

Electrochemical Studies and Square Wave Voltammetry of Paracetamol at Manganese Modified Carbon Paste Electrode

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Abstract

A square wave voltammetry (SWV) method for the determination of trace amounts of paracetamol at carbon paste electrode modified with manganese (Mn-CPE) is proposed. The results showed that the Mn-CPE exhibited excellent electro catalytic activity to paracetamol. A quasi-reversible redox process of paracetamol at the modified electrode was obtained. The concentration of paracetamol and measuring solution pH was investigated. This electrochemical sensor shows an excellent performance for detecting paracetamol with a detection limit of 6.8×10^{-10} mol.L⁻¹ with the relative standard deviation of 2.0% (n=7). The sensor was successfully applied to the determination of paracetamol in a real sample tablets with satisfactory results.

Keywords: Modified electrodes; SWV; Cyclic voltammetry; Manganese; Electrodeposition; Paracetamol

Introduction

Paracetamol (*N*-acetyl-*p*-aminophenol) is a commonly used analgesic and antipyretic drug these days [1]. Paracetamol (PC) was firstly introduced into medicine as an antipyretic/analgesic by Von Mering in 1893 and has been in use as an analgesic for home medication for over 30 years and is accepted as a very effective treatment for the relief of pain and fever in adults and children. It is the most used medicine after acetylsalicylic acid in many countries as an alternative to aspirin and phenacetin [2]. The analgesic-antipyretic effect of paracetamol is similar to aspirin, but paracetamol is normally preferred especially for the patients who are sensitive to acetylsalicylic acid [3]. Overdoses of paracetamol produce toxic metabolite accumulation that causes acute hepatic necrosis, inducing morbidity and mortality in humans [4]. Thus, it is very important to develop simple and accurate methods for detecting the paracetamol in pharmaceutical preparations.

A range of methods for the analytical determination of paracetamol have been reported in the literature such as titrimetry [5], spectrophotometry [6], spectrofluorometry [7], voltammetry [8], HPLC [9], TLC [10], colorimetry [11]. Fourier transforms infra red spectrometry [12], and many other methods are proposed for the determination of paracetamol. However, these methods suffer from some disadvantages such as high costs, long analysis times and requirement for sample pre-treatment, and in some cases low sensitivity and selectivity that makes them unsuitable for routine analysis.

Paracetamol is electroactive, and most electroanalytical techniques can be considered for the determination of paracetamol as a strong alternative to the above mentioned methods. Most electrochemical methods rely on the use of modified carbon based electrodes such as cobalt hexacyanoferrate modified graphite was composite electrodes [3], single-wall carbon nanotube-dicetyl phosphate film modified glassy carbon electrodes [13], polyaniline-multiwalled carbon nanotubes composite modified electrodes [14], carbon film resistor electrodes [15], C₆₀-modified glassy carbon electrodes [16], L-cysteine modified glassy carbon electrodes [17], carbon nanotubes based nanoelectrode arrays [18], boron-doped diamond thin film electrodes [19], pumice mixed carbon paste electrodes [20] and metalloporphyrin modified glassy carbon electrodes. However, carbon nanotube modified

electrodes have been used for detection of a variety of analytical and biological targets [20-26].

In this paper, we describe the research and development of a novel electrochemical sensor that was fabricated with manganese modified carbon paste electrodes (Mn-CPE), and the electrochemical properties of the sensor were investigated. A comparison of the voltammetric signals of paracetamol on manganese modified carbon paste electrode and bare carbon paste electrode. The results show that a Mn-CPE exhibits excellent performance for detecting paracetamol. The method is simple, rapid and sensitive and no preparation procedures were required for the analysis of paracetamol.

Experimental

Reagents

All chemicals were of analytical grade and were as received without any further purification. All solutions were prepared in double distilled water. Buffer solutions ($\mu=0.1$ M) at various pH values, were used as supporting electrolyte for the determination of paracetamol. Paracetamol and all reagents were purchased from Sigma. Carbon paste was supplied from (Carbone, Lorraine, ref 9900, French).

Preparation of the Mn-CPE

The modified carbon paste electrodes were obtained by electro deposition of manganese on a bar of carbon according to the method [21]; The cathode electrode was bar of carbon, was polished on wet Sic paper (grade 600) and immersed in H₂SO₄ solution for 5 min to dissolve the air-formed oxide film on the surface and the anode electrode was

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a platinum plate. The current was maintained by a galvanostat with a function generator. Then, the electrodes were immersed in electrolyte of manganese, and subjected to anodic oxidation by applying dc for 12 h at room temperature. The deposit of Mn on carbon surfaces was processed at 10.0 V.

Instrument

Cyclic and square wave voltammetry were carried out with a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes; using Mn-CPE as the working, platinum plate for counter and saturated Calomel (SCE) as reference electrodes. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel and French) was used for adjusting pH values.

Procedure

The initial working procedure consisted of measuring the electrochemical response at Mn-CPE at a fixed concentration of paracetamol. Standard solution of paracetamol was added into the electrochemical cell containing 50 mL of supporting electrolyte. The mixture solution was kept for 20 s at open circuit and deoxygenated by bubbling pure nitrogen gas prior to each electrochemical measurement. The square wave voltammetry was recorded in the range from -1.0 V to 1 V, for which the scan rate is 1 mV.s⁻¹, step potential 50 mv, amplitude 2 mV and duration 0.1 s. Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature.

Results

Surface characteristics

The surface structure of modified electrode was observed using scanning electron microscopy (Figure 1). On the surface of the Mn-CPE, it is recognized that manganese and carbon paste were attached and effectively modified. An examination of manganese modified carbon paste electrode indicates some kind of agglomeration [27].

Electrochemical behaviour of Mn-CPE

Figure 2 shows a cyclic voltammograms (CV) in the potential range -1 V to 2 V recorded, respectively, for carbon paste and manganese modified carbon paste electrode at 100 mV.s⁻¹. The voltammograms take different forms. No peak is observed in the case of Mn-CPE, it is recognized that carbon surface was effectively modified by manganese.

A CV was used to investigate the electrochemical behaviour of paracetamol on a Mn-CPE and a bare CPE in the buffer solution (pH-7.2) at scan rate of 100 mV.s⁻¹. At the bare CPE (Figure 3a), paracetamol shows an irreversible behaviour. However figure 3b shows, paracetamol exhibits a pair of redox waves on the Mn-CPE with E_{pa} (anodic peak potential)=0.4V and E_{pc} (cathodic peak potential)=-0.1 V. The effect of scan rates on the redox paracetamol at the manganese modified carbon paste electrode was investigated by cyclic voltammetry (Figure 4). The redox peak currents increased linearly with the scan rate in the range from 10 to 500 mV.s⁻¹ indicating that paracetamol is adsorbed onto Mn-CPE surface [27]. The linear regression equations:

$$I_{pa} = 1.0431 v + 129.39 \quad R = 0.9943$$

$$I_{pc} = -0.3026 v - 119.87 \quad R = 0.9912$$

Effect of pH

The effect of pH on the voltammetric response of paracetamol was studied in the range of pH 4.0-9.0. Figure 5 shows the cyclic voltammograms recorded at different pH values for 0.5 mM paracetamol. The pH of the solution has a significant influence on the peak potential of the catalytic oxidation of paracetamol. As can be figure 6 peak potential for paracetamol oxidation varies linearly with pH and is shifted to more negative potentials with increase in pH. The dependence of E_p on pH at manganese modified carbon paste electrode can be expressed by the relation:

$$E_p = -0.0509\text{pH} + 0.5298 \quad R^2 = 0.9831$$

The dE_p/dpH value of ~ 51 mV/pH indicates that equal number of protons and electrons are involved in the oxidation of paracetamol.

The redox mechanism of paracetamol according [27] was shown in scheme 1.

Analytical application

In order to evaluate the performance of the analytical methodology described above, the determination of paracetamol at Mn-CPE was carried out in commercial sample. The analytical curves were obtained by SWV experiments in supporting electrode (Figure 7). It was founded that the peaks currents increase linearly versus paracetamol added into the buffer solutions (Figure 8). The results obtained from the linear regression curves are included in table 1.

The reproducibility of the proposed methodology was determined from seven different measurements in the same solution containing 0.5 mM of paracetamol (Table 1).

According to Kachosangi et al. [27] the standard deviation of the mean current (S.D.) measured at reduction potential of paraquat for seven voltammograms of the blank solution in pure electrolytes was calculated from:

$$SD = \frac{1}{(n-2)} \sum_{j=0}^n (i_j - I_j)^2$$

Where, *i_j* is the experimental value of the experiment number *j* and *I_j* is the corresponding recalculated value, at the same concentration using the regression line equation. The calculated S.D. was used in the determination of the detection limit (DL, 3×S.D./slope) and the quantification limit (QL, 10×S.D./slope). From these values, the detection and quantification limits were, respectively, 1.87×10⁻⁸ mol/L and 0.57×10⁻⁷.

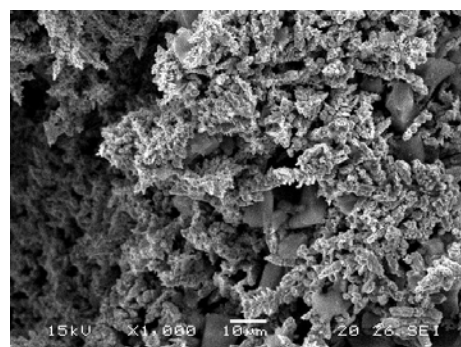


Figure 1: Scanning electron micrograph of manganese modified carbon paste electrode.

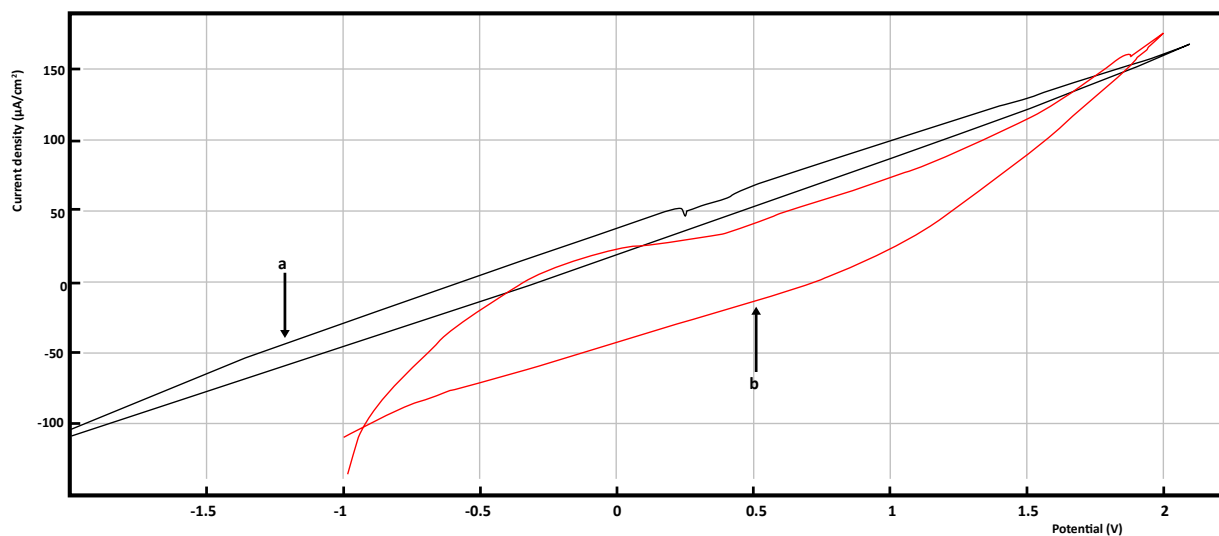


Figure 2: Cyclic voltammograms recorded for Mn-CPE (a) and bare CPE (b), in 0.1 M NaCl at 100 mV/s.

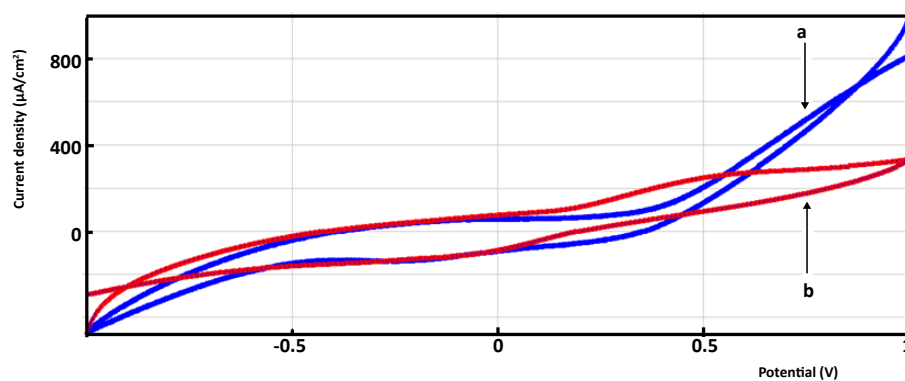


Figure 3: CVs recorded for 0.5 mM paracetamol at pH 7.2 at bare CPE (a) and Mn-CPE (b), scan rate: 100 mV/s.

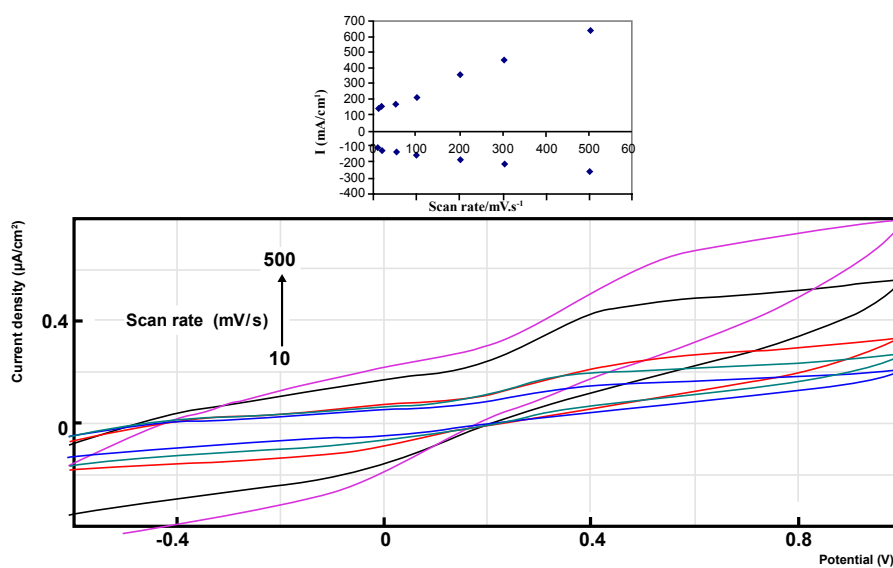


Figure 4: CVs acquired on Mn-CPE with 0.5 mM paracetamol in the buffer solution at different scan rates from 10 to 500 mV.s⁻¹. Inset is the plot of the peak current of paracetamol versus scan rate.

Conclusion

Electroanalytical techniques require only very small sample volumes, often in the microliter range. In this work, electrochemical behaviour of paracetamol was evaluated using the voltammetric measurements. A novel method is described for the determination of paracetamol which is simple, quick and sensitive with a low cost of analysis. The modifier is not soluble in water, non-toxic, and not a pollutant.

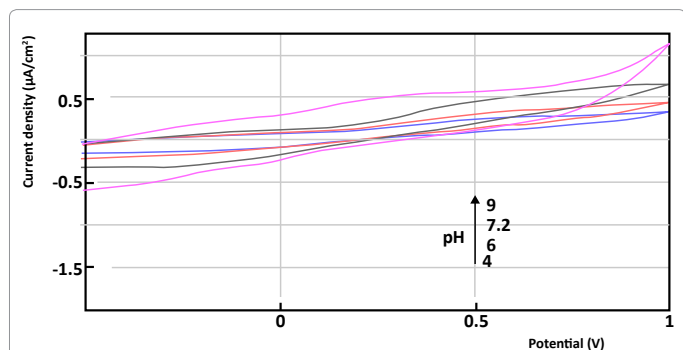


Figure 5: CVs for 0.5 mM paracetamol on Mn-CPE in buffer solution with pH values of 4, 6, 7.2 and 9.

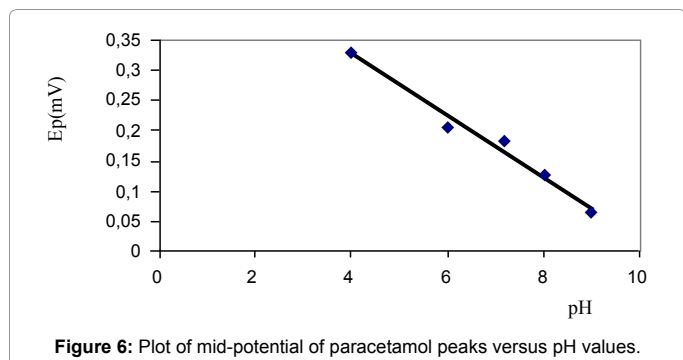


Figure 6: Plot of mid-potential of paracetamol peaks versus pH values.

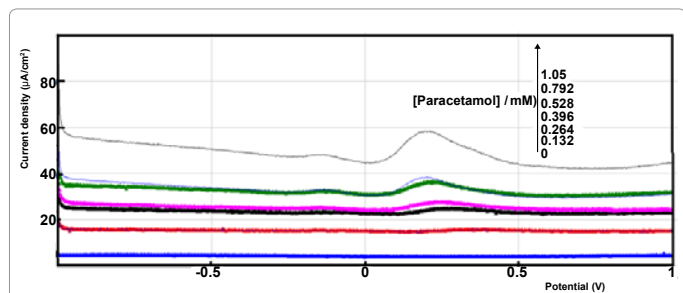
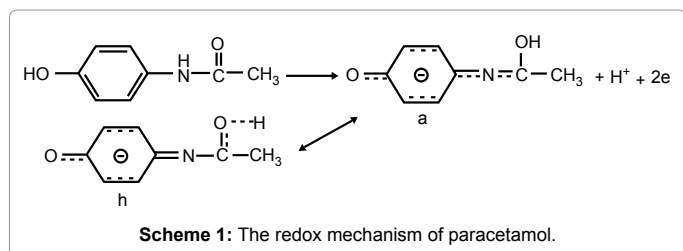


Figure 7: SWVs for additions of 0.132 mM, 0.264 mM, 0.396 mM, 0.528 mM, 0.792 mM and 1.05 mM paracetamol on a Mn-CPE in buffer solution (pH 7.2).

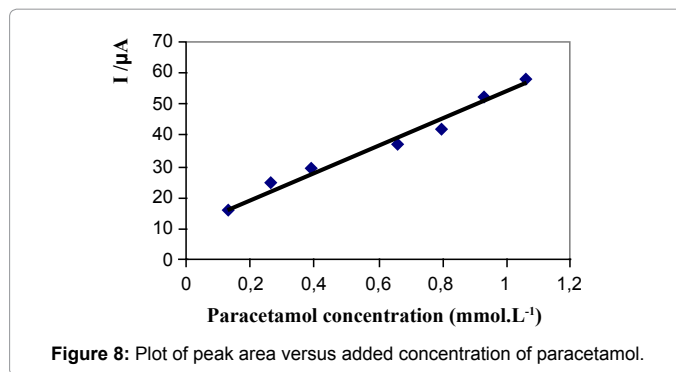


Figure 8: Plot of peak area versus added concentration of paracetamol.

| Parameters | Value |
|--|--------|
| R ² | 0.9895 |
| Slope (µA/mM) | 43.45 |
| Standard Deviation (x10 ⁻¹ A) | 36.15 |
| Relative Standard Deviation | 1.97 |

Table 1: Results obtained from the linear regression curves I=f([paracetamol]) for the determination of paracetamol at Mn-CPE.

The results obtained here show that the proposed SWV method is fast and better suits than conventional methods, like spectrophotometry or chromatography, to characterizing fast variations in concentration of dilute paracetamol aqueous solutions.

The observed reproducibility of the proposed methodology was below 2.0%. These values are considered to very satisfactory, thus confirming the practicality of the proposed method.

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