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A natural phosphate based electroanalysis sensor for sensitive detection of paracetamol

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ABSTRACT

An electrochemical sensor based on the electrocatalytic activity of functionalized natural phosphate for sensitive detection of paracetamol is presented. The electrochemical behaviors of paracetamol on natural phosphate modified carbon paste electrode (NP-CPE) were investigated by cyclic voltammetry and square wave voltammetry. The results showed that the natural phosphate modified electrode exhibited excellent electrocatalytic activity to paracetamol. A quasi-reversible redox process of paracetamol at the modified electrode was obtained. Such electrocatalytic behavior of natural phosphate is attributed to its unique physical and chemical properties, subtle electronic characteristics, attractive interaction, and strong adsorptive capability. This electrochemical sensor shows an excellent performance for detecting paracetamol. The sensor shows great promise for simple, sensitive, and quantitative detection and screening of paracetamol.

KEYWORDS

Modified electrodes;
Cyclic voltammetry;
Natural phosphate;
Paracetamol.

INTRODUCTION

It is very important to develop simple, sensitive, and accurate methods for detecting active ingredients since drug monitoring plays an important role in drug quality control, and this has a great impact on public health. 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 infrared 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[20-27]. In this paper, we describe the research and development of a novel electrochemical sensor that was fabricated with natural phosphate modified carbon paste electrodes (NP-CPE), and the electrochemical properties of the sensor were investigated. A comparison of the voltammetric signals of paracetamol on natural phosphate modified carbon paste electrode (NP-CPE) and bare carbon paste electrode. The results show that a NP-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

Apparatus and software

Voltammetric experiments were performed using 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) run under windows 2007. The three electrode system consisted of a chemically modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of Natural Phosphate (NP). The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was 0.1256cm2. Electrical contact was made at the back by means of a bare carbon.

Procedure

The initial working procedure consisted of measuring the electrochemical response at NP-CPE at a fixed concentration of paracetamol. Standard solution of paracetamol was added into the electrochemical cell containing 100 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 cyclic voltammetry was recorded in the range from -0.7 V to 1 V.

Optimum conditions were established by measuring the peak currents in dependence on all parameters. The square wave voltammetry (SWV) was recorded in the range from -0.7 V to1 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. All experiments were carried out under ambient temperature.

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RESULTS AND DISCUSSION

Surface characteristics

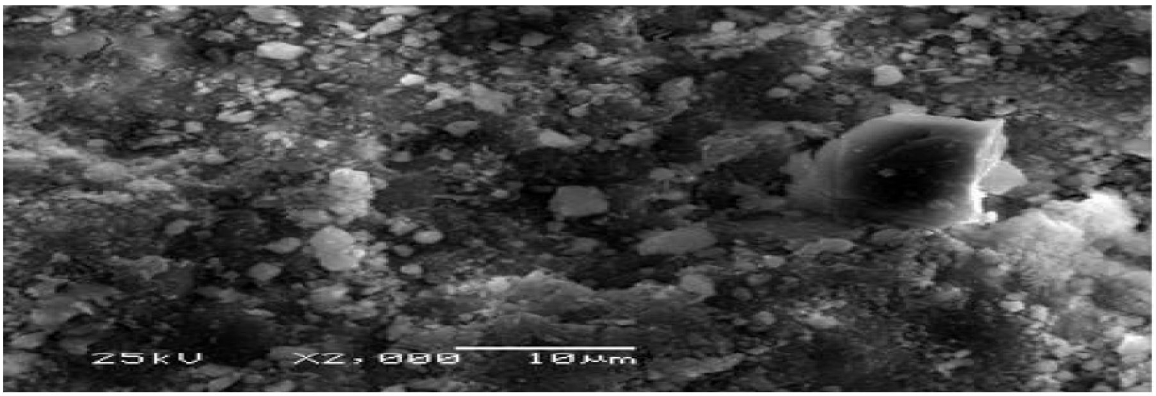
The surface structure of natural phosphate electrode was observed using scanning electron microscopy (Figure 1).

Voltammetric behavior of paracetamol

Cyclic voltammetry

Figure 2 shows a cyclic voltammograms (CV) in the potential range -0.7 V to 1 V recorded, respectively, for carbon paste and natural phosphate modified carbon paste electrode at 100mV.s^{-1}. The voltammograms take different forms. No peak is observed in the case of NP-CPE, it is recognized that carbon surface was effectively modified by natural phosphate.

Figure 3b shows as paracetamol exhibits a pair of well-defined redox waves on the NP-CPE with Epa = 0.26V and Epc = -0.1 V.



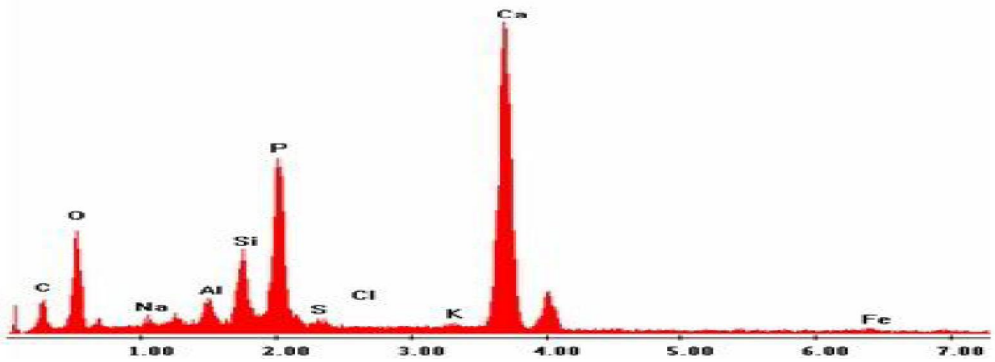


Figure 1 : Scanning electron micrograph of natural phosphate

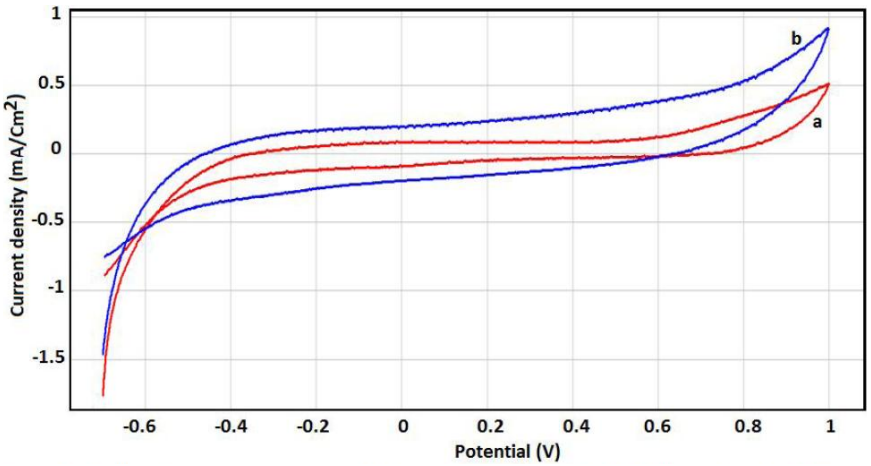


Figure 2 : Cyclic voltammograms recorded for CPE (a) and bare NP-CPE (b), in 0.1 M K_2SO_4 at 100 mV/s

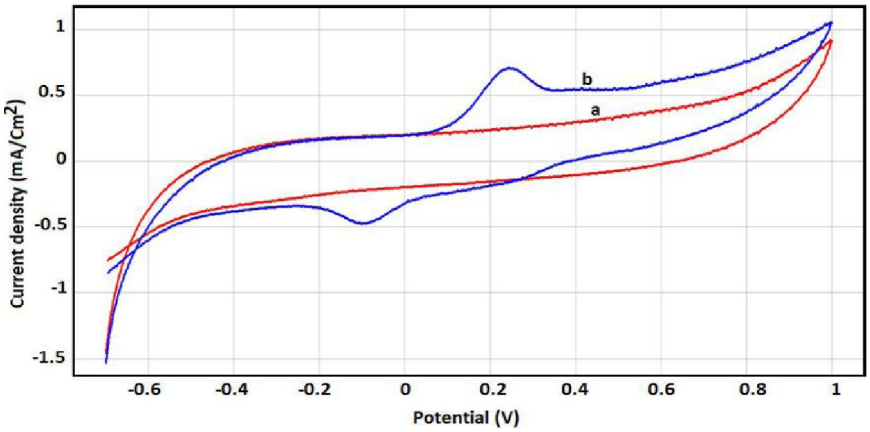


Figure 3 : CVs recorded for 2.64 mM paracetamol at pH=7 at bare NP-CPE (a) and NP- CPE/paracetamol (b), scan rate 100 mV/s, preconcentration time (tp)= 2min

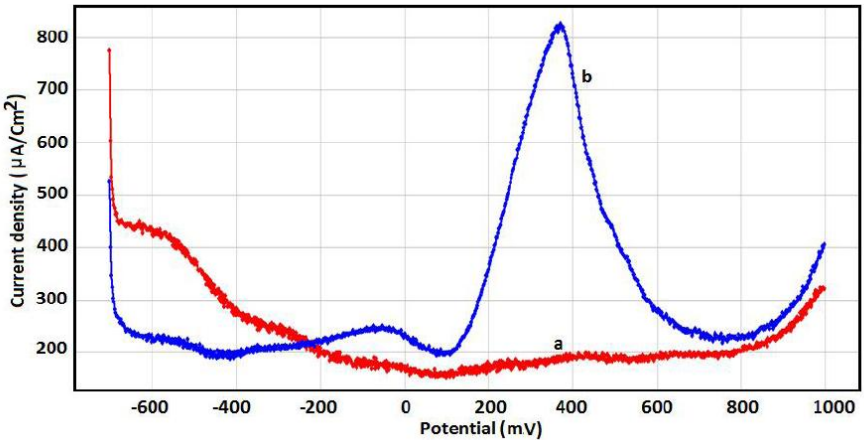
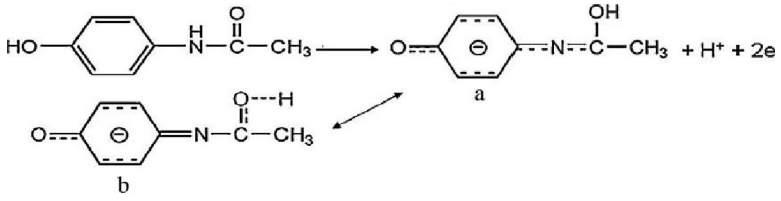


Figure 4 : SWV recorded for 2.64 mM paracetamol at pH=7 at bare NP-CPE (a) and NP- CPE/paracetamol (b), preconcentration time (tp)= 2min



Scheme : The redox mechanism of paracetamol

Square wave voltammetry

The pulse technique, square wave voltammetry is used for the further determination of paracetamol as it has several advantages including excellent sensitivity and the rejection of background currents. The square wave voltammograms recorded for 2.64mM paracetamol at bare NP-CPE in K_2SO_4 buffer solution at pH 7 are illustrated in Figure 4, this figure shows an oxidation peak at 0.33V paracetamol potential and a reduction peak potential to 0.1V.

The redox mechanism of paracetamol at NP-CPE

According to the discussion mentioned above, the redox of paracetamol belongs to a two-electron and one-proton process, and the possible redox mechanism of paracetamol on the NP-CPE was shown in scheme. During the redox process of paracetamol, the electric system was exchanged with p–π conjugation (reactant) and π – π conjugation (product). Compared with the reactant, the energy level of the product decreased, and the product was more stable, which may be because of the easily formed π – π interaction between the product molecules and the phosphate modified carbon paste elec-

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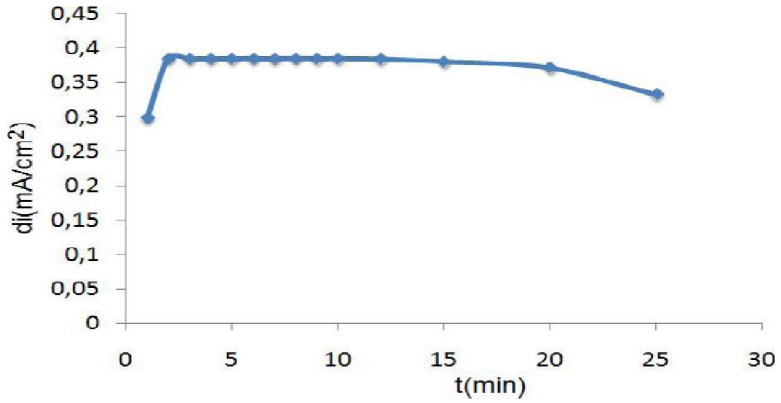

Figure 5 : Effects of accumulation time on oxidation peak currents of 3.96 mmol L^{-1} paracetamol at NP-CPE, supporting electrolyte is K_2SO_4 0.1M (pH=7)

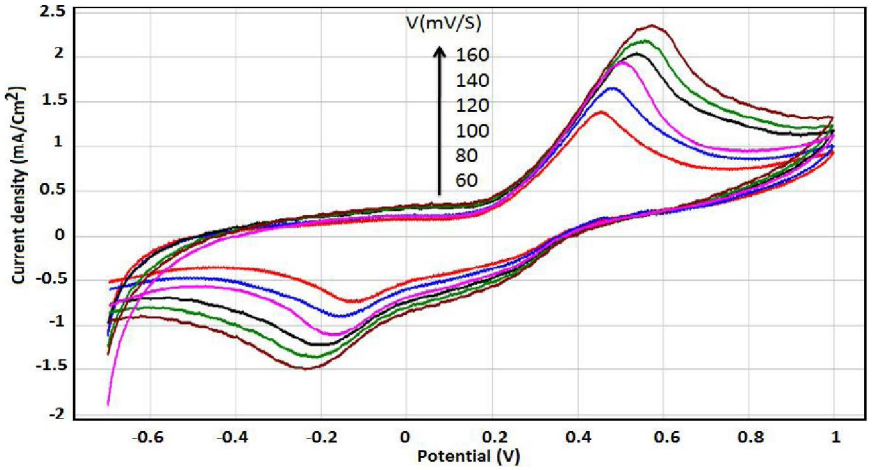

Figure 6 : CVs acquired on NP-CPE with 5.28 mM paracetamol in the buffer solution at different scan rates from 60 to 160mV.s^{-1}. Inset is the plot of the peak current of paracetamol versus scan rate

trode

Optimization of experimental conditions

Optimum conditions for the electrochemical response were established by measuring the peak current in dependence on all parameters.

Influence of accumulation time

The effect of the accumulation time is investigated (Figure 5); this significantly affects the oxidation peak current of paracetamol. The peak current of 3.96 mmol L^{-1} paracetamol increases greatly within the first 2min. Further increase in accumulation time does not increase the amount of paracetamol at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of NP-CPE that improves the ability of the electrode to adsorb electroactive paracetamol. Maybe this is attributed to the saturated adsorption of paracetamol on the NP-CPE surface. Taking account of sensitivity and efficiency, accumulation time was 2 min in the following experiments.

Effect of scan rate

The effect of scan rates on the redox paracetamol at the natural phosphate modified carbon paste electrode was investigated by cyclic voltammetry (Figure 6). The redox peak currents increased linearly with the scan rate in the range from 60 to 160mV.s^{-1} indicating that paracetamol is adsorbed onto NP-CPE surface.

The Figure 7 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of paracetamol at NP-CPE.

Calibration graph

A Figure 8 shows the CV curves of different concentration of paracetamol at NP-CPE was in-

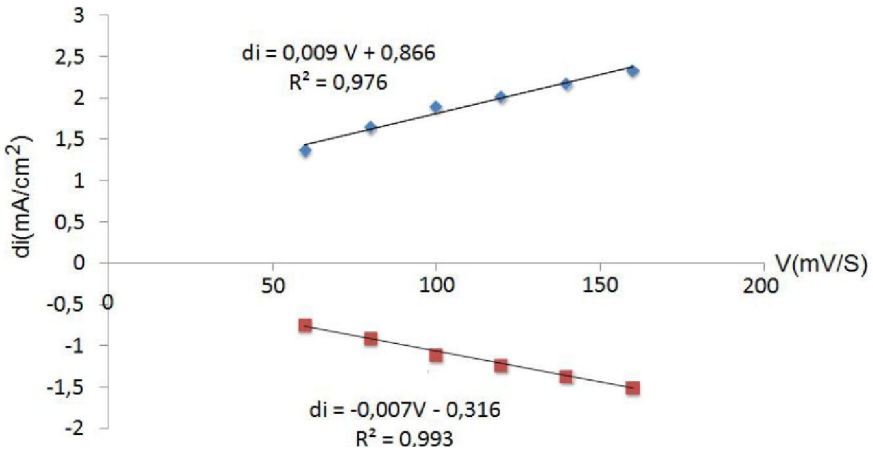

Figure 7 : Plot of peaks area versus scan rate

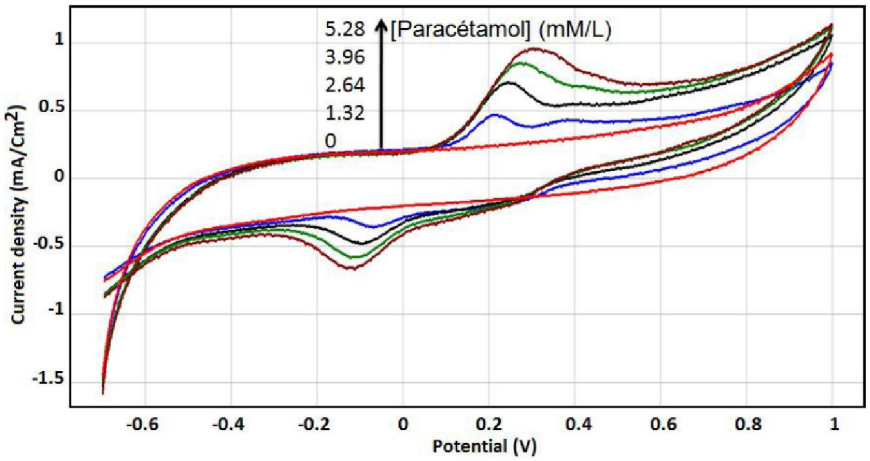

Figure 8 : Cyclic Voltammograms of different concentration of paracetamol (1.32mM to 6.6mM) at NP/CPE in 0.1 M K_2SO_4 PH=7, Scan rate 100 mV/s

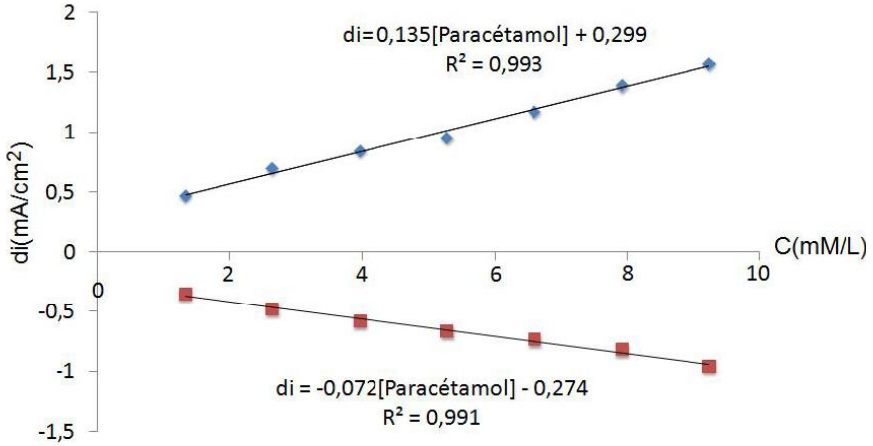

Figure 9 : Plot of peaks area versus added concentration of paracetamol

creased from 1.32 mM to 5.28 mM at pH 7. Both the anodic and cathodic peak current increases linearly with the concentration of paracetamol. The calibration curve for the CV peak current for paracetamol oxidation and reduction vs. paracetamol concentration, Figure 9 shows excellent linearity. Modification of carbon paste surface by natural phosphate remarkably improves the reactivity of NP-CPE towards the oxidation and reduction of paracetamol.

Influences of pH

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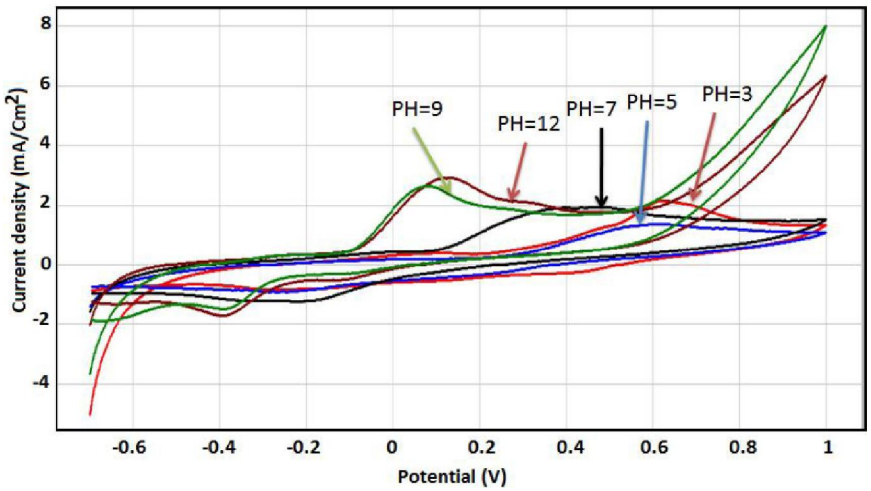

Figure 10 : Cyclic Voltammograms of different pH on the oxidation and the reduction of paracetamol at the NP modified CPE

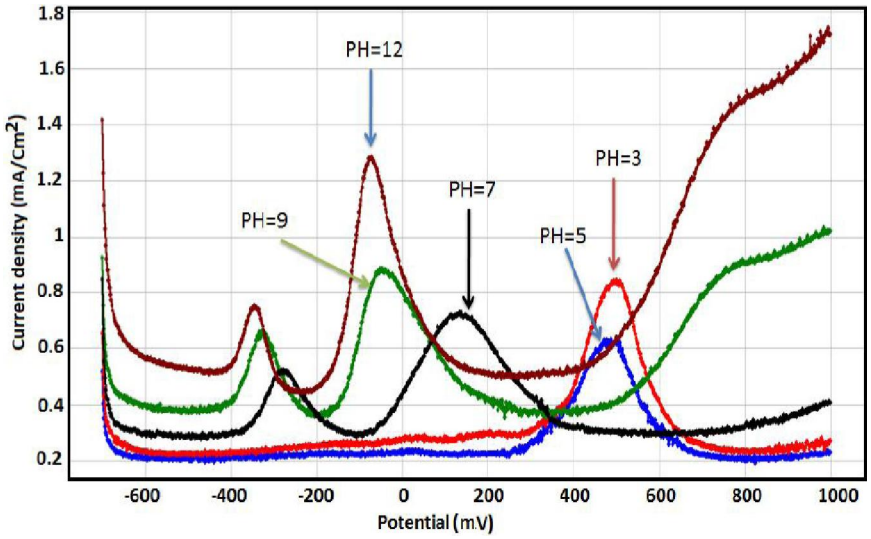

Figure 11 : Effect of pH on the oxidation of paracetamol at the phosphate modified CPE

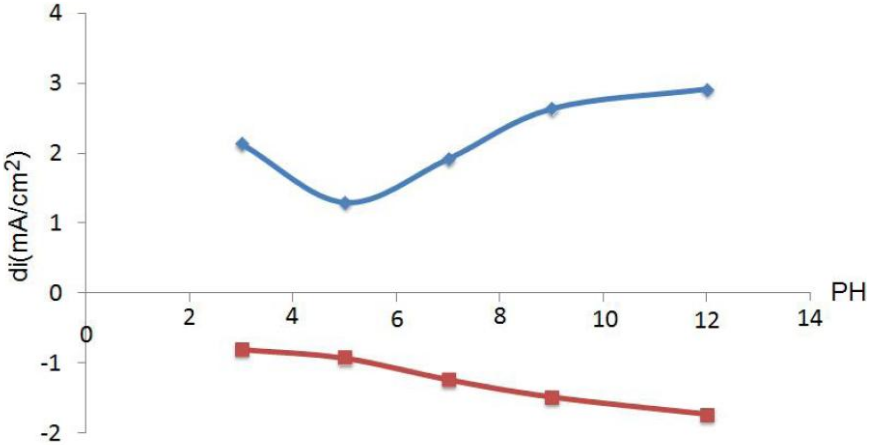

Figure 12 : Plot of the relationship between solution pH and the oxidation and reduction peak current

The effect of pH on the voltammetric response of paracetamol was studied in the range of pH 3-12. Figures (10,11) shows respectively the cyclic voltammograms and square wave voltammograms recorded at different values of pH to 6.24 mM paracetamol. The pH solution has a significant in-

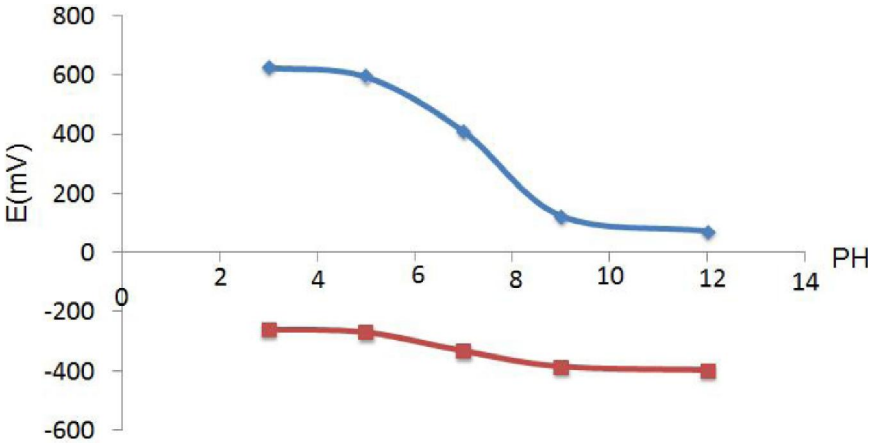

Figure 13 : Plot of mid-potential of paracetamol peaks versus pH values

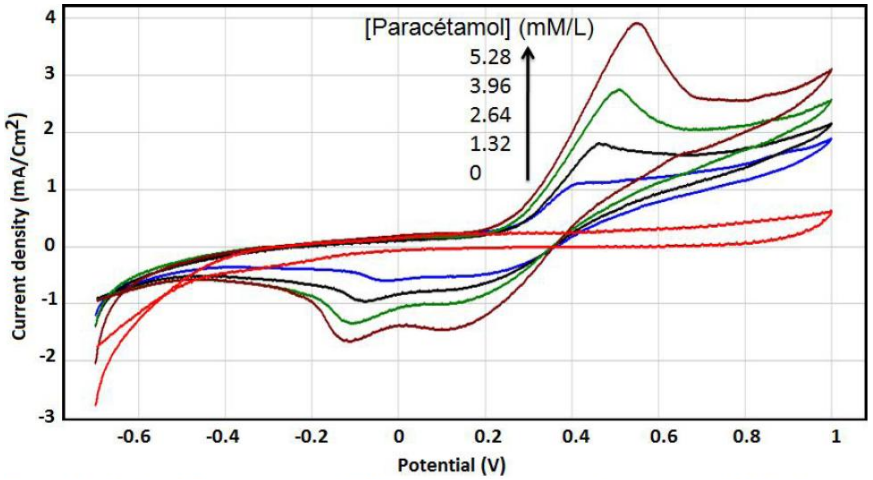

Figure 14 : Cyclic Voltammograms of different concentration of paracetamol (1.32mM to 6.6mM) at NP/CPE, Scan rate 100 mV/s

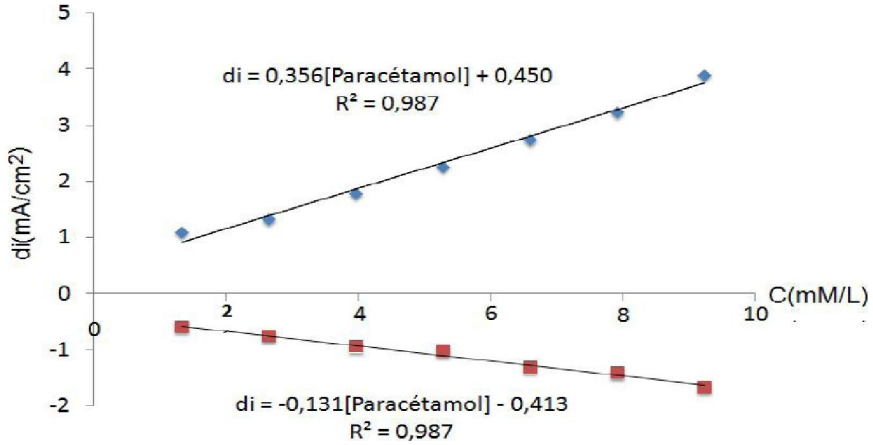

Figure 15 : Plot of peaks area versus added concentration of paracetamol

fluence on the peak current and the peak potential of the catalytic oxidation peak and the reduction peak of paracetamol. Figures (12,13) shows respectively the effect of pH on the current density and the peak potential for paracetamol oxidation and reduction.

PRACTICALAPPLICATION

The proposed method was applied to the determination of commercial paracetamol (doliprane

500mg) formulations. The tablets were weighed and finely pulverized.

The analytical curves were obtained by CV experiments in supporting electrode (Figure 14). It was founded that the peaks currents increase linearly versus paracetamol added into the buffer solutions (Figure 15). The analysis of the obtained responses allowed concluding that the drug excipients do not significantly interfere with the proposed method.

CONCLUSION

A novel method is described for the determination of paracetamol which is simple, quick and sensitive with a low cost of analysis. Thus, the proposed method using cyclic voltammetry is of beneficial use in analytical applications and in fundamental studies of electrode mechanisms.

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