

Cyclic voltammetric determination of 4-chloroaniline using natural phosphate modified carbon paste electrode

Tarik El ouafy, Abdelilah Chtaini*, Hassan Oulfajrite, Rachida Najih

Equipe d'Electrochimie Moléculaire et Matériaux Inorganiques, Faculté des Sciences et Techniques de Beni Mellal,
Université Sultan Moulay Slimane (MAROC)

E-mail : a.chtaini@usms.ma

ABSTRACT

A carbon paste electrode modified with natural phosphate (NP) was evaluated as an electrochemical sensor for 4-Chloroaniline (4-CA) in aqueous medium. The electrode was prepared by mixed natural phosphate and carbon powder. The influence of accumulation time and pH of the electrolytic solution were investigated. The calibration graph obtained under the optimized conditions was linear. The natural phosphate modified carbon paste electrode was applied to the determination of 4-CA in natural water samples. The results indicate that this electrode is sensitive and effective for the determination of 4-CA. © 2015 Trade Science Inc. - INDIA

KEYWORDS

4-Chloroaniline;
Cyclic voltammetry;
EIS;
Electrochemical detection;
Natural phosphate.

INTRODUCTION

Environmental pollution caused by the release of a wide range of compounds as a consequence of industrial progress has now assumed serious proportions. Thousands of hazardous wastes sites have been generated worldwide resulting from accumulation of xenobiotics in soil and water over the years^[1]. Anilines are extensively used in many industrial processes as solvents, as precursors for amino aromatic derivatives and in synthesis of dyes, plasticizers, pharmaceuticals, pesticides, polymers including polyurethane and rubber additives, photographic chemicals and varnishes^[2]. They are also formed during microbial transformation of nitroaromatic compound found in explosives, dinitroaniline, urea herbicides and nitropyrenes^[3]. For many years chloroanilines have been one of the most important industrially produced amines. In recent years, they have attracted increasing attention owing to their

widespread use, ubiquity in the environment and endocrine disrupting activity^[4]. As a consequence of this widespread use, they are detected in many industrial waste waters^[5]. 4-Chloroaniline is particularly toxic to aquatic organisms, which is due to their impediment on the oxygen carrying capacity of the blood supply; thus effectively suffocating the aquatic organisms^[6]. The primary toxic effect resulting from acute exposure to 4-chloroaniline, by inhalation or by oral route, is methemoglobinemia, usually accompanied with anoxia, erythrocyte damage and spleen effects^[7]. The environmental fate of chloroanilines is affected by a number of physicochemical processes, including evaporation, photo-oxidation and chemical binding^[8]. However, biodegradation is the main mechanism of chloroaniline removal in aquatic environment^[9]. In soils, mineralization of chloroanilines may occur slowly^[10] or they may react to form recalcitrant molecules such as azobenzenes and triazenes^[11]. *Moraxella* sp. strain G^[12-14] was the first strain

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isolated that could use 4-chloroaniline as sole source of carbon and energy. Other bacterial species such as *Pseudomonas*^[15-17], *Frauteria*^[18], *Delftia* sp. AN3^[19] and so many others have also been implicated. In this work, we present a simple and sensitive method of determination of 4-Chloroaniline based on their reaction.

EXPERIMENTAL

Reagent

4-Chloroaniline, sodium sulfate, and nitric acid were of analytical grade and from Aldrich.

A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco). Stock solutions of 4-Chloroaniline were prepared by dissolving 4-Chloroaniline in deionized water. All preparations and dilution of solutions were made with deionized water.

Provisions were made for oxygen removal by bubbling the solution with azotes gas for about 5 min then the solution was blanketed with azotes gas while the experiment was in progress. For reproducible results, a fresh solution was made for each experiment.

Instrumental

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. 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 measur-

ing the electrochemical response at NP-CPE at a fixed concentration of 4-CA. Standard solution of 4-CA 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 -1 V to 1,7 V.

Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature.

RESULTS AND DISCUSSION

Voltammetric and EIS of 4-Chloroaniline

Cyclic voltammetry

Figure 1 shows a cyclic voltammograms (CV) in the potential range -1 V to 1.7 V recorded, respectively, for carbon paste and natural phosphate modified carbon paste electrode at 100 mV.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 2b shows as 4-CA exhibits a pair of well-defined redox waves on the NP-CPE with

$E_{pa(1)} = 0.34V$, $E_{pa(2)} = 0.75$ and $E_{pc(3)} = 0.025$ V.

Electrochemical impedance spectroscopy (EIS)

An impedance spectroscopy study was performed in order to confirm the results obtained by the cyclic voltammetry tests. Figures 3 show the impedance diagram recorded for NP-CPE and NP-CPE/4-CA (1.96mM) respectively. at the absence of 4-CA EIS is right which means that there is a diffusion at the surface of the NP-CPE, for the presence of 4-CA the impedance curve observed decrease of the charge-transfer resistance means also that the modified electrode becomes more conductive, which can be explained by the presence of 4-CA.

Influence of accumulation time

The effect of the accumulation time is investigated

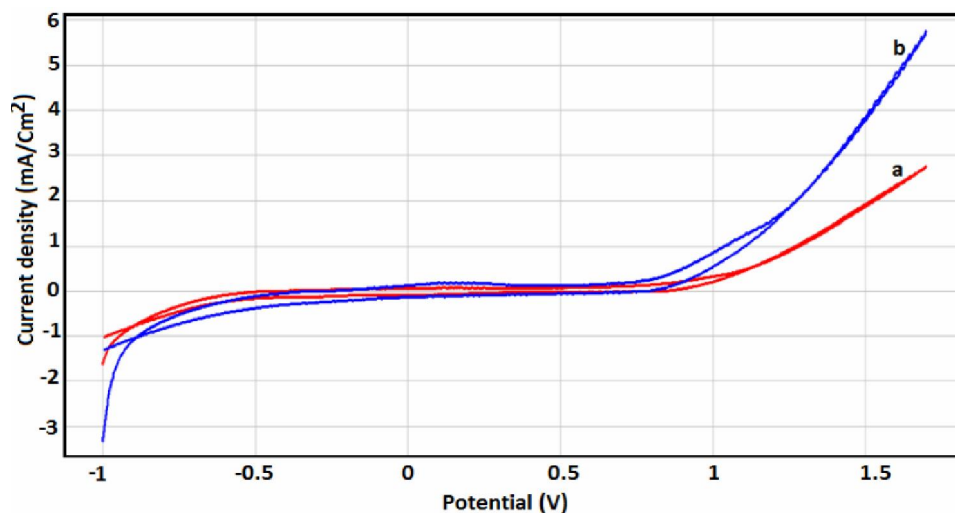


Figure 1 : Cyclic voltammograms recorded for CPE (a) and bare NP-CPE (b), in 0.1 M Na_2SO_4 at 100 mV/s

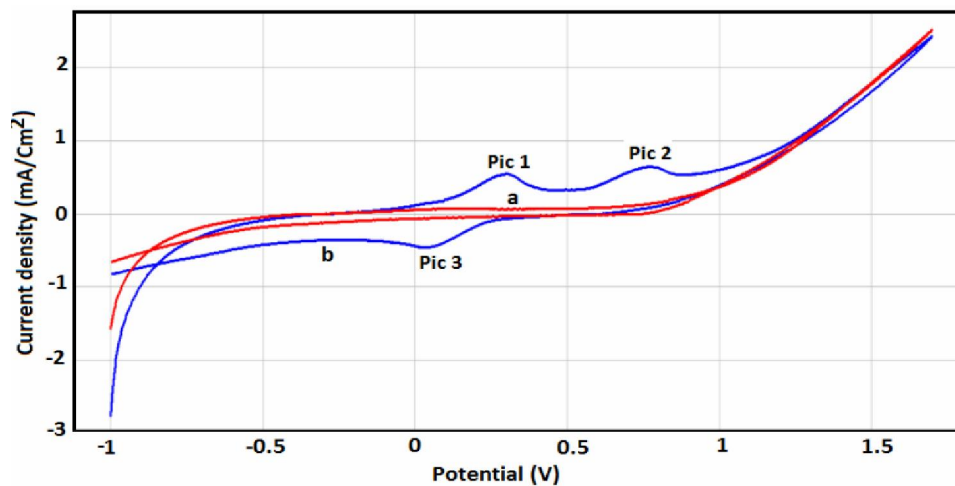


Figure 2 : CVs recorded for 0.78 mM 4-CA at pH=7 at bare NP-CPE (a) and NP-CPE/4-CA (b), scan rate 100 mV/s, preconcentration time (t_p)= 9min

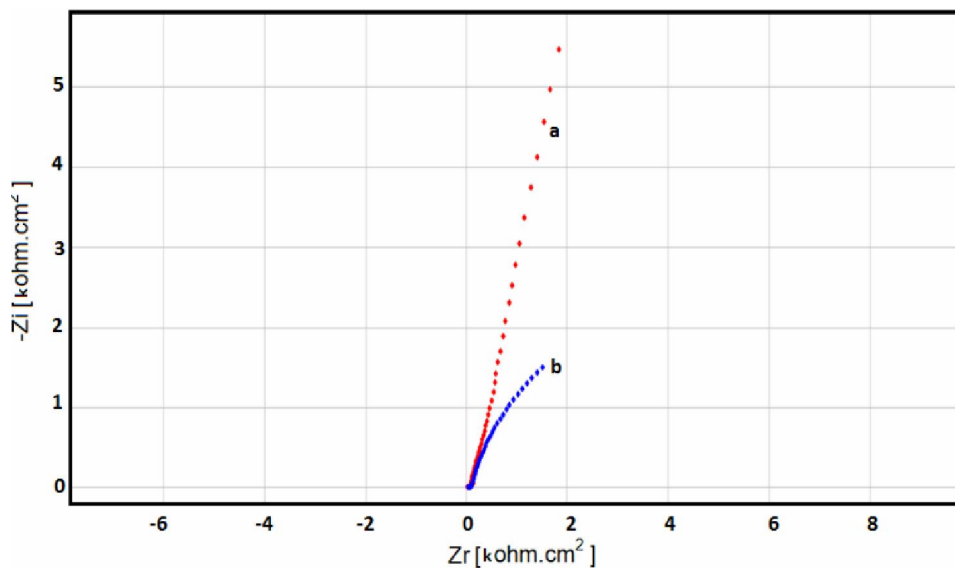


Figure 3 : Impedance spectra at 0 V C-CPE (a) and (4-CA)-C-CPE (b)

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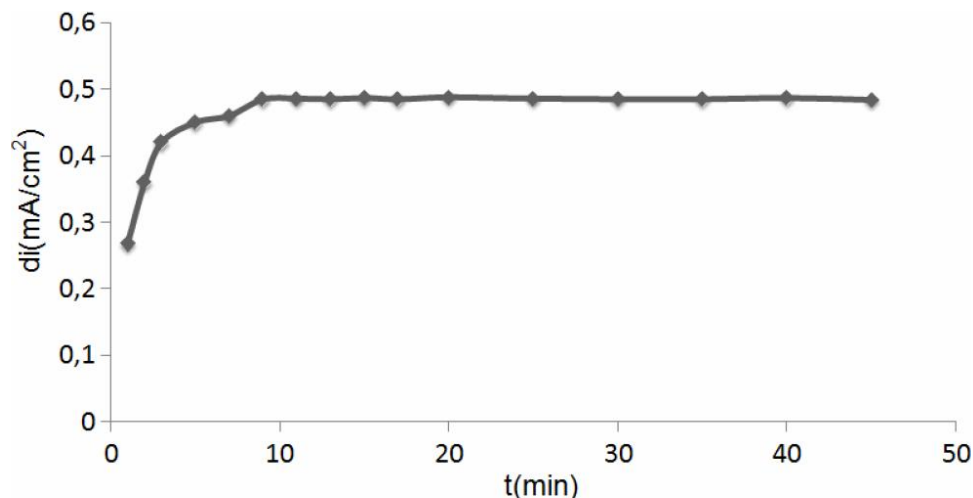


Figure 4 : Effects of accumulation time on oxidation peak currents of 0.4 mmol L^{-1} 4-CA (pH=7) at NP-CPE, supporting electrolyte is Na_2SO_4 0.1M

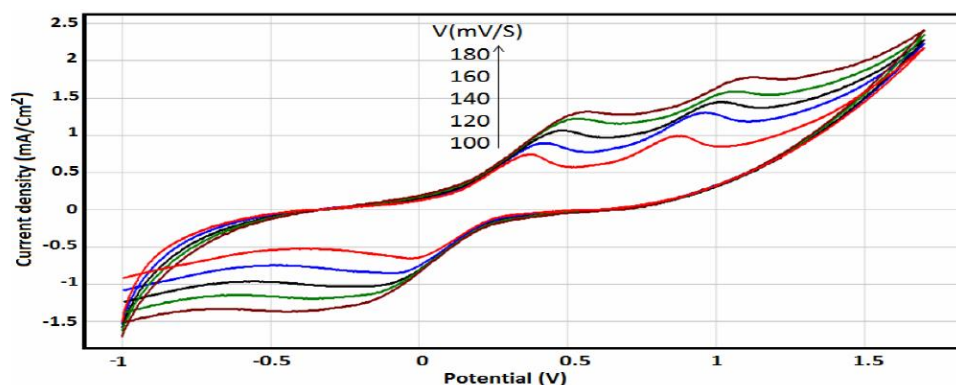


Figure 5 : CVs acquired on NP-CPE with 0.78 mM 4-CA in the buffer solution at different scan rates

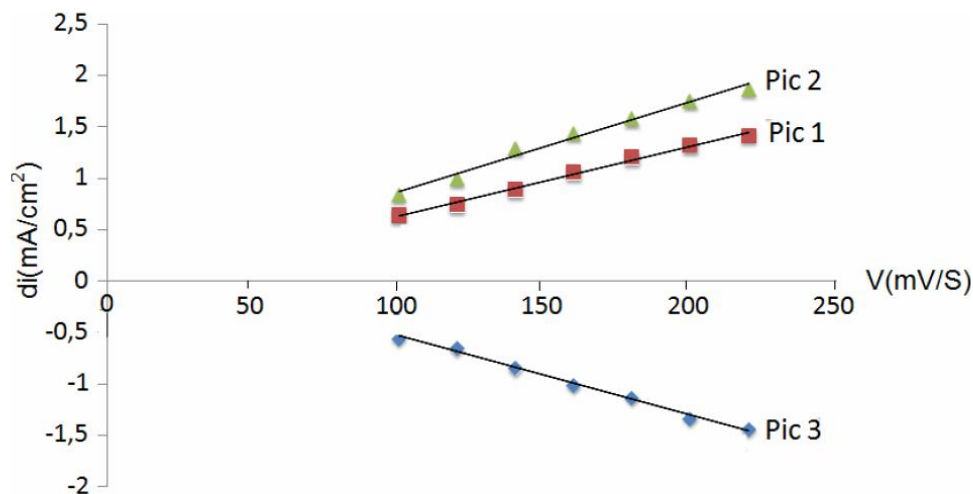


Figure 6 : Plot of peaks area versus scan rate

(Figure 4), this significantly affects the oxidation peak (Pic 1) current of 4-CA. The peak current of 0.4 mmol L^{-1} 4-CA, increases greatly within the first 9 min. Further increase in accumulation time does not increase the amount of 4-CA 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 4-CA. Maybe this is attributed to the saturated adsorption of 4-CA on the NP-

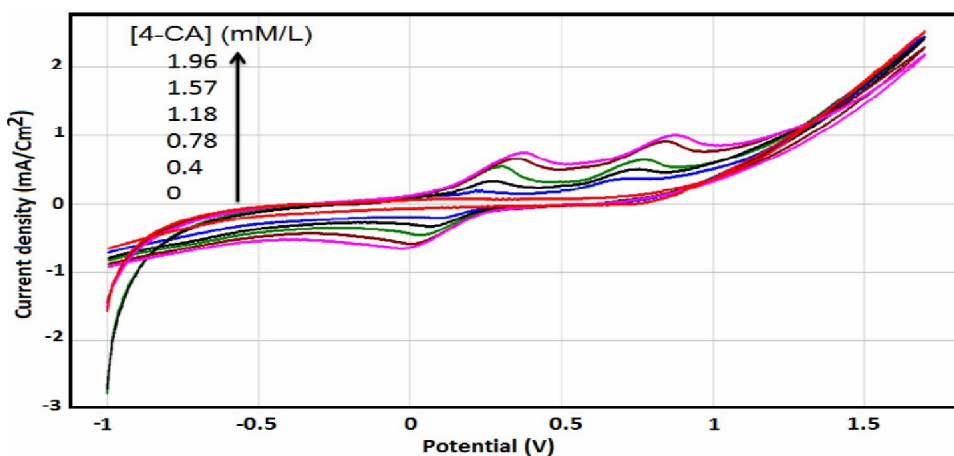


Figure 7 : Cyclic voltammograms of different concentration of 4-CA at NP-CPE in 0.1 M Na₂SO₄ pH=7, Scan rate 100 mV/s

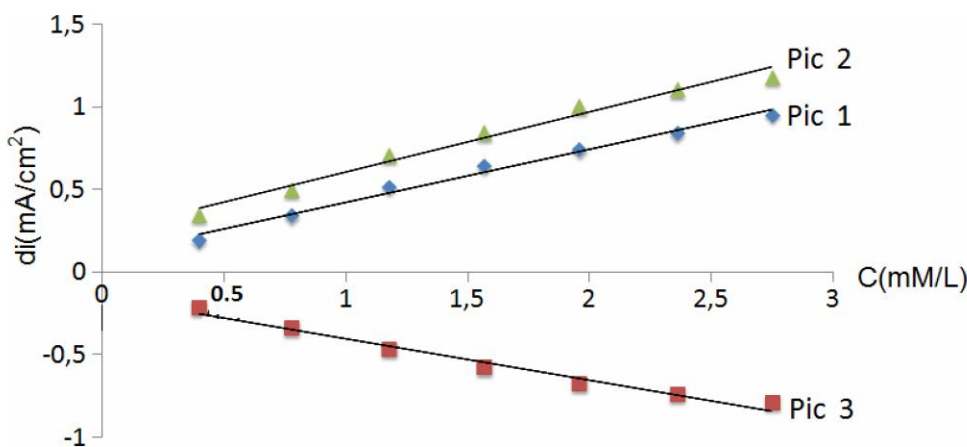


Figure 8 : Plot of peaks area versus added concentration of 4-CA

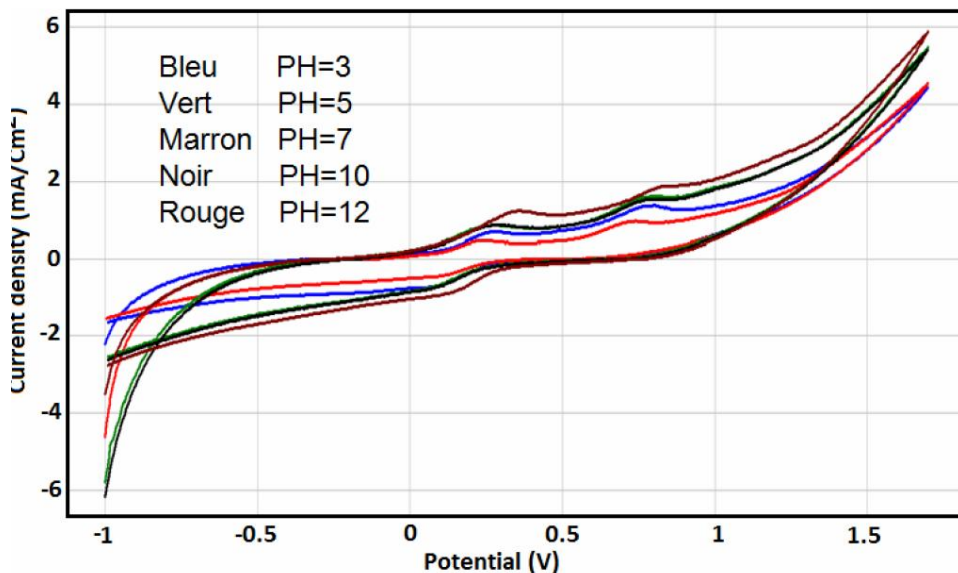


Figure 9 : CV of effect of pH on the redox of 4-CA at the NP-CPE

CPE surface. Taking account of sensitivity and efficiency, accumulation time was 9 min in the following experiments.

Effect of scan rate

The influences of scan rate on the redox of 4-CA was examined in 0.1 M Na₂SO₄ buffer solution of pH=7

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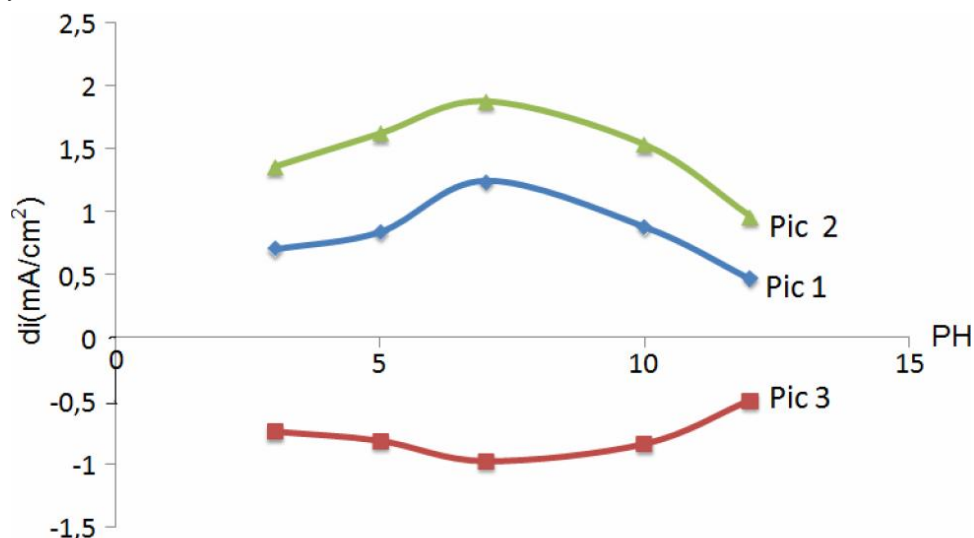


Figure 10 : Plot of the relationship between solution pH and the redox peak current

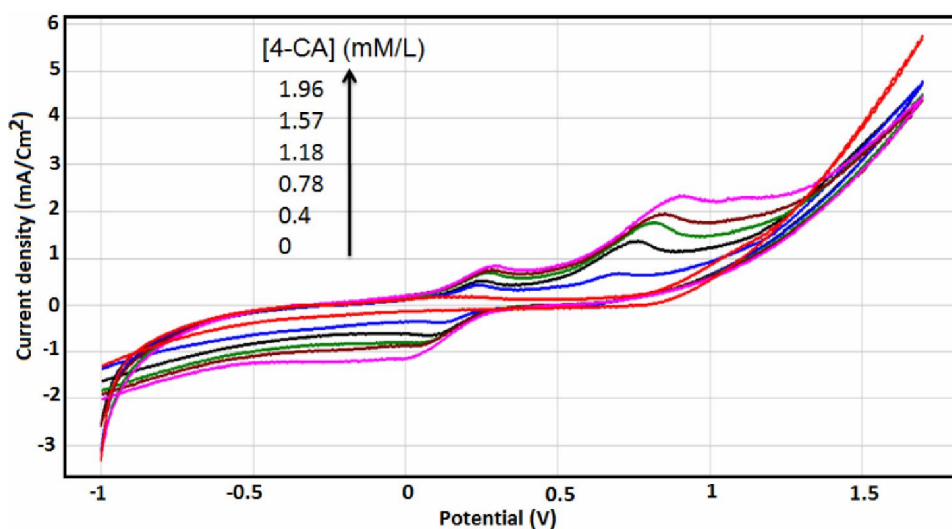


Figure 11 : Cyclic voltammograms of different concentration of 4-CA at NP-CPE in tap water

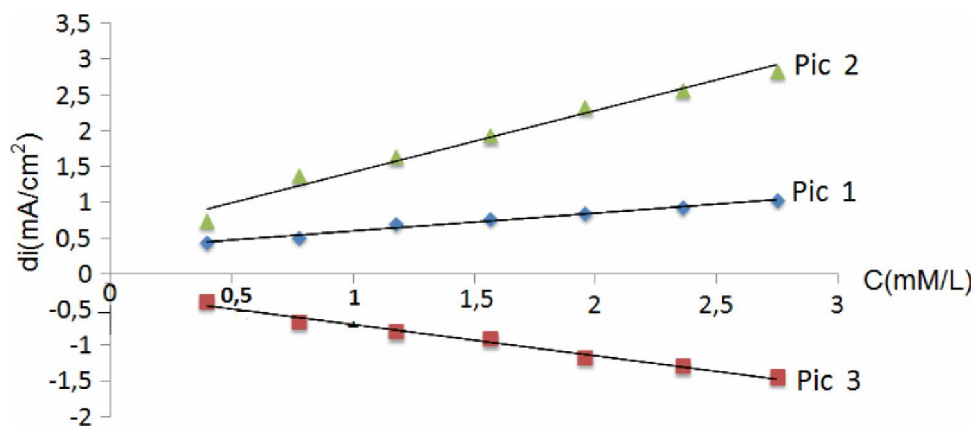


Figure 12 : Plot of peaks area versus added concentration of 4-CA

as a supporting electrode. The Figure 5 shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 100 to 180 mVs^{-1} .

The Figure 6 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of 4-CA at C-CPE. The linear regression equations:

$$I_{pa}(1)=0.006V-0.043 \quad R^2=0.994$$

$$I_{pa}(2)=0.008V-0.005 \quad R^2=0.983$$

$$I_{pc}(3)=-0.007V+0.223 \quad R^2=0.994$$

Calibration graph

Figure 7 show the CV curves of different concentration of 4-CA at NP-CPE was increased from 0.4 mM to 1.96 mM in 0.1 M Na₂SO₄ buffer solution at pH=7 at a sweep rate of 100 mVs⁻¹. Both the anodic and cathodic peak, current increases linearly with the concentraton of 4-CA. The Figure 8 shows the linear relationship between the 4-CA concentration and the anodic peak and the cathodic peak currents. The linear regression equations:

$$I_{pa}(1)=0.320 [4-CA] +0.097 \quad R^2=0.987$$

$$I_{pa}(2)=0.362 [4-CA] +0.244 \quad R^2=0.981$$

$$I_{pc}(3)=-0.249 [4-CA] -0.150 \quad R^2=0.976$$

Effect of pH

The Figure 9 shows the cyclic voltammograms of the 4-CA at different pH. The current of the peak depend on the solution pH. The Figure 10 shows the graph of different pH versus peak current.

ANALYTICAL APPLICATION

In order to evaluate the performance of NP-CPE by practical analytical applications, the determination of 4-CA was carried out in tap water. The analytical curves were obtained by CV experiments in supporting electrode (Figure 11). It was founded that the peaks currents increase linearly versus 4-CA added into the buffer solution (Figure 12). The linear regression equations:

$$I_{pa}(1)=0.256 [4-CA] +0.346 \quad R^2=0.982$$

$$I_{pa}(2)=0.853 [4-CA] +0.578 \quad R^2=0.979$$

$$I_{pc}(3)=-0.430[4-CA]-0.276 \quad R^2=0.984$$

CONCLUSION

We have demonstrated the use of phosphate modified carbon paste electrode for a greatly CV sensing of 4-CA compounds. The modified electrode increased the amplitude of the current signal of 4-CA and produced good response. The electrode construction was extremely simple and with low cost. No unstable or toxic reagents were used.

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