



Construction of a new electrochemical sensor based on molecular imprinting recognition sites on multiwall carbon nanotube surface for analysis of ceftazidime in real samples



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ABSTRACT

In this paper a new electrochemical sensor based on molecularly imprinted polymer immobilized on multiwall carbon nanotube surface was introduced for determination of ceftazidime. The sensor was constructed via synthesis of a molecularly imprinted polymer on glassy carbon electrode which has been modified with carboxyl-functionalized multiwall carbon nanotubes. Then, for increasing the sensitivity of the sensor, Ag dendrites (AgDs) nanobranch was deposited on polymer electrochemically. The resulting imprinted polymer-multiwall carbon nanotube composite showed high sensitivity, excellent stability and good specific recognition behavior towards template molecule. The morphology of AgDs/MIP/c-MWCNT/GCE was investigated by field emission scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy in detail. Under the optimal experimental conditions, the current response of the imprinted sensor was linear to the concentration of ceftazidime in the range of 2–500 and 500–7000 nM, with the limit of detection of 0.55 nM (S/N=3). The proposed sensor has also been examined for recognition of ceftazidime quantitatively, in complicated matrices real samples.

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1. Introduction

Ceftazidime (CFZ) is a third-generation cephalosporin antibiotic and it is highly stable to hydrolysis by most β -lactamases produced by gram-negative and gram-positive bacteria [1]. CFZ is widely used in the treatment of susceptible infections including respiratory-tract infections such as pneumonia and lung infections in patients with cystic fibrosis-urinary tract infections, skin and soft tissue infections, bone and joint infections, peritonitis and other abdominal infection [2]. It is reported that [3] CFZ is not metabolized and can be excreted unchanged principally in urine. The antibiotic CFZ is generally a well-tolerated medication, but in some cases, side effects do occur. Some of the most common ones include seizures, bloody diarrhea, hyperactivity, inflammation at the injection site, and irritation at the injection site. So determination of this drug in real sample such as biological fluids and pharmaceutical formulation, is very important. Therefore, several analytical methods have been described for the determination of CFZ, including chromatographic techniques [4–9],

spectrophotometric [10–14], colorimetric [15] and microbiological methods [16,17]. The determination of CFZ using chromatographic, spectrophotometric and colorimetric techniques show high sensitivity, but they also requires expensive instruments, pre-treatment steps, skilled operators and large quantity of organic solvents and also are time-consuming. CFZ is an electroactive compound therefore; the electrochemical techniques offer another possibility for the estimation of this compound. Electrochemical sensors have attracted more and more attentions in drugs analysis that may be due to their advantages such as reliability, fast response, low cost, simple operation, time saving, high sensitivity and good selectivity. There have been several reports on the electroanalytical determination of CFZ [18–26]. Literature survey showed that many of previous reports for CFZ detection are based on its irreversible reduction at the surface of mercury drop electrode and modified mercury drop electrode [18–23]. Unfortunately, the reduction peak current as electrode responses is encountered with interference of ease reducible substances. Thus, the electrooxidation of CFZ was suggested for its detection. Due to limitation of mercury in positive potential range, the electrooxidation must be carried out at the solid electrodes. It is generally believed that the direct redox reactions of biochemicals at bare electrode are irreversible, and therefore require high over potential and often produces pro-

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nounced fouling effect that results in rather poor selectivity and reproducibility. A promising approach to overcome these difficulties arising from over potential and fouling effect is to change the nature of the bare electrode by its modification. The chemically modified electrodes are very interesting tools for the analysis of many substances at trace level, using very sensitive electroanalytical techniques [27–29]. Up to now some modified electrodes have been used for electrooxidation of CFZ and its monitoring [24–26] but, these sensors have major drawbacks such as short linear range and high limit of detection. Therefore in this work a new material called molecular imprinted polymer (MIP) was used as a highly selective and sensitive sorbent for detection of CFZ in pharmaceutical forms as well as analysis in biological fluids.

MIPs have been widely regarded as novel materials as biomimetic molecular recognition elements. Stable and simple preparation and excellent binding character for MIPs are of particular attraction [30,31]. In other words, recognition sites were generated by polymerizing functional monomer together with the template molecules in the presence of a cross-linking agent. After removal of template from the polymers, the cavity complementary in size and shape to the template is obtained in the polymer network, which can rebind the template with high selectivity and affinity [32,33]. Several techniques have been employed in molecular imprinting, differing mainly from the type of interaction between the functional monomer and the template prior to polymerization. This may be covalent, non-covalent or semi-covalent nature [34]. The template may also be introduced in the system differently: it may stand free or be attached to a surface, thus creating, respectively, 3D or 2D imprinting environments. When the template was attached on the surface prior to polymerization, provides more accessible binding sites compared to the MIPs prepared by conventional bulk polymerization techniques.

Multi-walled carbon nanotubes (MWCNTs) serve as an excellent support for grafting of MIPs on its surface, because it possesses large specific surface area, highly porous nature and it consists of hollow structures [35–37]. Furthermore, the MWCNTs incorporation in coating helped enhancing the sensitivity of the electrochemical detection because of its high conductivity. Therefore MWCNTs have been used as supporting material for construction of electrochemical sensors modified by MIP [38–40].

Here in we attempt to fabricate a novel electrochemical sensor for determination of CFZ based on carboxyl-functionalized multiwall carbon nanotubes (c-MWCNTs) modified glassy carbon electrode (GCE) and imprinting of a CFZ-MIP, followed by deposition of Ag dendrites (AgDs) nanobranch on its surface. The prepared electrochemical sensor was characterized by field emission scanning electron microscopy (FE-SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The sensitivity and selectivity of AgDs/MIP/c-MWCNTs/GCE were evaluated using anodic stripping differential pulse voltammetry (ASDPV) and its successful application was investigated for CFZ monitoring in pharmaceutical and serum samples. To the best of our knowledge, the proposed method is the first application of MIP electrode for CFZ determination.

2. Experimental

2.1. Reagents

Carboxylated multiwall carbon nanotubes with purity 95% were obtained from Dropsens (Llanera, Spain). Cefexime (CEF), CFZ and Cefepime (CFP) were obtained from Merck (Darmstadt, Germany). The following materials, namely ammonium persulphate (APS), acrylamide (AAM), *N*-hydroxysuccinimide (NHS), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide

Table 1

Experimental conditions and results of central composite design.

Run	Variables		Responses		
	Factor 1	Factor 2	voltammetric responses		
	AAM (mmol)	NNMBA (mmol)	Actual	Predicted	Error (%)
1	15	1	25.2	25.060	−0.6
2	7.93	1	19.3	17.765	−8.0
3	20	0.7	11.3	11.775	4.2
4	15	1	24.2	25.060	3.6
5	10	0.7	19.7	21.077	7.0
6	15	1	23.7	25.060	5.7
7	15	1.42	20.0	19.259	−3.7
8	15	1	25.9	25.060	−3.2
9	20	1.3	16.8	17.223	2.5
10	15	1	26.3	25.060	−4.7
11	22.07	1	11.8	11.541	−2.2
12	15	0.58	19.3	18.493	−4.2
13	10	1.3	15.4	16.725	8.6

hydrochloride (EDC), $K_3Fe(CN)_6/K_4Fe(CN)_6$, $NaNO_3$, $AgNO_3$ and *N,N*-methylenebisacrylamide (NNMBA) were obtained from Merck (Darmstadt, Germany). Vial of CFZ (500 mg) was purchased from local pharmacies. Stock solutions of CFZ (1×10^{-3} M) were prepared in water. The solutions (1×10^{-3} M) of the CEF and CFP were prepared in methanol/deionized water by volume ratio of 2:1. Phosphate buffered solutions (PBS) (0.01 M) with different pH values were prepared by 0.01 M H_3PO_4 , 0.01 M KH_2PO_4 and 0.01 M K_2HPO_4 and then adjusting the pH with 0.2 M HCl or 0.2 M NaOH.

2.2. Instrumentation

Voltammetric measurements were carried out with a μ Autolab III potentiostat/galvanostat (Eco Chemie B. V. Netherlands) electrochemical and electroanalytical instrument having NOVA 1.10 software. The electrochemical cell consisted of unmodified and modified GCE as working electrode, Ag/AgCl and platinum wire were used as reference and counter electrodes. A Metrohm pH-meter (model 691) was also applied for pH measurements. Scanning electron microscopy (SEM) images were obtained with a field emission gun scanning electron microscope (TSCAN, Czech). All measurements were carried out at room temperature.

2.3. Experimental design

In order to increase the voltammetric response of the sensor, instead of one-factor-at-a-time design, which is adopted most frequently in the literature, the central composite design (CCD) along with response surface methodology (RSM) [41] was employed to optimize the MIP assembling during polymerization step with two important parameters (functional monomer and cross linker). The experimental conditions and results are shown in Table 1. The analysis was carried out using Design Expert Version 8.0.1 software (Stat-Ease Inc., Minneapolis, MN, USA).

2.4. Preparation of the MIP modified electrode

Prior to modification of MIP modified electrode, the bare GCE was polished with emery paper followed by alumina (1.0 and 0.05 μ m) and then thoroughly washed with distilled water. After each polishing, the electrode was sonicated in ethanol and double-distilled water for 5 min successively and allowed to dry at room temperature. In the beginning, the suspension of 1.0 mg/1 mL of c-MWCNTs in DMF was prepared by sonication, and then 5 μ L of the c-MWCNTs/DMF suspension was cast onto the GCE surface and dried slowly. The c-MWCNTs/GC electrode was immersed into PBS

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