Bioelectrochemistry 89 (2013) 42–49

Contents lists available at SciVerse ScienceDirect

Bioelectrochemistry

journal homepage: www.elsevier.com/locate/bioelechem

Simultaneous determination of ofloxacin and gatifloxacin on cysteic acid modified electrode in the presence of sodium dodecyl benzene sulfonate

Fenfen Zhang [b], Shuqing Gu [a,b], Yaping Ding [a,b,*], Li Li [a], Xiao Liu [a]

[a] Department of Chemistry, Shanghai University, Shanghai 200444, PR China
[b] School of Materials Science and Engineering, Shanghai University, Shanghai 200444, PR China

ARTICLE INFO

Article history:
Received 31 May 2012
Received in revised form 27 August 2012
Accepted 28 August 2012
Available online 12 September 2012

Keywords:
Ofloxacin
Gatifloxacin
L-Cysteine
Simultaneous determination
Differential pulse voltammetry

ABSTRACT

A novel cysteic acid modified carbon paste electrode (cysteic acid/CPE) based on electrochemical oxidation of L-cysteine was developed to simultaneously determine ofloxacin and gatifloxacin in the presence of sodium dodecyl benzene sulfonate (SDBS). Fourier transform infrared spectra (FTIR) indicated that L-cysteine was oxidated to cysteic acid. Electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) indicated that cysteic acid was successfully modified on electrode. The large peak separation (116 mV) between ofloxacin and gatifloxacin was obtained on cysteic acid/CPE while only one oxidation peak was found on bare electrode. And the peak currents increased 5 times compared to bare electrode. Moreover, the current could be further enhanced in the presence of an anionic surfactant, sodium dodecyl benzene sulfonate. The differential pulse voltammograms (DPV) exhibited that the oxidation peak currents were linearly proportional to their concentrations in the range of 0.06–10 μM for ofloxacin and 0.02–200 μM for gatifloxacin, and the detection limits of ofloxacin and gatifloxacin were 0.02 μM and 0.01 μM (S/N = 3), respectively. This proposed method was successfully applied to determine ofloxacin and gatifloxacin in pharmaceutical formulations and human serum samples.

1. Introduction

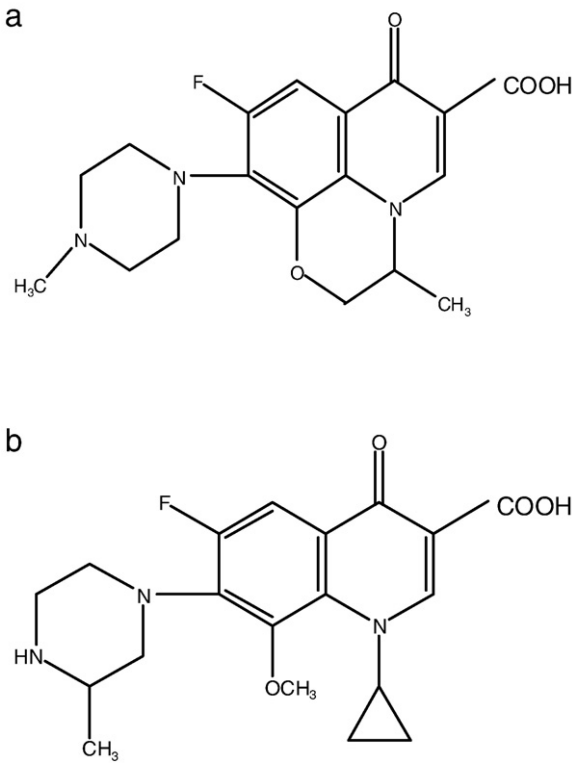
Fluoroquinolones (FQs) are important synthetic group of antibacterial agents which derived from nalidixic acid. They are quinolones with fluorine at position 6 and a piperazine substituent in position 7 of the naphthyridine ring [1], as fluorine atom and piperazine substituent broaden their activity spectrum against both Gram-negative and Gram-positive pathogens [2–6]. Different fluoroquinolone agents are obtained by substitution at the 1-nitrogen position of the quinolones and the para position of the piperazino group [7]. Although the structure varies, the therapeutic mechanism of their activity is based on the inhibition of bacterial DNA gyrase [8,9]. Ofloxacin [9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7-oxo-7H-pyrido[1,2,3-de]-1,4-benzox acine-6-carboxylic acid] (Scheme 1a) and gatifloxacin [1-cyclopropyl-6-fluoro-8-methoxy-7-(3-methyl-1-piperazinyl)-4-oxo-1,4-dihydro-quinoline-3-carboxylic acid] (Scheme 1b) are second and fourth generation fluoroquinolones respectively, which are commonly used for the treatment of urinary tract infections, respiratory tract infections, osteomyelitis, gastrointestinal, skin and soft tissue infections, peritonitis and gonorrheal [10,11] because of their high potency, low minimal inhibitory concentration, low toxicity, long half-life, and high stability.

Due to the similarity of structures, simultaneous determination of gatifloxacin, ofloxacin and other fluoroquinolones in both biological fluids and pharmaceutical formulations was generally performed with spectrophotometric methods [12,13], high-performance liquid chromatography (HPLC) [2,12,14,15], liquid chromatography (LC) [16], liquid chromatography–mass spectrometry (LC–MS) [17], fluorescence methods [18] and capillary electrophoresis [19]. Some of these methods have been found to be cumbersome, possessing poor precision and specificity and uneconomical [12]. Electrochemical method was an alternative approach with the advantages of simple, quick and low cost. However, few electroanalysis methods [20] have been reported for simultaneous determination of gatifloxacin and ofloxacin owing to the close peak potential positions of both analytes.

Recently, conductive polymer film modified electrode has received increasing attention because of its easier fabrication and better reproducibility than monolayer modified electrodes, and different polymer film-modified electrodes were constructed to enhance the sensitivity and selectivity of electrode than bare electrode [21,22]. L-Cysteine (CySH) is an important amino acid owing to its crucial roles in biological systems. Because of having sulfhydryl, L-cysteine could be electrochemical oxidated to cysteic acid, which form a novel thin film material at surface of electrode. Wang et al. have utilized cysteic acid modified electrode to determine some drugs, such as terbinafine [23], sinomenine [24], dopamine [25], nimesulide [26], meloxicam [27], and other drugs including adenine [28] and theophylline [29] were also detected on cysteic acid modified electrode. However, to the best of our knowledge,

* Corresponding author at: Department of Chemistry, Shanghai University, Shanghai 200444, PR China. Tel.: +86 21 66134734; fax: +86 21 66132797.
E-mail address: wdingyp@sina.com (Y. Ding).

1567-5394/$ – see front matter.
http://dx.doi.org/10.1016/j.bioelechem.2012.08.008



Scheme 1. The structure of ofloxacin (a) and gatifloxacin (b).

cysteic acid modified carbon paste electrode for simultaneous detection of ofloxacin and gatifloxacin has not been reported.

Sodium dodecyl benzene sulfonate (SDBS) is a kind of anionic surfactant which was commonly used in electroanalysis to improve the sensitivity and selectivity of analysis, since the surfactant molecules can spontaneously adsorb on the interfaces of two phases with different polarities or associate into micelles in solutions which can improve the property of the electrode/solution interface [30–32].

In this paper, cysteic acid modified carbon paste electrode was prepared by electrochemical oxidation of L-cysteine on the surface of the electrode and used to detect ofloxacin and gatifloxacin in the presence of SDBS. It was found that the oxidation potentials of ofloxacin and gatifloxacin were separated on cysteic acid/CPE while it was one potential position on bare CPE, and the peak current further enhanced in the presence of sodium dodecyl benzene sulfonate (SDBS). Based on this, the cysteic acid/CPE was successfully employed to simultaneously/individually detect ofloxacin and gatifloxacin in the presence of SDBS. This method was also successfully used to detect the concentration of ofloxacin and gatifloxacin in pharmaceutical formulations and human serum samples.

2. Experimental

2.1. Apparatus and reagents

All electrochemical experiments were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua Co. Ltd., China), with a conventional three-electrode system including a cysteic acid/CPE as working electrode, a Pt wire counter electrode and a saturated calomel electrode (SCE) reference electrode. All potential values given below were referred to the SCE. Fourier transform infrared spectra (FTIR) were carried out on AVATAR 370 Fourier transform infrared spectrometer (USA). The electrochemical impedance spectroscopy (EIS) was recorded on Solartron 1255B Frequency Response analyzer/SI 1287 electrochemical interface (Scribner Associates, Inc., USA). A digital pH/mV/Ion meter (CyberScan model 2500, USA) was used for the preparation of the buffer solution.

All chemicals and reagents used in this work were of analytical grade and used as received without further purification. Gatifloxacin and ofloxacin were purchased from Wuhan Yuancheng Gongchuang Technology Co., Ltd. (China). L-Cysteine, graphite powder (spectral reagent), sodium dodecyl benzene sulfonate, paraffin oil, HCl, HNO_3, and C_2H_5OH were purchased from the Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. Fresh serum samples obtained from healthy person were provided by Shanghai University Hospital.

2.2. Fabrication of CPE and cysteic acid/CPE

Graphite powder and paraffin oil were mixed at the ratio of 3:1 (w/w) in the agate mortar for 20 min. The mixture was firmly packed into the glass tube (i.d. = 3.0 mm) which had been sonicated in HNO_3, NaOH solution and double distilled water in turns, and then the copper wire was inserted from another end of the tube. The electrode was polished with a piece of weighing paper and rinsed with double distilled water.

Cysteic acid/CPE was prepared by electrochemical oxidation of L-cysteine through dipped CPE in 0.1 M PBS (pH 7.0) containing 10 mM L-cysteine in the potential range of −0.8 to 2.2 V at 100 $mV \cdot s^{-1}$ for 20 cycles. Finally, the cysteic acid/CPE was carefully washed with double distilled water for use.

2.3. Experimental measurements

For FTIR spectroscopy analysis, the cysteic acid was obtained using the method in Section 2.2, except that the working electrode was replaced to a polished aluminum sheet. EIS was performed at bare CPE and cysteic acid/CPE in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl using an alternating current voltage of 10 mV and was recorded at a bias potential of 200 mV within a frequency range of 10^{-1}–10^5 Hz. Cyclic voltammetry was carried out in quiescent solution at a scan rate of 100 $mV\ s^{-1}$. Differential pulse voltammetry was performed in an electrochemical cell filled with 10.0 mL 0.1 M PBS.

2.4. Treatment and determination of samples

2.4.1. Tablets

Five tablets of ofloxacin and gatifloxacin were weighed and powdered in a mortar individually. A quantity equivalent to one tablet was weighed, dissolved into double distilled water, transferred to a 100 mL volumetric flask, and diluted to the mark with double distilled water. This solution (1 $mg \cdot mL^{-1}$) was diluted with double distilled water to obtain working concentrations in the range of 0.01–200 μM.

2.4.2. Human serum samples

Blood sample obtained from healthy person was supplied by Shanghai University Hospital. For 1 mL blood sample, 0.15 mL perchloric acid was added, vortex-mixed for 1 min and centrifuged at 2500 rpm for 15 min. And then, the supernatant was directly injected to pH 4.5 PBS to give a total volume of 10 mL.

3. Result and discussion

3.1. The role of materials modified on the CPE

The electrochemical determination of CySH has been studied by many researchers [33,34]. And it is widely accepted that the reaction occurs by the following oxidation reaction mechanism on electrodes [34–37].

$$CySH \rightarrow CyS^{-} + H^{+}. \quad (1)$$