HQ concentration of 1.0 × 10⁻³ mol L⁻¹ (0.1 mol L⁻¹ PBS, pH = 2) by the cyclic voltammetry (see Fig. 2a).

From the CVs at the modified electrode, both the values of redox peak currents ($I_{pa}$ and $I_{pc}$) are linearly proportional to the increase of scan rates (see Fig. 2b). A linear fit demonstrates that the oxidation process of HQ on the AC-CPE surface is a typical adsorption-controlled process. Therefore, the peak current could be correlate with the scan rate by Eq. (3) [27]:

$$I_p = \frac{n^2F^2A\Gamma}{4RT}v$$

where $\Gamma$ represents the surface coverage concentration (mol cm⁻²), $v$ the scan rate, $A$ (0.1256 cm²) the electrode surface area and $I_p$ is the peak current. The number of electron transfer ($n$) can be calculated as 2.2 in terms of the following equation (Eq. (4)):

$$\Delta E_{p}/2 = E_p - E_{p1/2} = \frac{2.3RT}{nF} = \frac{59}{n} \text{mV (25°C)}$$

Thus, the calculated surface concentration of AC-CPE is $\Gamma = 1.76 \times 10^{-8}$ mol cm⁻².

Fig. 2c shows the linear variation of $E_{pa}$ and $E_{pc}$ with the logarithm of the scan rate. This linear variation makes it possible to calculate the charge transfer coefficient ($\alpha$) and the apparent heterogeneous electron transfer rate constant ($k_s$). The two linear equations of $E_{pa}$ and $E_{pc}$ on log $v$ are plotted and expressed as:

$$E_{pa} (V) = 0.062 \log v + 0.3607 \quad (R^2 = 0.9689)$$

$$E_{pc} (V) = -0.0521 \log v + 0.2632 \quad (R^2 = 0.9737)$$

According to the Tafel’s equation, the slopes of the graph of the anode and cathode potential as a function of log $v$ are −2.3RT/nF and 2.3RT/(1−$\alpha$) nF, respectively. These slopes can be used to calculate the kinetic parameters. The anodic transfer coefficient ($\alpha_a$) was estimated out to be 0.53. This value was then inserted into (Eq. (5)) [28] to calculate the electron transfer rate constant ($k_s$).

where $k_s$ is transfer rate constant, $\alpha$ is the charge transfer coefficient, $n$ is the number of electron transfer and $v$ is the scan rate.

The effect of the pH value of the electrolyte solution on the electrochemical reactivity of hydroquinone was also investigated. The responses of the 1.0 × 10⁻³ mol L⁻¹ HQ were studied in the wide pH range from 2.48 to 11.41 (see Fig. 2d). As shown in Fig. 2e, the obtained results indicate that there is a linear displacement of the oxidation peak potentials to the negative potentials that is a function of the increase in the pH of the medium. The value of the line slope obtained is 48.8 mV per pH. This result according to the formula the Nernst [29]:

$$dE_{pa}/d\text{pH} = 2.303 \frac{\text{mV}}{\text{pH}}$$

where $n$ and $m$ are respectively the numbers of electrons and protons; $m/n$ was calculated to be 1.07 for the HQ oxidation process. This means that the number of protons and electron are (almost) equal.

3.4.2. Chronoamperometric studies

The catalytic performance of AC-CPE was also examined by the chronoamperometry (see Fig. 3). Chronoamperograms were recorded at a potential of 250 mV in the phosphate buffer solution.
Fig. 2. (a) CVs of $1.0 \times 10^{-3}$ mol L$^{-1}$ HQ in 0.1 mol L$^{-1}$ PBS (pH = 2) on AC–CPE in the scan rates range of 10–400 mV s$^{-1}$; (b) Variation of $I_p$ with of scan rate; (c) Variation of $E_p$ with log $v$; (d) CVs of AC–CPE at different pH values; $1.0 \times 10^{-3}$ mol L$^{-1}$ of HQ in 0.1 mol L$^{-1}$ PBS; (e) Plot of $E_{pa}$ vs. pH value.

Fig. 3. Chronoamperograms obtained at AC-CPE in PBS (pH 2.0, 0.1 mol L$^{-1}$) for HQ concentrations of $1.0 \times 10^{-6}$ (1), $1.0 \times 10^{-5}$ (2), $5.0 \times 10^{-5}$ (3), $1.0 \times 10^{-4}$ (4), $5.0 \times 10^{-4}$ (5) and $1.0 \times 10^{-3}$ (6) mol L$^{-1}$. Insets: (a) plots of $I$ versus $t^{1/2}$, (b) plot of slopes of straight lines against HQ concentration, and (c) dependence of $I_C/I_L$ on $t^{1/2}$. 

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3.5. Analytical performance

3.5.1. Linearity range and the detection limit

Differential pulse voltammetry (DPV) was used for the determination of HQ using the activated carbon modified electrode. The various experimental parameters were studied to achieve the maximum assay performance. The best shift of the peak current was reached using a percentage of 2% for mixing AC into the carbon paste, a preconcentration time of 3 min, a pH of 2, a step width of 200 ms, a pulse width of 20 ms and a pulse height of 150 mV. These experiments were conducted using AC-CPE at 1.0 × 10⁻⁴ mol L⁻¹ HQ.

The DPV response observed at potential of 0.429 V was found amplified by increasing the HQ concentration (0.05–1000 μM). This peak potential is related to the oxidation of HQ, which is similar to that described in the literature [32]. It can be seen clearly from Fig. 4 inset, that the DPV response of HQ is linear over the concentration range from 0.05 to 1000 μM with a regression equation of \( I_{pa} (\mu A) = 0.7946 [HQ] \text{ μmol.L}^{-1} + 1.7761 (R^2 = 0.995) \). The limit of detection (LOD) was calculated as 3.6 × 10⁻⁶ mol L⁻¹ using the IUPAC recommendations 3σ/m [33], where σ is the standard deviation of the blank signal (obtained based on 8 measurements on the blank solution) and m is the slope of the calibration curve (m = 3.3373 μA μmol L⁻¹). To demonstrate the novelty and the analytical advantages of the proposed method, the analytical characteristics of the sensor, such as the sensitivity, the linear response range and the LOD were compared with those of the previously reported AC sensors (see Table 1) [10,34–38]. The comparative results demonstrate that the AC-CPE has a higher sensitivity, a low LOD and a wider linear response range toward HQ than previously reported HQ sensors.

3.5.2. Stability, repeatability and selectivity

The stability of the modified electrode was investigated by examining its response to the 1.0 × 10⁻⁵ mol L⁻¹ HQ in the PBS (1.0 × 10⁻¹ mol L⁻¹, pH = 2). However, the stability of storage of AC-CPE was explored by comparing the current responses of the modified electrode after storing in the laboratory at room temperature for 30 days. Initial responses were retained more than 94.6%, clearly indicating the good stability of the fabricated electrode. The repeatability of the activated carbon modified paste carbon electrode was also estimated from the voltammetric current response to HQ for eight successive assays by the same electrode under the solution containing 1.0 × 10⁻⁶ mol L⁻¹ HQ. The relative standard deviation was found to be 4.84%, indicating good repeatability of the sensor preparation.

The selectivity is an important parameter for a sensor as it indicates the ability to discriminate between the interfering species commonly present in the similar physiological environment and the target analyte. Therefore, the determination of HQ in the presence of several interfering species is very important for the

\[
I = n F A D^{1/2} C \pi^{1/2} \tau^{-1/2}
\]

\( (pH = 7) \) containing hydroquinone at range of concentrations from 1.0 × 10⁻⁶ mol L⁻¹ to 1.0 × 10⁻³ mol L⁻¹. Fig. 3a shows the evolution of the current density as a function of the inverse of the square root of time at different concentrations of HQ. The quasi-linear relationship between the current density and \( t^{-1/2} \) indicates that oxidation process of HQ on the AC-CPE surface is well controlled by a diffusion phenomenon (Eq. (6)) [30]. Based on the Cottrell equation and using the slope of the linear relation, the diffusion coefficient of HQ was estimated to be \( D = 3.99 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \).

Using the chronoamperometric data and the Galus equation (see Fig. 3c) [31], the catalytic rate constant \( (K) \) for the reaction between the HQ and the AC-CPE was determined. The average value of \( K \) was found to be 5.89 × 10⁻⁴ mol⁻¹ L s⁻¹. This value explains quite well the sharp feature of the catalytic peak observed for catalytic oxidation of HQ at the surface of AC-CPE.

Table 1

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Linear range (μmol.L⁻¹)</th>
<th>Detection limit (μmol.L⁻¹)</th>
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cosmetic point of view. The recovery rates obtained for successive additions of the 1.0 × 10⁻⁶ mol L⁻¹ HQ in the presence of different concentrations of inorganic ions and organic compounds are recorded in Table 2.

The result shows that 100-fold of Ag⁺, Al³⁺, Ca²⁺, Cd²⁺, Co²⁺, Cu²⁺, Fe²⁺, Mg²⁺, Ni²⁺, Zn²⁺, Pb²⁺, Na⁺, 50-fold of phenol, paracetamol, resorcinol, 2-nitrophenol, 4-nitrophenol, 3-aminophenol and 4-aminophenol did not interfere with the oxidation signal (peak current change < ±5%). However, the HQ determination was affected in the presence of catechol, dopamine and ascorbic acid in these conditions. Therefore, a separation procedure is required before determination such as optimization of the modifier content and pH.

3.6. Analysis of HQ in real samples

The newly modified electrode was used for the determination of HQ in samples of various skin whitening creams. Three commercial skin bleaching creams were analyzed for their hydroquinone contents. The results for all cream samples with 2% and 4% HQ on the label are listed in Table 3. The obtained recovery results indicate that AC–CPE modified electrode can be successfully used for the determination of the hydroquinone concentration in the skin whitening cosmetics samples.

4. Conclusion

Process optimization of the activated carbon from date stones was successfully conducted by the Box–Behnken design (BBD). The experimental values obtained for ΔE were found to be in good agreement with those predicted by the quadratic models. The maximum desirability value was obtained at a pyrolysis time of 120 min and at the activation temperature of 800 °C for 80 min. Under these conditions, the predicted value for ΔE was 255.19 mV. It was observed that the physical activation could be expected as a very effective method to prepare activated carbon. Therefore, the CPE modified with AC was prepared and used for electrocatalytic determination of HQ. The high current sensitivity and low detection limit of the AC for the detection of HQ were obtained using the DPV method. These properties indicate the applicability of the AC-CPE to determine the hydroquinone concentration in cosmetic samples with satisfactory recoveries.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jsamd.2019.07.003.
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