Trade Science Inc.

January 2008 Volume 7 Issue 2

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 7(2) 2007 [110-115]

Adsorptive stripping voltammetry determination of ofloxacin using carbon paste electrode

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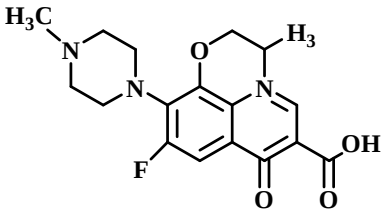
Received: 24th June, 2007 ; Accepted: 29th June, 2007

ABSTRACT

The electrochemical behavior of antibiotic drug (ofloxacin), at carbon paste electrode CPE, is thoroughly investigated. Chemical and electrical parameters affecting the adsorptive voltammetric measurements are optimized. Deferential pulse DP is swept over potential range from -1000 to +400mV in the presence of Britton-Robeson buffer pH 7, with accumulation time 30s, scan rate 50mV/s and pulse amplitude 50mV. The responses are linear over the concentration range 1.65-23.1μg/ml with correlation coefficient .0.998 while the limit of detection is 0.17μg/ml. The method has been applied successfully for the determination of active ingredient in the Egyptian pharmaceutical products and in spiked urine with mean recoveries of 100.025±2.33, and 98±2.38 respectively.

INTRODUCTION

Quinolones have emerged as one of the most important classes of antibiotics of the past decade. Ofloxacin (OFLX) {(±)-9-fluoro-2,3-dihydro-3-methyl-10-(-methyl-1-piperzinyl)-7-oxo-7H-pyrido-[1,2,3-de]1,4-benzoxazine-6-carboxylic acid}(Figure 1) is a synthetic racemate flouroquinolone derivative, which has demonstrated broad-spectrum activity against many pathogenic gram-negative and positive bacteria.



Ofloxacin

It is widely used in the treatment of urinary infections with good localized action on infected sites. About 75% of the oral dose is excreted unchanged in the urine within 24h, thus producing high urinary concentrations[1]. Therefore various techniques have been utilized for the determination of ofloxacin either in pharmaceutical tablets or in biological samples. These include HPLC[2-12], LC[13-15], TLC[17,18], electrophoresis method [19-24], UV spectrophotometric[25-28] spectrofluorometry[29-31], flow-injection chemiluminescence[32-37], conductometry and acid-base potentiometric titration using glass electrode[38], PVC membrane coated glass electrode[39] or PVC membrane coated carbon selective electrode[40]. Polarographic and voltammetric techniques[41-46], on the other hand, have also been conducted. However, due to the hazardous effects on using mercury electrodes, solid electrodes specifically carbon electrodes have been afforded alternative solution. Glassy carbon electrode, without[47] or with[48] coated DNA film, has been applied for determining levofloxacin which is the L-isomer of the racemate ofloxacin. Carbon paste electrode CPE can be used alternatively which is characterized by low cost and easy fabrication[49]. Irrespective the low sensitive method reported for determining levofloxacin using CPE modified by DNA[48], in the present work, CPE without any organic modifiers has

been applied successfully for determining the cited ingredient in pharmaceutical tablets and in urine samples as described here.

EXPERIMENTAL

Reagent and materials

All chemicals used are analytical grade. Twice distilled water was used throughout all experiments. Two pharmaceutical products, namely Tarivid(Hoechst Oriented S.A.E. Egypt) and Kirrol(Glaxowellcom, Egypt), containing 200mg ofloxacin per tablet were used. A stock solution of ofloxacin(0.3mg/ml) was prepared by dissolving in absolute ethanol. The buffer solutions were prepared in distilled water. The modified Britton-Robinson BR buffer solutions over the range pH 3-11 were prepared.

Preparation of carbon paste electrode

Carbon paste was prepared by mixing thoroughly 250mg synthetic carbon powder 1-2 micron (ALDRICH) with 0.1ml paraffin oil, in a small hand mortar. A portion of the paste was packed into the tip of the electrode assembly. This made from a Teflon tube with a hole of 2.5mm diameter and 3cm length moving through it a screwed stainless steel metal. The electrode then soaked in distilled water. Whenever regeneration of the electrode was required, a tiny portion of the paste was cut off and polished with filter paper.

Apparatus

All different modes of adsorptive stripping voltammograms(deferential pulse DP, square wave SW, and alternating current AC) were recorded using Metrohm 693VA processor(Switzerland) and VA 694 stand equipped with three electrodes Ag/AgCl-3M KCl, a platinum electrode and carbon paste electrode(CPE). The pH measurements were carried out with digital pH-meter Metrohm.

Procedure

The working electrode was first electrochemical activated by sweeping in 10ml BR buffer solution at pH 7, six times, over the potential range -1000 to 400mV,. A known volume of the analyte was transferred into 10ml calibrated flask containing 5ml of BR buffer(pH 7) and completed to the mark with distilled water. The solution was transferred into the voltammetric cell and de-aerated with pure nitrogen gas at 1 atmosphere for 2min, the accumulation potential at -1000mV is applied to a new surface of carbon paste electrode whilst still stirring the solution(2000rpm). Following the accumulation period(30s), the stirring is stopped and allowed to equilibrate for 10s. The differential pulse voltammogram is obtained by scanning from -1000 to 400mV with scan rate 80mV/s and pulse amplitude 50mV.

Procedure for spiked urine

Different volumes of ofloxacin solution were spiked into 10ml calibrated flask containing 1 ml human urine, 5ml of BR buffer(pH 7) and completed to the mark with distilled water. The final concentrations obtained should be in the range 2-20ug/ml. The solution is then transferred into the voltammetric cell and the experiment is completed as described before.

RESULTS AND DISCUSSION

Ofloxacin is readily adsorbed onto the hanging mercury drop electrode HMDE and displayed two definite cathodic and anodic peaks as shown in figure 1. The cathodic peak is depicted more sharp and height than anodic peak, but it will be hampered totally on using carbon electrodes. Although both peaks revealed in a cyclic voltammogram, at -1400 and -450mV, corresponding to reduction and oxidation of the adsorbed species, respectively, ofloxacin behalves irreversible reactions at HNDE as proved by long distance between

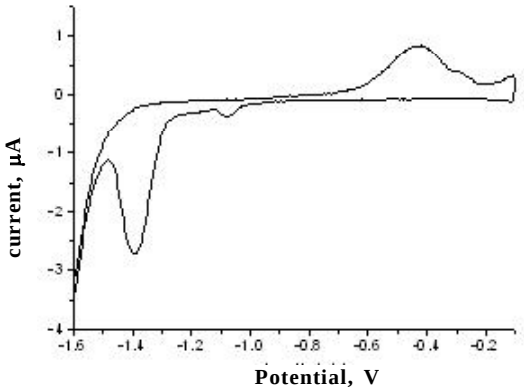


Figure 1 : Cyclic voltammogram for 22µg/ml ofloxacin on the HMDE and scan rate 100 mV/s.

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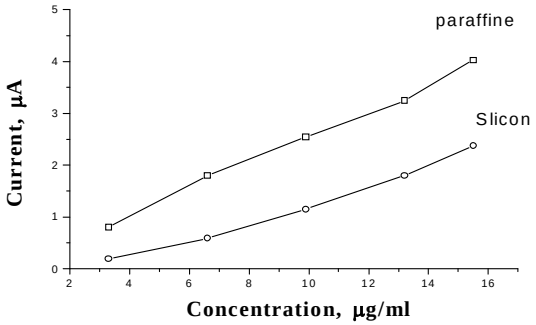

Figure 2 : Influence of the pasting oil type on the sensitivity of CPE for deferent concentrations of ofloxacin, using pH 7 BR, t_{acc}=30s and DP-mode, ΔE=50mV, α=50mV/s

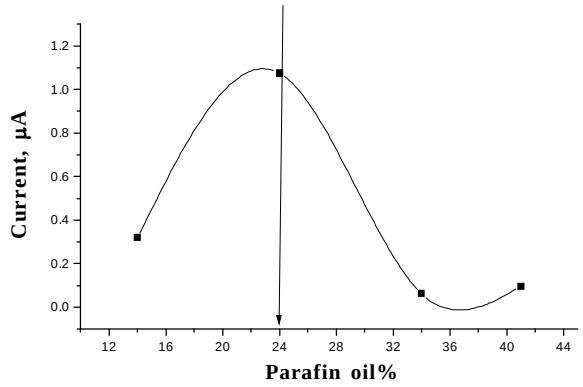

Figure 3 : Variatoin paraffin oil percentages composed in CPE and peak current of 22µg/ml ofloxacin, using pH 7 BR, t_{acc}=30s and DP-mode, ΔE=50 mV, ν=50mV/s

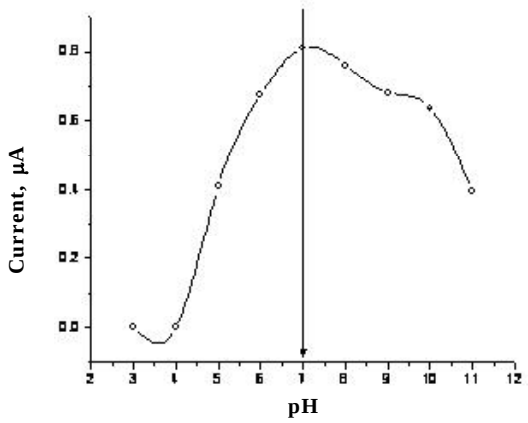

Figure 4 : The relation between pH and peak current value, at concentration 6µg/ml ofloxacin and using pH 7 BR, t_{acc}=30s and DP-mode, ΔE=50 mV, ν=50mV/s

them. In fact, similar irreversible behaviors are reported for fluoroquinolone derivatives and all are characterized either by reduction of quinolone at cathodic sweep using mercury electrode or oxidation of piperazine at anodic direction using solid electrodes.

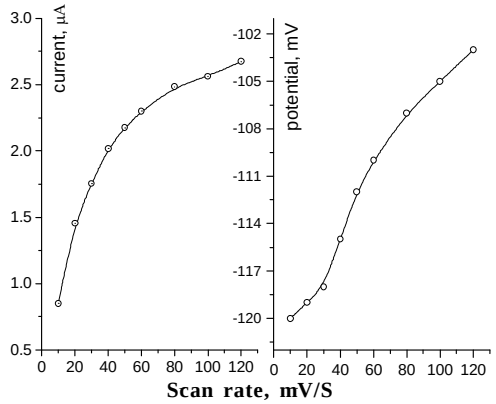

Figure 6 : Effect scan rate ν, on the peak current and potential, using pH 7 BR, t_{acc}=30s and DP-mode, ΔE=50mV

The influence of the composition of water-immescible oganic binders (pasting liquids), viz. paraffin and silicon oils, on the electrochemical behaviour of carbon paste electrode was investigated. Figures 3 and 4 illustrates the 24% paraffin oil emerged linear and high linear responses towards the ofloxacin concentrations.

The composition of supporting electrolytes such as Briton Robinson BR, borate, phosphate, ammonia buffer and potassium chloride, was studied and the highest peak was obtained with 0.04M BR. The effect of pH, varying from pH 3 to 11, was also studied for 6µg/ml ofloxacin solution following 30s accumulation at -1000mV and DP sweep. The maximum size peak was obtained with pH 7 of 0.04M BR buffer, Figure 4.

The variation of scan rate from 10 to 120mV/s, revealed that the diffusion current is increased with the scan rate, figure 5 and plotting log I versus log ν gave up straight line over the range 10 to 100mV/s with a slope 0.96(r=0.97) which is very close to the theoretical expected of unity for an ideal adsorptive reaction of species[50,51]. The peak potential is also shifted to less negative with increasing the scan rate confirming the irreversibility of the oxidation process. This result obtained is in accordance with that obtained by using glassy carbon electrode[39]. The scan rate, 50mV/s, is selected for the following studies.

Also, figure 7, illustrates increasing the oxidation current with increasing pulse amplitude ΔE, noting that a second broader peak (about -750mV) begins to reveal at ΔE=40mV and upward, indicating a second oxidation process occurred likely at carboxylic group.

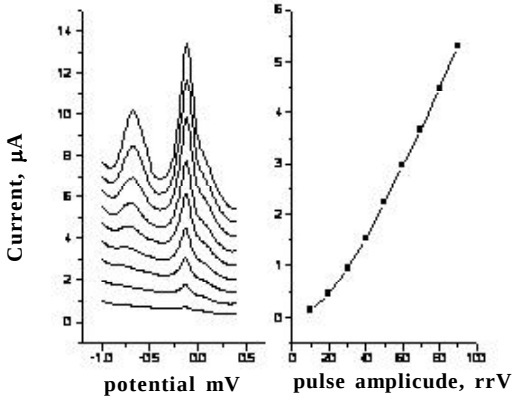

Figure 7 : Effect pulse amplitude ΔE, on the peak current, using pH 7 BR, t_{acc}=30s and DP-mode, ν=50 mV/s

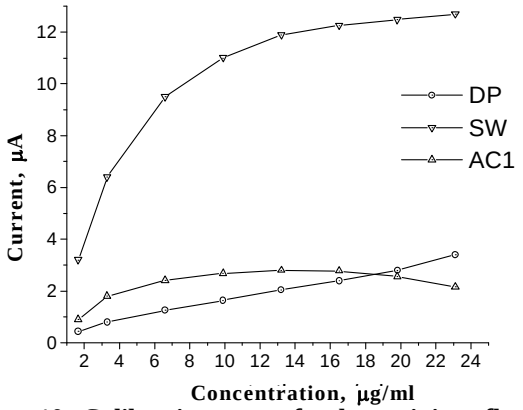

Figure 10 : Calibration curves for determining ofloxacin using different modes of sweep at pH 7 BR, t_{acc}=30s, ΔE=50 mV, ν=50mV/s

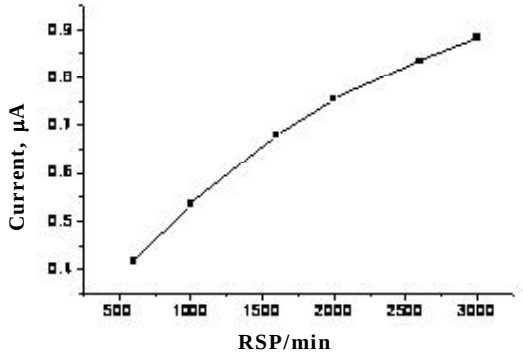

Figure 8 : Effect of rotating speed on the peak current, using pH 7 BR, t_{acc}=30s and DP-mode, ΔE=50mV, ν=50 mV/s

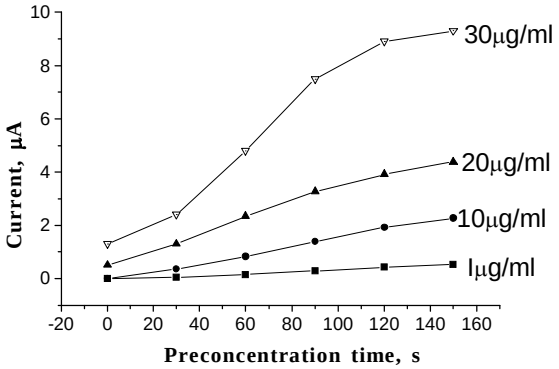

Figure 9: Show the relation between preconcentration time and peak current at different concentrations, of ofloxacin using pH 7 BR, t_{acc}=30 s and DP-mode, ΔE=50 mV, ν=50 mV/s

The ΔE=50mV, was chosen as optimum value for the next studies.

The speed of rotation within the accumulation time was also studied; the peak current increased linearly with the speed of rotation as shown in figure 8 and the value 2000rsp/min was selected.

Effect of the preconcentration time on the peak height at four different concentrations of ofloxacin, viz. 1, 10, 20 and 30µg/ml, was studied. The peak height increases linearly with deposition time up to 120s for all concentrations studied. Above that time, the deviation from the linearity is observed because of the formation of multilayer on the surface of the electrode. The time 30s is selected in this experiment.

Based on the optimized parameter mentioned above, the calibration curves are constructed using different modes of sweep, viz. differential pulse DP, square wave SW and first harmonic alternating current AC, for the comparison purpose, over the concentration range 1.65-23.1µg/ml ofloxacin. As shown in figure 9, the DP mode gave highest proportionality compared with other modes used(r=0.998, 0.910 and 0.717 for DP, SW and AC, respectively) and the limit of detection by DP was 0.17µg/ml.

The optimized parameters were also applied for determining cited compound in pharmaceutical products, viz. Tarivid and Kirol containing 200mg ofloxacin per tablet, as will as in urine samples spiked by different concentrations of ofloxacin solutions mentioned in the above procedure.

CONCLUSION

In the present work, carbon paste electrode CPE has been proved to be economic, effective and accu-

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rate tool as alternative mercury-free electrode for determining ofloxacin down to 1.6μg/ml either in pharmaceutical products or in urine samples.

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