

Investigation of Electrochemical Behavior of 3-Hydroxytyramine Hydrochloride Modified Pencil Graphite Electrode: Usability in Determination of Paracetamol

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Abstract – In this study, in order to determine Paracetamol (PAR), a widely used antipyretic and analgesic drug active ingredient due to its cheapness and easy availability, 3-hydroxytyramine hydrochloride (3-HT) molecule was modified to pencil graphite electrode (PGE) surface with cyclic voltammetry (CV) technique in +0.3/+2.0 V potential range and 100 mV s⁻¹ scan rate for 10 cycles. The electrochemical and spectroelectrochemical behaviors of 3-HT on PGE surface were investigated by CV, electrochemical impedance spectroscopy (EIS) and linear scanning voltammetry (LSV) techniques. After modification and chemical bonding processes, surface characterizations were compared with bare PGE and 3-HT modified PGE surfaces by using ferrocene in nonaqueous medium and ferricyanide solutions in aqueous medium with CV technique. Characterization studies performed by CV technique were supported by EIS technique. Studies conducted at pH 2.0 in BR buffer solution using square wave voltammetry (SWV) technique showed that PAR could be directly determined on the 3-HT modified PGE surface.

Keywords – Paracetamol, 3-hydroxytyramine hydrochloride, pencil graphite electrode, cyclic voltammetry, square wave voltammetry.

I. INTRODUCTION

Paracetamol (Acetaminophen, N-acetyl-p-aminophenol, N-(4-hydroxyphenyl) acetamide) (PAR), an antipyretic and analgesic drug active ingredient, is widely used because it is cheap and easily available [1]–[3]. PAR has weak acid properties. It has three functional groups in its structure: amide group (-HN-CO-R), aromatic benzene ring and hydroxyl group (-OH).

Techniques such as spectrophotometry, chromatography, electrophoresis and chemiluminescence are used to determine PAR. Some techniques have disadvantages such as time-consuming, high cost and low

sensitivity. But electrochemical methods are frequently preferred due to their features such as high sensitivity, selectivity, low cost, little equipment and speed. In recent years, PAR determination has been performed using different electrochemical techniques such as SWV, differential pulse voltammetry, square wave adsorptive stripping voltammetry and differential pulse adsorptive stripping voltammetry.

II. MATERIALS AND METHOD

2.1. Instruments and Chemicals

All experiments in our study were performed using GAMRY Reference 600+ potentiostat/galvanostat/ZRA (Gamry Instruments, Warminster, USA) using cyclic voltammetry, linear sweep voltammetry, electrochemical impedance spectroscopy and square wave voltammetry electroanalytical techniques. Conventional three-electrode BAS (Bioanalytical Systems Inc., West Lafayette, USA) brand C3 cell stand was used in all voltammetry and impedance experiments. Ag/Ag⁺ (BAS Model MF-2052) was used as a reference electrode in non-aqueous studies, Ag/AgCl/3M KCl reference electrode (BAS Model MF-2063) was used as a reference electrode in aqueous studies, platinum wire electrode (BAS Model MW-1034) was used as an auxiliary electrode and pencil graphite electrode (0.7 2B pencil) (PGE) was used as a working electrode. For each new voltammetric measurement, a new pencil tip with a clean surface that had not been subjected to any previous treatment was used as the working electrode. The pH 106BNWP combined glass pH electrode was measured with a VWR Leuven pH 1100 L model pH ion meter.

The chemicals and solvents used in this study were purchased commercially from Sigma-Aldrich, Merck, Acros Organics in high purity and were used without any pre-purification.

For the 3-HT solution prepared at 1 mM concentration, phosphate buffer (PBS, pH 7.2) was prepared as the supporting electrolyte by making calculations and mixing Na₂HPO₄ and KH₂PO₄. For the PAR solution prepared at 1 mM concentration, appropriate amounts of H₃PO₄, CH₃COOH and H₃BO₃ were prepared as the supporting electrolyte for Britton-Robinson (BR, pH 2.0) buffer solution.

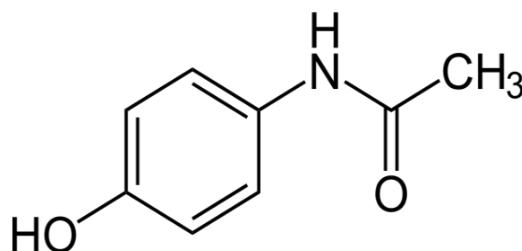


Fig. 1 Chemical structure of PAR

III. RESULTS AND DISCUSSIONS

3.1. Modification of 3-HT on PGE Surface

In our study, CV, EIS and LSV techniques were used for 3-HT solution prepared as 1 mM in PBS (pH 7.2) using PGE as working electrode in the modification and characterization processes of 3-HT. In the modification of 3-HT on PGE surface, amine oxidation method was selected due to -NH₂ functional group in its structure and positive (anodic) scanning was performed. Electrochemical modification of 3-HT was applied in +0.3 V/+2.0 V potential range, 100 mV s⁻¹ scan rate with CV technique for 10 cycles.

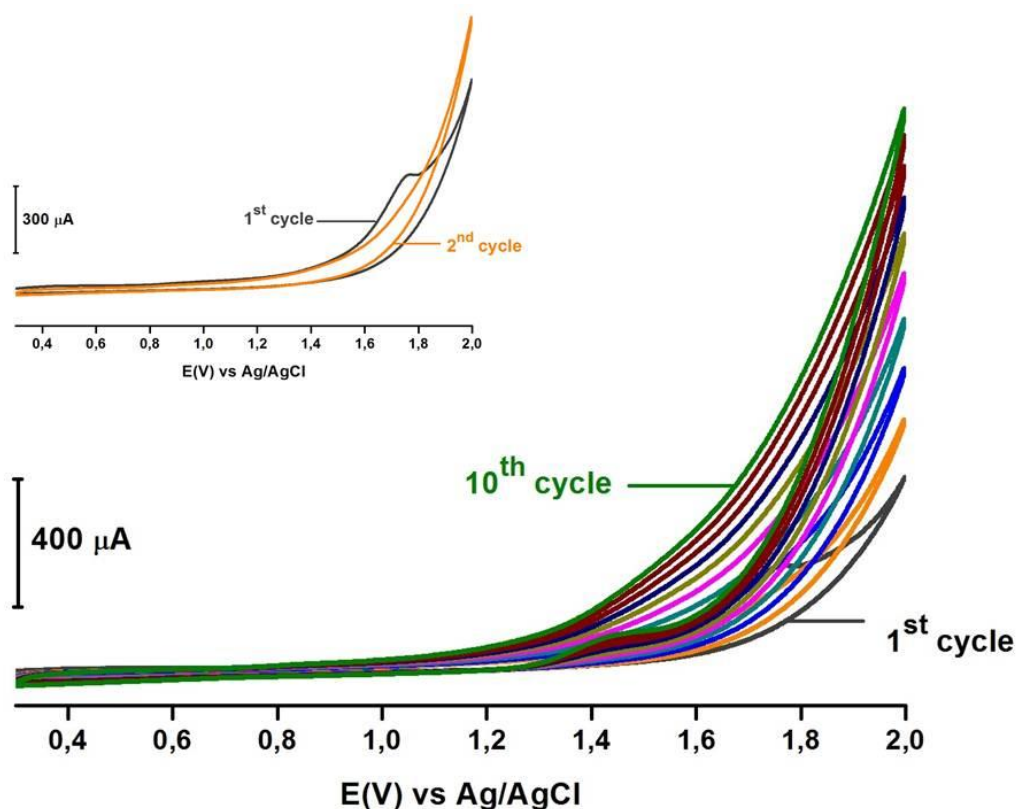


Fig. 2 Modification voltammogram of 3-HT onto PGE surface

When the modification voltammogram of 3-HT in the +0.3 V/+2.0 V potential range was examined in Figure 2, it was seen that it was modified on the electrode surface starting from the 2nd cycle.

3.2. Characterization of 3-HT on PGE Surface

1 mM ferrocene (Figure 3A) prepared in 100 mM tetrabutylammonium tetrafluoroborate (NBu_4BF_4) in a non-aqueous media and 1 mM ferricyanide (Figure 3B) prepared in 100 mM H_2SO_4 solution in an aqueous media were utilized for characterization after modification. Ferrocene test for characterization was carried out in the potential range of +0.1 V/+0.6 V at a scan rate of 100 mV s^{-1} on bare PGE and modified PGE surfaces, while ferricyanide test was carried out in the potential range of +0.5/-0.2 V at a scan rate of 100 mV s^{-1} on bare PGE and modified PGE surfaces.

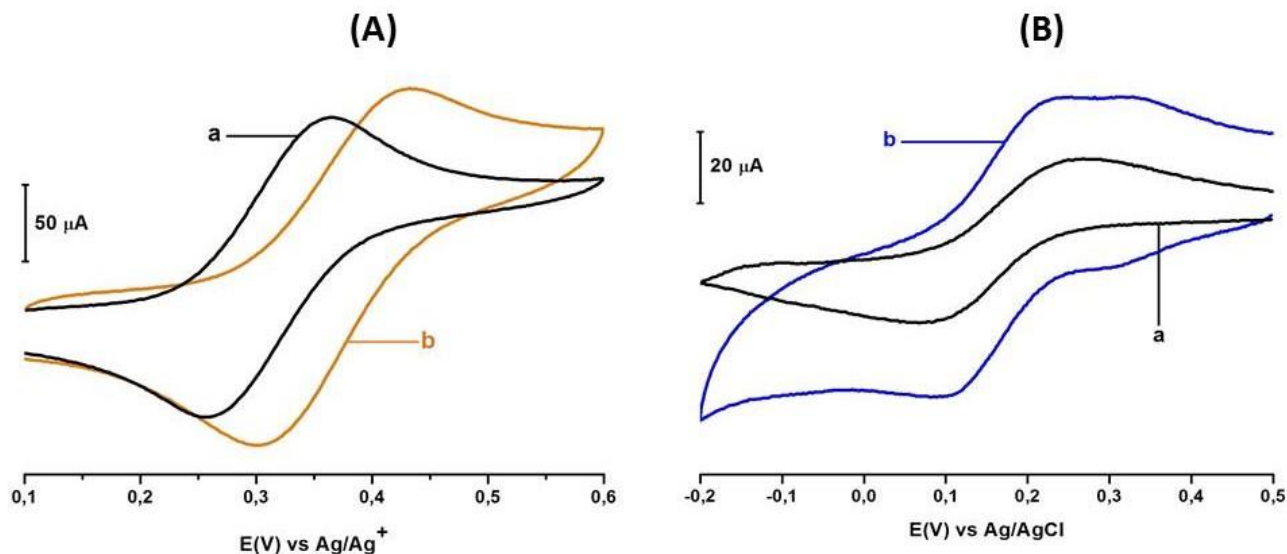


Fig. 3 Voltammograms of surface characterization A) Ferrocene, B) Ferricyanide redox probe for 3-HT (a) bare PGE, b) 3-HT modified PGE surfaces)

The voltammograms of bare PGE and 3-HT modified PGE were interpreted by superimposing ferrocene and ferricyanide redox probes using the CV technique. Since the peak currents of the 3-HT modified electrode surface were higher than the bare surface, it was decided that 3-HT modified PGE surface was more electroactive.

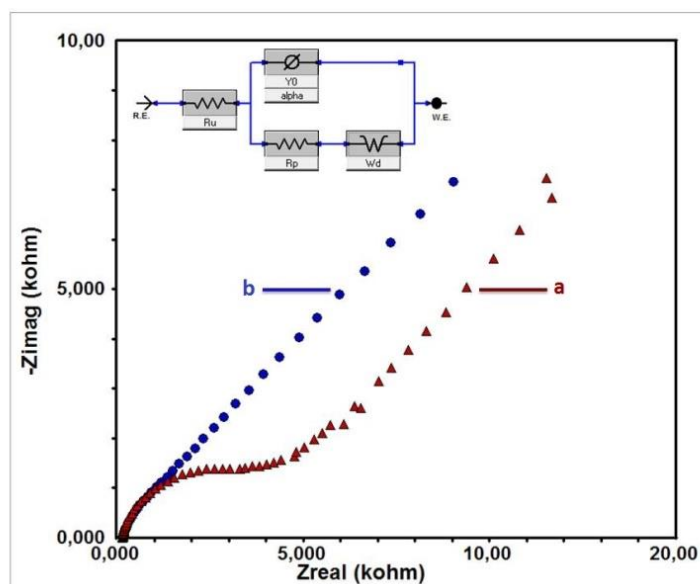


Fig. 4 Overlying Nyquist plots for electrochemical impedance spectra of (a) bare PGE and (b) 3-HT modified PGE's surfaces

Nyquist plots of bare PGE and 3-HT modified PGE were superimposed using the EIS technique at a frequency range of 100.000–0.01 Hz and a wave amplitude of 10 mV using 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple solution in 100 mM KCl solution. When the obtained Nyquist plots were examined, it was seen that the results were compatible with the ferrocene test and ferricyanide test (Figure 4).

After examining the electrochemical behavior of 3-HT on the PGE surface, 1 mM 3-HT solution was prepared in PBS (pH 7.2) and single scan voltammograms were taken with LSV technique in the potential range of +0.3 V to +1.2 V at different scanning rates (10, 25, 50, 100, 150 and 200 mV s^{-1}) and superimposed to understand whether the molecule was transported to the electrode surface in a diffusion-controlled manner (Figure 5A). The peak current (I_p) values read from the voltammograms were plotted

against the square root of the scan rates (v) ($I_p - v^{1/2}$). The linearity of the graph in Figure 5B showed that 3-HT was transported to the PGE surface in a diffusion-controlled manner during the modification.

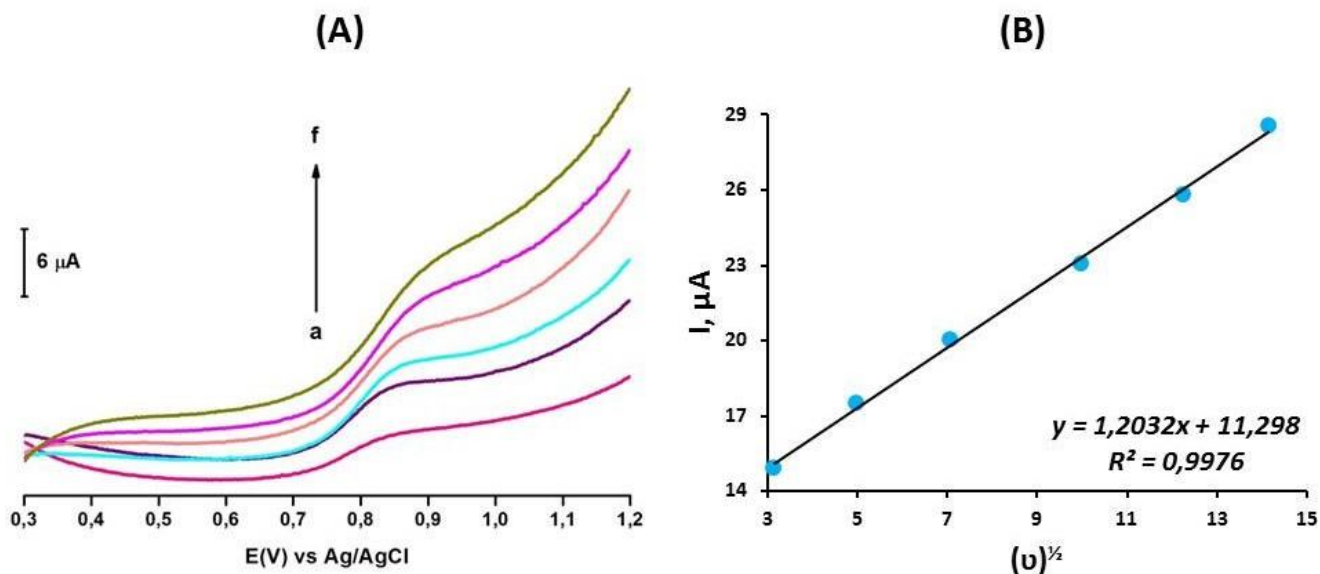


Fig. 5 **A)** LSV voltammograms on PGE surface of 3-HT at various scan rates of 10, 25, 50, 100, 150 and 200 mV s^{-1} . **B)** Graph drawn between $I_p - v^{1/2}$

3.3. Examination of 3-HT modified PGE for detectability of PAR

The usability of 3-HT modified PGE in PAR determination was investigated with SWV technique. In our previous studies, 1 mM PAR solution was prepared and used in BR buffer solution (pH 2.0) selected as optimum pH [4]. SW voltammograms of the modified electrode and supporting electrolyte were taken in the potential range of -0.2 V to +0.9 V (Figure 6). When the superimposed voltammograms using SWV technique were examined, it was seen that the peak current of PAR was approximately 0.6 V and the supporting electrolyte did not give a peak at this potential.

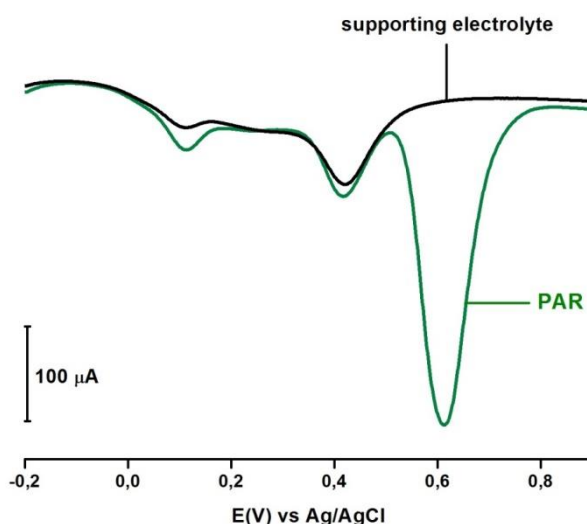


Fig. 6 Overlaid SW voltammograms of 3-HT modified PGE in the potential range of -0.2 V to +0.9 V in 1 mM PAR and supporting electrolyte solution

III. CONCLUSION

PAR is a widely used antipyretic and analgesic drug active ingredient due to its cheapness and easy availability. In this study, cyclic voltammograms were taken with CV technique on the 3-HT molecule

PGE surface in the potential range from +0.3 V to +2.0 V, at a scan rate of 100 mV s⁻¹ for 10 cycles. The modified electrode was characterized with CV and EIS techniques and the effect of the scan rate was investigated. In our study, the usability of the 3-HT modified PGE sensor electrode for the determination of PAR at pH 2.0 was investigated. In our ongoing study, the determination of PAR in different samples containing PAR is aimed.

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