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ORIGINAL ARTICLE

Application of experimental design for quantification and voltammetric studies of sulfapyridine based on a nanostructure electrochemical sensor

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Abstract In the present paper, differential pulse voltammetry (DPV) coupled with experimental design, as a new method, was developed for determination of sulfapyridine (SP). These measurements were carried out in a 0.2 M Britton–Robinson (B–R) buffer solution at the surface of multi-walled carbon nanotubes modified carbon paste electrode (MWCNT/CPE). Operating conditions were improved with central composite rotatable design (CCRD), involving several chemical and instrumental parameters such as pH, MWCNT amount, scan rate, step potential and modulation amplitude. DPV, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were applied for characterizing of the modified electrode. The modified electrode showed enhanced effect on the oxidation peak current of SP. The electron transfer coefficient ($\alpha = 0.77$), exchanging current density ($j_0 = 1.82 \times 10^{-11}$ A cm^{-2}) and diffusion coefficient ($D = 2.03 \times 10^{-5}$ cm^2 s^{-1}) of SP were calculated by linear sweep voltammetry (LSV) and chronoamperometry methods, respectively. Some analytical parameters such as repeatability, linear dynamic range (5.96–161.07 M) and detection limit (DL) (49.55 nM) for SP were also obtained. Finally, the proposed method was successfully applied for determination of SP in plasma samples.

1. Introduction

The classical method based on one factor at a time may be effective in some processes, but fails to consider the combined effects of several variables involved. When there are various independent variables affecting the responding factors, it is probably that the operational variables interact and influence each other's effects on the response. Thus, it is necessary to apply an optimization strategy that can determine all factors and possible interactions between these independent variables, so that a set of experimental optimal conditions can be determined (Cui et al., 1994). The design of experiments (DOE) fulfills this requirement. The DOE based on the statistical models, started with agricultural experiments in 1920s (Sir Ronald Fisher), followed by chemical experiments in 1950s (George Box) (Patil et al., 2012). In the statistical evaluation and

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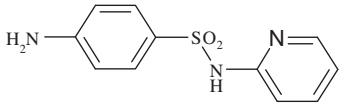
experimental design, response surface methodology (RSM) can be applied for process modeling and analytical optimization (Khuri and Cornell, 1996; Myer and Montogomery, 2002; Körbahti and Rauf, 2008; Ölmez, 2009). RSM is a useful modeling tool with a group of statistical and mathematical techniques that can be applied to improve, develop and optimize processes when the responses are influenced by several factors. It characterizes the effect of the independent factors, alone or in combination regarding the studied processes. Furthermore, this experimental methodology develops a mathematical model which is presented in a graphical form (Bas and Boyac, 2007). RSM permits to accomplish optimization study easily as it helps to decrease the number of experimental trials needed as minimum as possible. Thus, it is less laborious and time-consuming than other methods.

Sulfonamides (sulfa drugs) are an important kind of antibiotics widely applied in human and veterinary medicine to treat urinary bronchitis, ear infections, tract infections, skin and soft tissue infections. Important sulfa drugs used for these applications include sulfapyridine (SP) (Scheme 1), sulfamethoxazole, sulfamerazine, sulfamethazine, sulfadiazine and sulfathiazole (Dost et al. 2000; Long et al. 1990; Marek, 1998; Nhat et al. 2012). A variety of methods such as HPLC-UV and HPLC-FLD (Fischer et al., 1983; Teshima et al., 2002), ESI-MS/MS (Pastorini et al., 2008), potentiometric (Nazer et al., 2001), GC (Assassi et al., 2005) and LC–ESI-MS/MS Guang-Zhi et al. (2011) have been applied to measure sulfonamides. But only a few electrochemical methods have been reported for the detection of sulfonamide drugs (Abdullin et al., 2002; Braga et al., 2010; Preechaworapun et al., 2006). Electrochemical methods have attracted a lot of interest in many cases, and these methods can be fast in detections, low in cost, with merits of high accuracy and low detection limit (Ghoreishi et al., 2012a,b).

Carbon pastes are one of the most convenient materials for the preparation of modified electrodes. By adding mediator materials in carbon paste can improve the electrode sensitivity and selectivity (Ghoreishi et al., 2012a,b). Chemically modified carbon paste electrode is mainly used in the field of voltammetric determination (Ghoreishi et al., 2013; Lin et al., 2008; Švancara et al., 2007). Carbon nanotubes (CNTs) are composed of graphitic sheets rolled into closed concentric cylinders with length of micrometers and diameter of the order of nanometers. Since the discovery of CNTs in 1991 (Iijima, 1991), they have been applied more and more in chemical, physical and material science fields due to their unique chemical stability, electrical conductivity and high mechanical strength and modulus. CNTs are able to promote electron transfer in electrochemical reactions when used as the electrode material. Therefore using CNTs, a new manner of electrode surface modification as new electrochemical sensors is obtained (Khoobi et al. 2013; Yao et al., 2006).

In the present work, RSM based on central composite rotatable design (CCRD) was used to design experiments and determine the optimum experimental conditions for desirable responses. The main purpose of this work was investigation of the effect of parameters simultaneously for voltammetric determination of SP in mixed samples and human plasma. This paper is the first report about sensitive determination of SP by the differential pulse voltammetry (DPV) method based on a multi-walled carbon nanotubes modified carbon paste electrode (MWCNT/CPE) in Britton–Robinson (B–R) buffer solution. Additionally, we also determined kinetic parameters of SP with other voltammetric methods.



Scheme 1 Structure of sulfapyridine.

2. Experimental

2.1. Chemicals and reagents

All solutions were freshly prepared with deionized water. Sulfapyridine was of analytical grade from Sigma–Aldrich. Graphite fine powder (Merck) and paraffin oil (DC 350, density = 0.88 g cm^{-3}, Merck) as the binding agent were applied for preparing the pastes. Multi-walled carbon nanotubes with o.d. between 5 and 20 nm, i.d. between 2 and 6 nm, and tube length between 1 and 10 m were purchased from the Chinese Academy of Science and were purified using nitric acid treatment. All other reagents were of analytical grade from Merck. The buffer solutions of 0.2 M B–R were prepared from orthophosphoric acid, acetic acid and boric acid by adjusting the pH with NaOH solution in the pH range of 2.0–10.0.

2.2. Apparatus and procedures

The cyclic voltammetry (CV), linear sweep voltammetry (LSV) chronoamperometry and differential pulse voltammetry experiments were carried out using a Sama 500 potentiostat (Isfahan, Iran). Electrochemical impedance spectroscopy (EIS) measurements were carried out by an Autolab potentiostat–galvanostat PGSTAT 35 (Eco chemie Utrecht, Netherlands), equipped with NOVA 1.6 software. Storage and processing of data were carried out by a personal computer (Pentium IV). For preparing buffer solutions with adjusted pH a Metrohm 691 pH/meter was applied. An ultrasound bath (Bandelin Sonorex, Germany) at a constant frequency of 35 kHz was used for dispersing of MWCNT during experiments. A three electrode cell system was applied at 25 ± 1 °C. The MWCNT/CPE, an Ag/AgCl/KCl(sat) and a platinum wire were used as the working, reference and auxiliary electrodes, respectively. A polyethylene tube with a rod (2 mm diameter and 5 mm deep) bored at one end was used as the body of the carbon paste working electrode. For electrical contact a copper wire was placed through the center of the rod. The working electrode was pretreated by pushing paste out of the tube, removing the excess, and mechanically polishing the surface with weighing paper.

2.3. Preparation of the electrodes

For preparation the modified carbon paste electrode, 6.0 mg (optimal amount) of purified MWCNT was added to 5.0 ml deionized water and sonicated for 30 min with an ultrasonic bath to obtain a stable and homogeneous suspension. This suspension was added to graphite powder (500.0 mg) in a small mortar, and allowed to evaporate water at room temperature

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