Application of multivariate curve resolution alternating least squares method for determination of caffeic acid in the presence of catechin interference

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ABSTRACT

In the current article, preparation and application of a graphene oxide nanosheets-based sensor for electrochemical determination of caffeic acid (CA) in the presence of catechin is described. This measurement was performed using the differential pulse voltammetry (DPV) technique and chemometric methods such as multivariate curve resolution–alternating least squares (MCR–ALS). The modified sensor was characterized by various techniques such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, ultraviolet–visible, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Operating conditions and influencing variables (involving several chemical and instrumental variables) were optimized with central composite rotatable design and response surface methodology. The second-order electrochemical data were generated by changing the pulse height in DPV, and after potential shift correction MCR–ALS was applied. Under the optimized conditions, the dynamic range for CA was from 0.5 to 100.0 μM and the detection limit was found to be 1.1×10^{-9} M. The results revealed that the modified electrode shows an improvement in anodic oxidation activity of CA due to a marked enhancement in the current response compared with the bare carbon paste electrode. The modified electrode demonstrated good sensitivity, selectivity, and stability. The proposed method was successfully applied in determination of caffeic acid in the presence of unexpected electroactive interferences with a very high degree of overlapping such as catechin in real samples.

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During recent years, graphene and its derivatives such as graphene oxide (GO)[1] have attracted great attention due to their unique and fascinating electronic and transport properties [1–3]. The interesting properties of GO have attracted considerable attention among scientists to explore the possibilities of using them in the processes of developing new nanoscale devices for future industrial, biological, medical, and bioelectronics applications [4–6].

Differential pulse voltammetry (DPV) is one of the most interesting techniques from the analytical viewpoint. However, conventional DPV cannot provide the necessary information to resolve a system with severe voltammograms overlap. Chemometric methods for extraction of analytical information from multivariate data have been proposed. Multivariate curve resolution–alternating least squares (MCR–ALS) is able to resolve different sources of variance in a particular data set, and it allows determining two or more components in a mixture with intense overlapping peaks.

Flavonoids are a group of naturally occurring phenolic compounds [7] that are well-known antioxidants due to their radical scavenging abilities [8]. Caffeic acid (CA) is one of the most protective antioxidants because of its effectiveness against immunoregulation diseases, asthma, and allergic reactions [9]. Catechin (Cat) has been acknowledged to be an antioxidant and radical scavenger [10]. It has been linked with many health benefits, including prevention of DNA damage due to oxidation and improvement in blood flow and liver function [11].

Traditional flavonoid analysis is mainly carried out by instrumental analysis [12–15]. However, such analysis is generally performed at centralized laboratories, requiring extensive labor and analytical resources, and often results in a lengthy turnaround time [16]. But a few electrochemical methods have been reported for the quantitative determination of CA [17–19,9,20,21]. Electrochemical

methods propose certain advantages, such as not being time-consuming and not requiring sample preparation, and also are simple, fast, sensitive, and low-cost methods compared with other analytical methods. However, voltammetric signals assisted by MCR–ALS give extra information that allows their better resolution [22].

In this article, we describe the preparation and application of a GO nanosheets-modified carbon paste electrode (GO/CPE) as a sensor for the determination of CA in the presence of Cat using experimental design and MCR–ALS. The aim of this study was to apply central composite rotatable design (CCRD) and response surface methodology (RSM) for optimization of instrumental and chemical variables. In the optimized experimental conditions, voltammetric determination of CA in the presence of Cat with a very high degree of overlapping peaks was performed by MCR–ALS.

Materials and methods

Instruments, materials, and software

The electrochemical measurements were carried out at 25 ± 1 °C using a three-electrode system (Sama 500 potentiostat, Iran) with an Ag/AgCl reference electrode and a platinum wire counter electrode. The working electrode was a modified carbon paste electrode.

A Metrohm pH meter model 691 was also used for pH measurements. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet magna FTIR-550 infrared spectrometer. A field emission scanning electron microscopy (FESEM) image of GO nanosheets was obtained using a Hitachi S4160 FESEM system. X-ray diffraction (XRD) patterns of the GO powder were carried out using a Philips X'Pert PRO system equipped with Cu Kα_1 radiation (λ = 1.5406 Å). Ultraviolet–visible (UV–Vis) absorption spectrum was recorded with a UV–PerkinElmer spectrophotometer (Lambda 2S). To verify the quality of the GO, Raman spectroscopy was carried out using a dispersive SENTERRA Raman Microscope (Bruker) equipped with a charge-coupled device (CCD) detector.

The pure forms of Cat and CA were purchased from Merck. The phosphate buffer solutions at different pH values were prepared from a 0.1-M solution of phosphoric acid and a concentrated solution of NaOH. Graphite fine powder (Merck) and paraffin oil (Merck, density = 0.88 g/cm^3) were used as binding agents for the graphite pastes.

The statistical software package MINITAB (release 16), developed by Minitab (USA), was used for calculating optimized parameters in CCRD. Voltammetric data were analyzed in the MATLAB environment. MCR–ALS was performed using the graphical user interface provided by R. Tauler [23]. Correlation optimized warping (COW) written in MATLAB [24] was used for alignment of electrochemical signals.

Synthesis of GO

GO was synthesized directly from graphite by a modified Hummers method [25]. According to this method, at first 1.0 g of graphite was stirred in 30 ml of H$_2$SO$_4$ (98%) in an ice bath for 5 h. KMnO$_4$ (6.0 g) and NaNO$_3$ (1.0 g) were slowly added while keeping the temperature under 20 °C. The mixture was then stirred at 50 °C for 45 min. Next, 100 ml of demineral water was added and the mixture was heated at 70 °C for 30 min. The reaction was terminated by the addition of demineral water (100 ml) and 30% H$_2$O$_2$ solution (5 ml). The resulting mixture was washed by repeated centrifugation and filtration, first with 10% HCl aqueous solution and then with demineral water. Finally, the GO product was obtained after the drying process.

Preparation of the modified electrode

The carbon paste was made by mixing of 0.5 g of graphite powder with an appropriate amount ($\sim$0.2 ml) of paraffin oil in a mortar. For preparing modified CPE, the different amounts of GO (0.5, 2.0, 5.0, 8.0, and 10.0 mg) were dispersed in 5 ml of demineral water by an ultrasonic bath for 40 min and then were added to carbon paste. After vaporizing water, the paste was mixed well for 30 min until a uniformly and homogeneously wetted paste was obtained. The modified carbon paste was packed into the end of a Teflon syringe. Electrical contact was made with a copper wire through the center of the rod screwed to the device (Scheme 1). A new surface was obtained by pushing an excess of the paste out of the syringe and polishing with a weighing paper.

Design of experiment

The optimization of effective chemical and instrumental variables on the determination of CA was studied by RSM. This method is a collection of statistical and mathematical techniques that is suitable for analysis and modeling of problems in which a response is influenced by several variables. It defines the effect of the independent variables alone or in combination regarding the studied processes. The main advantage of RSM is that it reduces the number of experimental trials required to evaluate multiple variables and their interactions and provides the information necessary for design and process optimization. In addition, this experimental design generates a mathematical model that is presented in graphical form [26,27].

The CCRD is a useful method for optimization of the effective variables through analyzing the interaction between them in a minimal number of experiments. This design process consists of three parts: (i) a full factorial or fractional factorial design; (ii) an additional design, often a star design in which experimental points are at a distance α from its center; and (iii) a central point. Full uniformly rotatable central composite designs present the following characteristics: (i) they require an experiment number according to $N = 2^f + 2f + r$, where f is the number of factors, r is the replicate number of the central point, and $2f$ is points fixed axially at a distance α from the center to generate the quadratic terms; (ii) α values depend on the number of variables and can be calculated by $\alpha = \pm 2^{f/4}$; and (iii) all factors are studied in five levels [28]. The experiments are often carried out in randomized order so as to minimize the effects of unexplained variability in the actual responses due to extraneous factors [29]. The response behavior could be related to the selected independent factors by a second-order polynomial. The generalized response surface model is shown in Eq. (1) for instrumental and chemical variables:

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_{12} + \beta_{22} x_{22} + \beta_{12} x_1 x_2, \tag{1}$$

where y_i is the predicted response, x_i is the independent variable, β_0 is the intercept (constant), and β_i, β_{ii}, and β_{ij} are the linear, quadratic, and interaction coefficients, respectively. In this work, we used the CCRD method to evaluate the relevance of two instrumental factors (scan rate and step potential) and two chemical factors (pH and GO nanosheets content) effective on the DPV response (a significance level of 95% was set for the mathematical model and surface response).

Results and discussion

Characterization of the prepared GO

The GO was characterized using FTIR, Raman spectroscopy, UV–Vis, SEM, and XRD (Figs. 1 and 2). The prepared GO was dispersed