

# Electrocatalytic Oxidation Study of Theophylline on a Copper Nanoparticles-Modified, Carbon Paste Electrode Based on Cyclic Voltammetry

**Ghaemi Amiri, Fateme; Aghaie, Hossein\*<sup>+</sup>**

*Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, I. R. IRAN*

**Giahi, Masoud**

*Department of Chemistry, Lahijan Branch, Islamic Azad University, Lahijan, I. R. IRAN*

**Mozaffari, Majid**

*Department of Chemistry, Shahrood Branch, Islamic Azad University, Shahrood, I. R. IRAN*

**ABSTRACT:** *In this study, the Cu nanoparticles were prepared by reducing CuSO<sub>4</sub>. These particles were used in making copper nanoparticles modified carbon paste electrode (nano-CPE). The electrochemical characteristics of this electrode (nano-CPE) were investigated. The results of the electrocatalytic oxidation of theophylline (TP) on nano-CPE, using cyclic voltammetry technique showed that nano-CPE, has more reactivity and more effective surface area, as compared to the unmodified carbon paste electrode (un-CPE). The investigation of voltammograms obtained from oxidation of TP at different scan rates on the nano-CPE confirmed a cyclic mediated redox mechanism followed by reducing Cu(III) which is a chemical reaction (EC mechanism). These species formed in more positive potentials and act as a redox intermediate for TP oxidation. There was a linear relationship between the oxidation peak current and the square root of scan rate, showing that the oxidation reaction of TP at nano-CPE might be due to the diffusion-controlled process.*

**KEYWORDS:** *Theophylline; Cu nanoparticle; Electrochemical oxidation; Cyclic voltammetry; Modified carbon paste electrode.*

## INTRODUCTION

Theophylline (1, 3-dimethyl-7H-Purine-2, 6-dione; TP) (Scheme 1) is a methyl xanthine drug used to treat respiratory diseases, such as asthma and acute pulmonary infections [1-4].

This drug causes relaxation in bronchial airway,

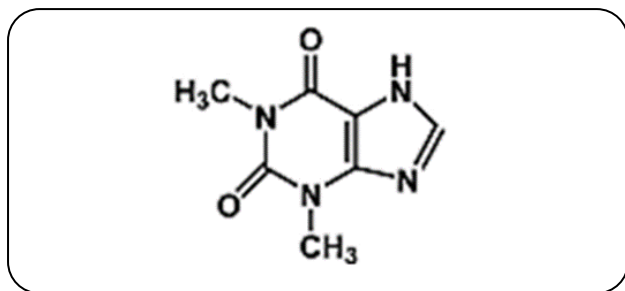
smooth muscle and the pulmonary vasculature. It also reduces spasm of the bronchus and increases the air flow rate and vital capacity [5-8]. Its plasma concentration should be between 20 and 100  $\mu\text{M}$  [2, 9]. If the TP level in the plasma is more than this rate, it can cause nausea,

---

\* To whom correspondence should be addressed.

+ E-mail: hn\_ghaie@yahoo.com

1021-9986/2020/4/99-112 14/\$/6.04



Scheme 1: Chemical structure of TP.

insomnia, irritability, seizure or even death [10-13]. Therefore, monitoring its concentration in the patient's blood plasma is essential, to ensure that it is not higher than the normal concentration in order to avoid drug toxicity. Some analytical methods, including spectrophotometry [14], ElectroSpray Ionisation Ion Mobility Spectrometry (ESI-IMS) [15], High Performance Liquid Chromatography (HPLC) [16-17], fluorescence polarization [18], Capillary Electrophoresis (CE), and immunoassay [19] were reported in the literature for measuring TP levels in plasma. Electrochemical methods have attracted a lot of attention in comparison to other methods due to advantages such as cheaper devices, easier operation, high speed, high sensitivity, excellent selection, and fast response.[20-26].

Several researches have focussed in electrochemistry, by preparing nanoparticles in connection with electrochemical sensors [27-31]. Carbon paste have been widely used to manufacture various electrochemical sensors[32-34], due to the wide range of anodic and cathodic potentials from -1.4 to 1.3 volts[35]. These electrodes are inexpensive and easily constructed, and their surfaces can easily be renewed with a simple polishing, so that for each measurement a new surface is provided and the problem of electrode fouling due to the adsorption of the products or reaction intermediates is eliminated [36]. The residual current of these electrodes are one-tenth of the glassy carbon electrode or noble metallic electrodes [37]. Most importantly, it is easy to modify it by adding different materials to the bulk of carbon paste in order to improve the efficiency of the electrode [38-40].

Nowadays, electrochemical scientists have used some nanostructures such as multiwalled carbon nanotubes [41-42] and different types of nanoparticles, in the form of metal [43-45], oxide [46-47], hydroxide [48]

semiconductor[49-50],alloys[51], and composite[52-55] to modify electrodes with the aim of achieving better responses. Nanoparticles show different physicochemical properties in comparison to their bulk forms, owing to their small size. The most important role of nanoparticles is to catalyze electrode processes by reducing the electrode overpotential[56]. The very small size, the high surface to volume ratio, and increasing the number of atoms on the surface are the most important reasons for the emergence of catalytic properties in nanomaterials. The absorption of reactants on the surface of the catalyst is the beginning of a heterogeneous catalytic reaction that culminates the breakdown or loosening of intra-molecular bonds. Then, adsorbed species on the surface often react in several consecutive steps [57].

There are many reports in the literature about electrocatalytic oxidation of theophylline with different modifiers such as multiwalled carbon nanotube [1], *Yu Jun Yang* and *Wikun Li*, modified a glassy carbon electrode with multiwalled carbon nanotube and manganese oxide nanoparticles and studied electrocatalytic oxidation of theophylline on this electrode[58]. Some researchers used nano composites to improve the electrode sensitivity for theophylline [59], *Tajik, S. et. al.* used a new ferrocene-derivative for modified graphene paste electrode to increase the peak currents of the electrocatalytic oxidation of theophylline [60], *Sevci, G. et. al* constructed an electrode modified with Imprinted sol-gel film immobilized on carbon nanoparticle layer as a sensor for theophylline [61]. *Yangyang Gao et.al.* designed an electrode modified with large mesoporous carbon and nafion composite and investigated the electrochemical activity of theophylline[62]. Many researchers have used silver [59], manganese oxides[6, 58], gold and platinum nanoparticles[10], in order to improve the electrode's efficiency. *Gungming Yang et al.* used gold nanoparticle and chitosan- ionic liquid to modified the electrode and enhanced the electrochemical sensing[63].

Various studies have shown that copper nanoparticles exhibit strong catalytic properties for oxidizing various compounds [64]. These particles have been used to modify the electrode surface for advantages such as wide array of reactivities, alternative selectivities relative to other metall catalysts and relatively inexpensive and low toxicity [65]. *Luo, J. et al.* applied Cu nanoparticle

to modify graphene sheets electrode as a non-enzymatic glucose sensor [66]. H. Helli et al. modified carbon paste electrode with copper nanoparticles and studied the oxidation of acetylcholine on it [67]. Nagashree, K.L. et al. designed an electrode which was modified with Cu nanoparticles in order to study the electrocatalytic oxidation of methanol in alkaline medium [68]. As far as we know, there is no report about electrocatalytic oxidation of theophylline on a copper nanoparticles modified carbon paste electrode in acidic medium (pH 3.0). Carbon paste electrodes modified by nanoparticles have great advantages when compared with the unmodified carbon paste due to the high mass transfer rate, catalytic activity, and high effective surface area [69]. The application of cyclic voltammetry is usually for qualitative studies [70-76]; and quantitative studies are usually done by techniques such as amperometry or differential pulse voltammetry, etc [77-78]. This research has been done with the aim of obtaining new qualitative results on the basis of physical chemistry view point. In this study, the carbon paste electrode was modified by using copper nanoparticles and the electrode was used for qualitative study of TP electrocatalytic oxidation by cyclic voltammetry.

## EXPERIMENTAL SECTION

### Reagents

The chemicals used in this study were Copper(II) sulfate anhydrous ( $\text{CuSO}_4$ ), disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ), and mono sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) as the products of Merck; polyvinylpyrrolidone (PVP), hydrazine hydrate, graphite powder, paraffin oil, and theophylline were purchased from Sigma-Aldrich and were used without further purification. Phosphate buffer solutions with different pH were prepared by adding appropriate amounts of HCl or NaOH solutions to a solution of 0.02 M  $\text{Na}_2\text{HPO}_4$  and 0.02 M  $\text{NaH}_2\text{PO}_4$ . A stock solution of TP (0.01 M) was prepared and stored in a refrigerator at 4°C. The working solutions of TP (0.1 mM) were made daily from the stock solution.

### Apparatus

The electrochemical experiments were performed in a glass container with a cap having holes for introducing electrodes. The reference electrode was an Ag/AgCl electrode; the counter electrode was a Pt wire

and the self-made carbon paste electrode as a working electrode, powered by potentiostat/galvanostat Autolab (Nova software model PG stat 302N, Metrohm, Netherlands) together with a personal computer. All the potentials given in this paper were recorded using the Ag/AgCl (3 M KCl) reference electrode. Transmission Electron Microscopy (TEM) was performed using a Philips EM 208 to study the shape and size of copper nanoparticles. The electron microscope was operated using a 100 kV accelerated voltage. Samples were prepared by suspending the nanoparticles in ethanol and dripping one drop on Cu grid (200 mesh) and evaporating solvent on it. Absorption spectra was recorded on CARY 100 Conc UV-Visible spectrophotometer, using 1cm quartz cell and scanning from 500 to 800 nm.

### Preparation of copper nanoparticles

PVP (10 mg) was added to 30 mL hydrazine 50% and was stirred to obtain the desired solution. Then 0.02 mol  $\text{CuSO}_4$  powder was added to the solution smoothly by stirring it. The reaction mixture was stirred using magnetic stirrer for 3 h, until a dark brown mixture was obtained. Subsequently, it was deposited using centrifugation and by being washed several times with double distilled water and smoothed with a filter paper and a bokhner funnel connected to the vacuum pump. It was later dried at 25°C for 24 h in a vacuum oven. Then, it was grounded in the mortar to obtain a fine powder. The TEM images showed that the diameters of copper nanoparticles are fairly less than 60 nm with near-spherical shape (Fig. 1).

The Optical absorption spectra of the Cu nanoparticles which was dispersed in a mixture of hydrazine hydrate and polyvinylpyrrolidone (PVP), was recorded in the range of 500 - 800 nm. As shown in Fig. 2, its absorption at 596 nm is due to the surface resonance phenomenon (SRP). The absorption bands of copper nanoparticles have been reported to be in the range of 550 - 600 nm [79-80].

### Electrode preparation

The unmodified Carbon Paste Electrode (un-CPE) was prepared by hand mixing graphite powder with paraffin oil (80/20% (w/w) ratio) according to the literature [67, 69]. These materials were mixed well homogeneously in a mortar for 20 min. The resulting paste was carefully

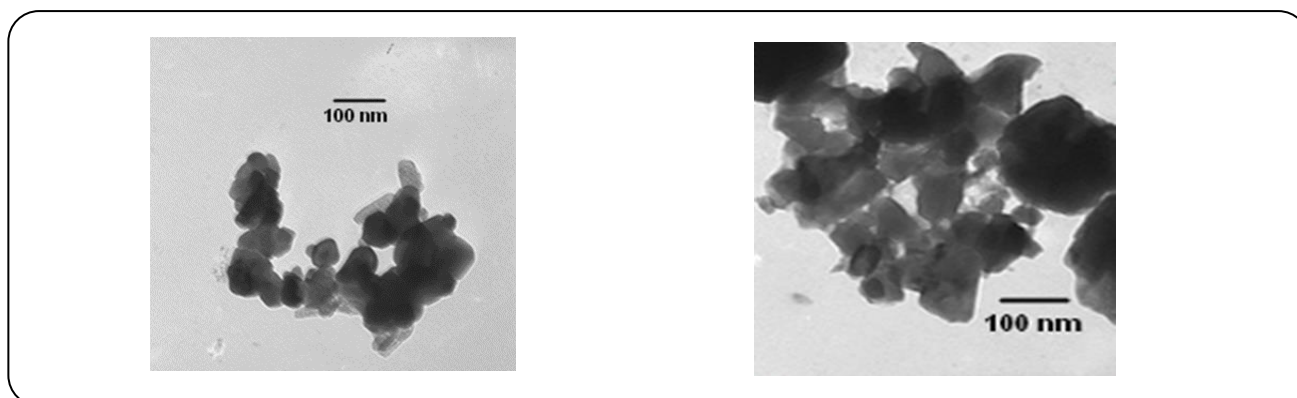


Fig. 1: TEM images of Cu nanoparticles.

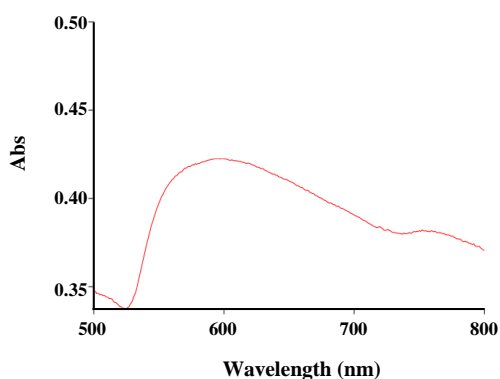


Fig. 2: UV-vis Spectrum of Cu nanoparticles in a mixture of hydrazine hydrate and polyvinylpyrrolidone (PVP).

poured into a tube of an insulin syringe and was packed firmly in it. A copper wire was inserted into the carbon paste to provide the electrical connection. Before each use, the surface of the electrode was smoothed by slipping it gently onto a weighing paper. This procedure was used to create a new surface before any experiment, and the surface fouling was ceased. Copper nanoparticle-modified carbon paste electrode (called nano-CPE) was prepared in a similar fashion, by mixing graphite powder, copper nanoparticles, and paraffin oil in a 60/20/20% (w/w) ratio. This optimized ratio was used on the basis of the previous published papers [67, 69]. The electrode area was calculated using cyclic voltammetric technique, at different scan rates, in a mixture of 6 mM  $K_4Fe(CN)_6$  and 1 M  $KNO_3$  (Figs. 3 to 5).

For a redox reversible system, the Randles-Sevcik formula can be used [81].

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C \quad (1)$$

where  $I_p$  is the anodic peak current (maximum current) at "298 K",  $n$  is the number of transferred electrons,  $A$  is the surface area of the electrode,  $D$  is the respect diffusion coefficient,  $\nu$  is the scan rate, and  $C$  is the concentration of the respective species. For 6 mM  $K_4Fe(CN)_6$  in 1 M  $KNO_3$  electrolyte,  $n=1$ ,  $D=1 \times 10^{-6} \text{ cm}^2/\text{s}$ , the slope of the plot of  $I_p$  versus  $\nu^{1/2}$ , is  $3.7 \times 10^{-4}$  and  $1.97 \times 10^{-3} \mu\text{A} (\text{Vs}^{-1})^{-1/2}$  for un-CPE and nano-CPE, respectively and the calculated area of the electrode is 0.23 and 1.22  $\text{cm}^2$  for un-CPE and nano-CPE, respectively.

### Influence of pH

The effect of the pH solution on the oxidation of TP in the nano-CPE was examined in the pH range of 3 to 11 to determine the appropriate pH for the TP oxidation (Fig. 6).

As shown in Figure 6, the current peak intensity is decreased by increasing the pH solution, so that there is a linear relationship between the oxidation peak current and the pH solution in the range of pH 3 to 9 (Fi. 7), which is expressed by the following equation:

$$I_p (\text{mA}) = 0.76 - 0.074 \text{ pH} \quad r^2 = 0.9169 \quad (2)$$

As shown in Fig. 6, the highest current intensity of oxidation peak was obtained at pH 3. So, this pH was selected as the appropriate pH for TP oxidation.

The TP oxidation potential goes up to positive potentials by increasing pH. The peak-oxidation potential diagram vs. pH shows a linear relationship within the pH range of 3 to 6 and is not pH dependent above pH 6 (Fig. 8).

The linear relationship between  $E$  and pH (3 to 6) is expressed by the following equation:

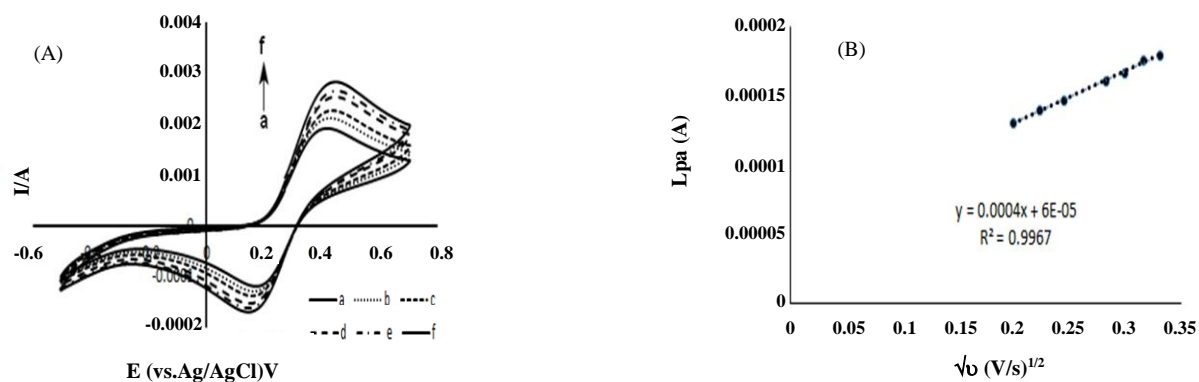


Fig. 3: (A) CVs of 6mM  $K_4Fe(CN)_6$  in 1M  $KNO_3$  recorded at un-CPE at various scan rates (from curve a to f): 0.04, 0.05, 0.06, 0.08, 0.09, 0.1  $Vs^{-1}$ . (B) Dependence of peak currents versus the square root of scan rate.

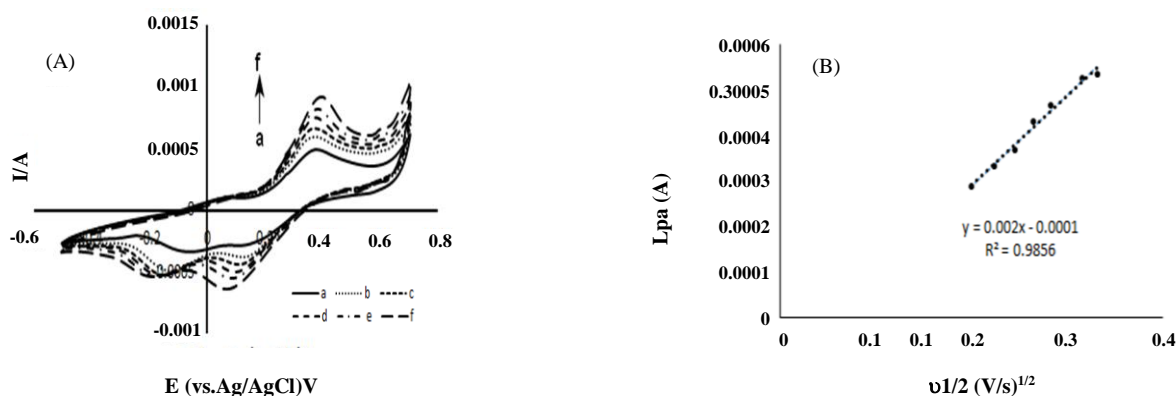


Fig. 4: (A) CVs of 6mM  $K_4Fe(CN)_6$  in 1M  $KNO_3$  recorded at nano-CPE at various scan rates (from curve a to f): 0.04, 0.05, 0.06, 0.08, 0.09, 0.1  $Vs^{-1}$ . (B) Dependence of peak currents versus the square root of scan rate.

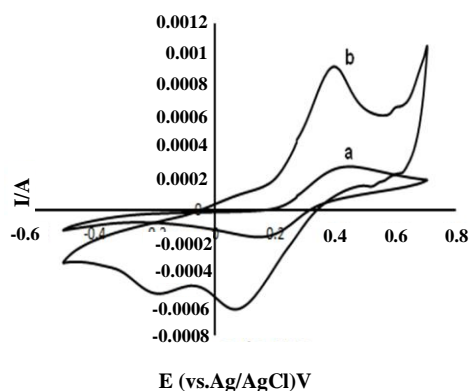


Fig. 5: CVs of 6mM  $K_4Fe(CN)_6$  in 1M  $KNO_3$  recorded at un-CPE (a) and nano-CPE (b) at scan rate 0.1  $Vs^{-1}$ .

$$E_p (V) = 0.39 - 0.03 \text{ pH} \quad r^2 = 0.948 \quad (3)$$

where the gradient is 0.03 V/pH. This value is very close to that theory of 0.059 V/pH and it can be concluded that the number of transferred electrons and the number of hydrogen ions in the electrode process are almost equal [82].

### Procedures

At first, the nano-CPE was activated in phosphate buffer pH 3.0 on the basis of cyclic voltammetric sweeps; the electrode potential was varied in a linear fashion between -0.50 and 1.30 V, while the scan rate was 0.05 V/s. After reaching the stable cyclic voltammogram, the electrodes were transferred to another cell having equal

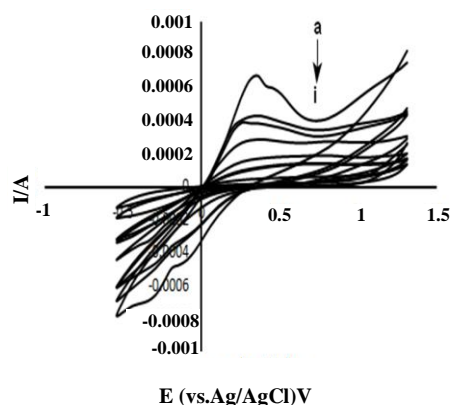


Fig. 6: Cvs of TP on nano-CPE , in the potential range of -0.5 to 1.3 V in phosphate buffer solutions, pH 3.0 to 11.0 (curve a to i). at scan rate 0.08V/s.

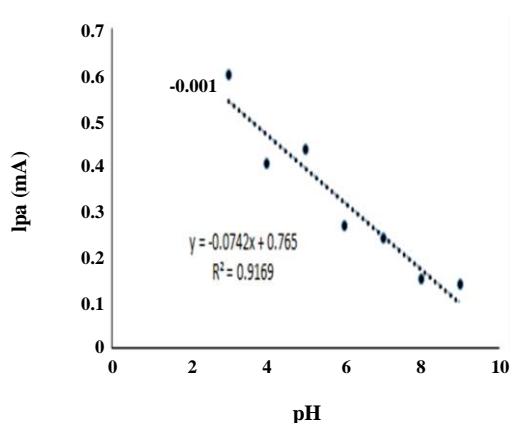


Fig. 7: Oxidation peak Current function vs.pH, for 0.1 mM TP in phosphate buffer solution on nano-CPE using CV.

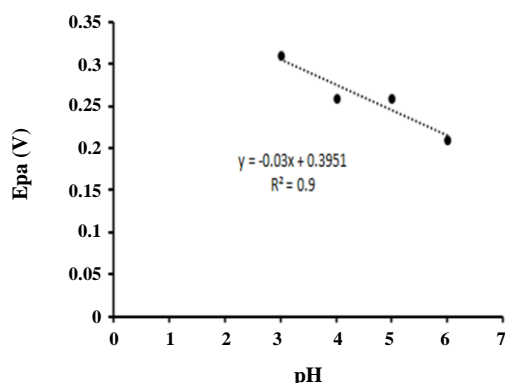


Fig. 8: Oxidation peak potential function vs.pH, for 0.1 mM TP in phosphate buffer solution on nano-CPE using CV.

amounts of pH 3.0 phosphate buffer solution and TP (0.1 mM ) and the respect experiment was performed.

## RESULTS AND DISCUSSION

### Electrochemical characterization of Nano-CPE

The voltammograms of un-CPE and nano-CPE in a phosphate buffer solution, pH 3.0 in the potential range of -0.50 to 1.30 V, with a scan rate of 0.08 Vs<sup>-1</sup> are shown in Fig. 9.

At the un-CPE (curve d), the redox peak was not observed, but at the nano-CPE (curve c) two anodic peaks at +0.32 and +0.56 V and three cathodic peaks at +0.1, -0.22, and -0.42 V were observed, revealing that Cu nano particles are electroactive particles in the selective potential range. It seems that the produced anodic flow is probably due to the conversion of Cu (III)/Cu (II) [66, 83]. This phenomenon usually happens when using electrodes modified with copper nanoparticles. The presence of redox couple Cu (II)/Cu (III) in voltammogram anodic peak has been reported in alkaline solutions [69, 84-85]. In this study, the experiments were performed in a phosphate buffer solution pH 3.0 (acidic solution) and electroactivity properties from Cu nano particles were observed, such that during the sweeping of the potential, different types of copper ions were formed on the surface of the electrode.

### Electrochemical behaviour of theophilline

The electrochemical behaviour of TP in pH 3.0 PBS was investigated in the potential range of -0.5 to 1.3 V on un-CPE and nano-CPE with the scan rate of 0.08 V/s using the CV technique.

Fig. 10 shows that in un-CPE, there were no anodic peaks, only a current was observed associated with the solvent electric discharge at the end of the curve related to the anodic scan (curve a ). But in nano-CPE, there was a large oxidation peak current (curve b ). In other words, the electrooxidation of TP at the modified electrode surface had a larger anodic current density than the un-CPE, which can be as a result of the electrocatalytic role of copper nanoparticles [66-69]. It can be said that the electrode modified by nanoparticles can make the transfer of the electrons from TP easier than unmodified electrode and nano-CPE has high reactivity and high effective surface area as compared to un-CPE [81-87]

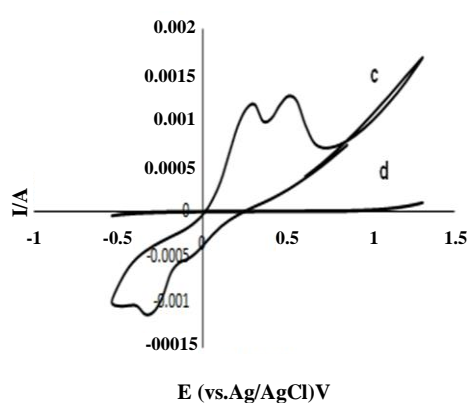


Fig. 9: Cvs of un-CPE (d) and nano-CPE (c), (-0.5 to 1.3 V, 0.08 V/s) in pH 3.0 phosphate buffer solution.

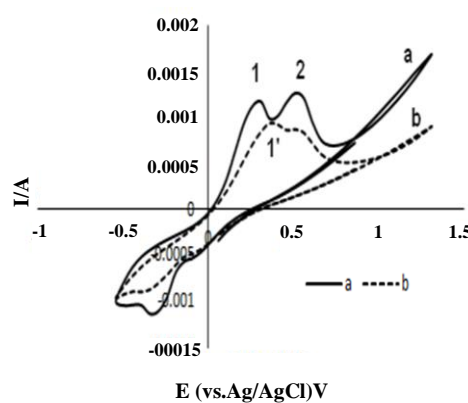


Fig. 11: CVs of nano-CPE (-0.5 to 1.3 V, 0.08 V/s) in 20 mM PBS pH 3.0 in the absence (a) and presence (b) of 0.1 mM TP.

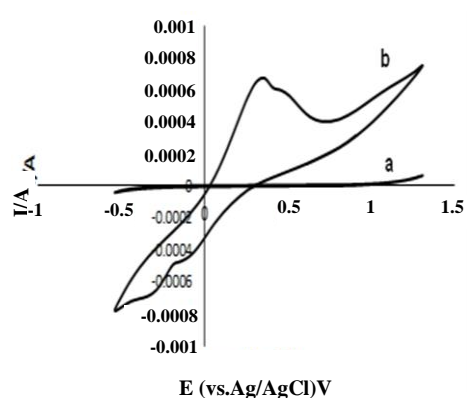


Fig. 10: Cvs of TP on un-CPE (a) and nano-CPE (b), (-0.5 to 1.3 V, 0.08 V/s) in pH 3.0 phosphate buffer solution.

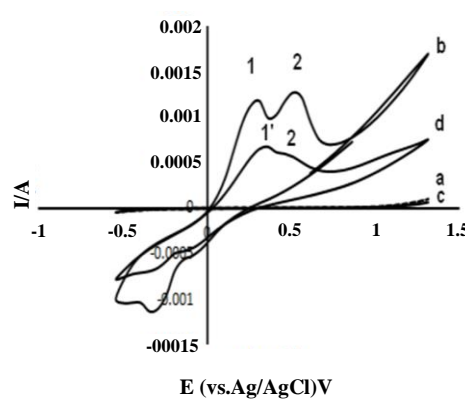


Fig. 12: Cvs of un-CPE (a, c) and nano-CPE (b, d) (-0.5 to 1.3 V, 0.08 V/s) in 20 mM PBS pH 3.0 in the absence (a, c) and presence (d, b) of 0.1 mM TP.

Nano-CPE in the presence of TP when compared with the blank buffer solution, showed two overlapped lower anodic peaks. It was also observed that in the reverse sweep, the cathodic peak current decreased. The location of the anodic peaks of nano-CPE in direct sweep in the presence of TP (indicated by 1' and 2 in Fig. 11) was +0.39 and +0.56 V. It has been reported that Cu (III) active species has the ability to oxidize some organic compounds by performing a chemical reaction [83-87].

This shows that the active species of Cu (III) is likely to oxidize this compound through an intermediate electron transfer process, by electrochemical reaction with TP [66-67]. It can be concluded from four voltammograms as shown in Fig. 12 that TP was oxidized onto electrodes containing copper nanoparticles in the potentials in which active Cu (III) species are formed.

Such that, a new anodic peak associated with the elimination of the peak 1 and diminished peak 2 can be observed, and then the cathodic peak current is decreased in the reverse sweep, which is related to the reduction of Cu (III) to Cu (II) and Cu (III) to Cu species, because Cu (III) has been consumed by the oxidation of TP and itself, becomes Cu (II).

The location of peaks can be seen in the same range of potentials by drawing the derived diagram ( $di/dt$ ) and comparing it with the voltammogram. In Fig. 13, diagrams c and d are the diagrams derived from the current intensity based on time, in which both peak locations and peak heights are more clearly distinguishable in the presence and absence of TP.

On the other hand, TP cyclic voltammograms at different potential scan rates in nano-CPE (Fig. 14) show

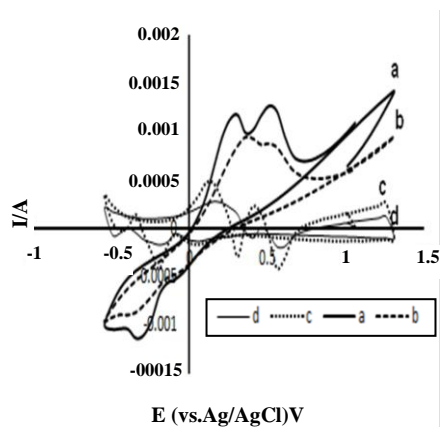


Fig. 13: CVs (a, b) and derivative voltammograms (di/dt) (c, d) of nano-CPE (-0.5 to 1.3 V, 0.08 V/s) in 20 mM PBS pH 3.0 in the absence (a, c) and presence (b, d) of 0.1 mM TP.

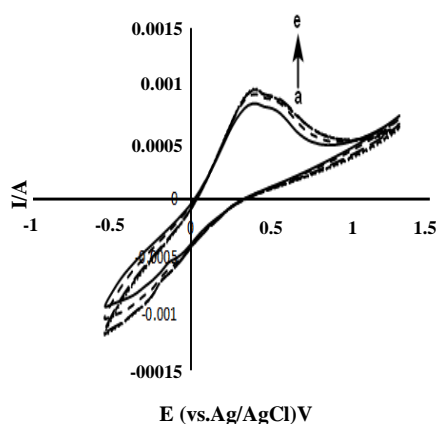


Fig. 14: CVs of nano-CPE measured at various potential scan rates: 0.06, 0.08, 0.12, 0.14, 0.16 V/s (a to e) in the presence of 0.1 mM TP, in the PBS pH 3.0.

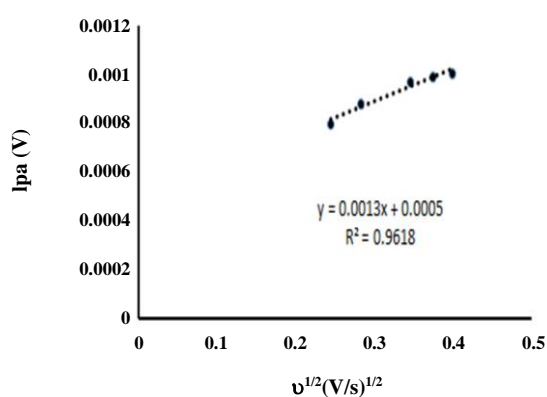


Fig. 15: Linear relationship between  $I_{pa}$  and  $v^{1/2}$  for 0.1 mM TP in PBS pH 3.0 on nano-CPE using CV. scan rates: 0.06, 0.08, 0.12, 0.14, 0.16 V/s.

a linear relationship between the square root of the scan rate and the oxidation peak current and it admits an intermediate redox mechanism that is followed up through a chemical reaction between Cu (III) and TP (EC mechanism) [88].

Cu (III) species is produced in more positive potentials and plays the role of a redox intermediate in the oxidation of TP. At fairly fast sweep rates, each anodic peak being labelled according to the electron transfer process causing it. At very high sweep rates, where the chemical reaction (reaction of TP with Cu (III)) does not occur to any appreciable extent during a single sweep, peak 1 will not be seen and a new peak 1' will appear at a more positive potential. While peak 2 is being depleted, as  $v$  is increased, peak 2 decreases faster by increasing the scan rate and peak 1' decreases slower than the dependency on the square root of scan rate, because the chemical process of the destruction of Cu (III) species and the production of Cu (II), have no opportunity to occur by increasing the scan rate, and the anodic peak of this process (peak 2) can be seen more sharper at the lower scan rates. Therefore, it seems that low valence states of copper (Cu (I) and Cu (II)) do not oxidize TP and they only adsorb it on the electrode surface, while the Cu (III) species formed at the more positive potentials acts as a redox species in the oxidation of TP. In previous reports concerning to the oxidation of some organic compounds in copper electrodes, the production of Cu (III) species from copper oxy- hydroxide is proposed [67-89].

#### Influence of scan rate

The effect of the scan rate on the TP oxidation in PBS pH 3.0 was examined at the nano-CPE. When the scan rate was increased from 0.06 to 0.16  $\text{vs}^{-1}$ , the intensity of the oxidation current of the TP was also increased (Fig 14).

The intensity curve of the oxidation current ( $I_{pa}$ ) versus the square root of the scan rate was linear (Fig. 15) and expressed as the following equation, which shows that the TP oxidation in the nano-CPE, maybe a diffusion controlled process [77].

$$I_p \text{ (mA)} = 0.5 - 1.137 v^{1/2} \text{ (mVs}^{-1}) \quad r^2 = 0.9616 \quad (4)$$

Also, as shown in Fig. 16,  $\log I_p$  versus  $\log v$  as a linear graph can be expressed as the following equation:

$$\text{Log} I_p \text{ (A)} = -2.79 + 0.24 \log v \text{ (Vs}^{-1}) \quad r^2 = 0.9677 \quad (5)$$



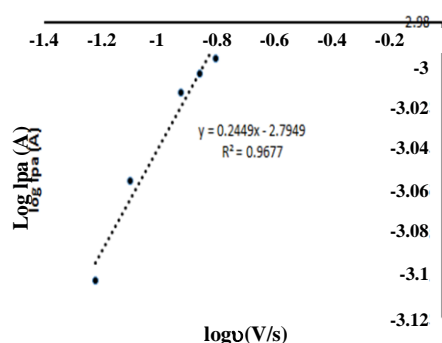


Fig. 16: Oxidation peak current logarithm function vs. logarithm of the potential scan rate for 0.1 mM TP in phosphate buffer solution pH 3.0 on nano-CPE using CV.

Since the slope of 0.24 A.s/V is close to the value of 0.25 which is related to the process that is fully controlled by diffusion [90], it can be concluded that the TP oxidation process on the electrode surface is more controlled by diffusion than adsorption (or kinetics).

## CONCLUSIONS

The optimized nano modified carbon paste electrode was prepared and used to study the oxidation of TP at the optimum conditions using cyclic voltammetric method. The anodic current density of TP oxidation at nano-CPE was considerably higher than that of un-CPE. This is as a result of the characteristic of copper nanoparticles which has high reactivity and high effective surface area as compared to un-CPE. From the obtained cyclic voltammograms, one can conclude that TP is oxidized on the surface of the modified electrode with Cu nanoparticles in the potential region where the active Cu (III) species exist and these species act as intermediates in the oxidation of TP, and this process is more affected by diffusion than adsorption (or kinetics). Therefore, the lower valence states of copper oxides did not participate in TP oxidation and it may only adsorb TP on the surface of the electrode. In fact, the Cu (III) species that formed in more positive potentials, acts as a fairly powerful oxidant in the TP oxidation process.

## Acknowledgements

The authors acknowledge for financial support of Zakariya Razi Laboratory, Islamic Azad University, Science and Research Branch.

Received : May 20, 2014 ; Accepted : Apr. 3, 2019

## REFERENCES

- [1] Malode S.J., Shetti N.P., Nandibewoor S.T., Voltammetric Behavior of Theophylline and Its Determination at Multi-Wall Carbon Nanotube Paste Electrode, *Colloids and Surfaces B: Biointerfaces*, **97**: 1-6 (2012).
- [2] Zi L., Li J., Mao Y., Yang R., Qu L., High Sensitive Determination of Theophylline Based on Gold Nanoparticles/L-Cysteine/Graphen/Nafion Modified Electrode, *Electrochimica Acta*, **78**: 434-439 (2012).
- [3] Alizadeh T., Ganjali M. R., Zare M., Norouzi P., Development of a Voltammetric Sensor Based on a Molecularly Imprinted Polymer (MIP) for Caffeine Measurement, *Electrochim. Acta*, **55**: 1568-1574 (2010).
- [4] Yin H., Meng X., Su H., Xu M., Ai S., Electrochemical Determination of Theophylline in Foodstuff, Tea, and Soft Drinks Based on Urchin-Like CdSe Microparticles Modified Glassy Carbon Electrode, *Food Chemistry*, **134**: 1225-1230, (2012).
- [5] Riahi S., Mousavi M. F., Bathaie S. Z., Shamsipur M., A Novel Potentiometric Sensor for Selective Determination of Theophylline: Theoretical and Practical Investigation, *Anal. Chim. Acta*, **548**: 192-198 (2005).
- [6] Mansouri Majd S., Teymourian H., Salimi A., Hallaj R., Fabrication of Electrochemical Theophylline Sensor Based on Manganese Oxide Nanoparticles/Ionic Liquide/Chitosan Nano Composite Modified Glassy Carbon Electrode, *Electro Chimica Acta*, **108**: 707-716 (2013).
- [7] Ferapontova E.E., Eva M.O., An RNA Aptamer-Based Electrochemical Biosensor for Detection of Theophylline in Serum, *J. Am. Chem. Soc.*, **130**: 4256-4258 (2008).
- [8] Igarashi T., Iwakawa S., Effect of Gender on Theophylline Clearance in the Asthmatic Acute Phase in Japanese Pediatric Patients, *Biol. Pharm. Bull.*, **32**: 304-307 (2009).
- [9] Ahn J.K., Park K.S., Won B. Y., Park H. G., A Novel Electrochemical Methode to Detect Theophylline Utilizing Silver Ion Captured Within Abasic Site-Incorporated Duplex DNA, *Biosensors and Bioelectronics*, **67**: 590-594 (2015).

- [10] Gowthaman N.S.K., Kesavan S., John S.A., [Monitoring Isoniazid Level in Human Fluids in the Presence of Theophylline Using Gold@Platinum Core@Shell Nano Particles Modified Glassy Carbon Electrode](#), *Sensors and Actuators*, **B 230**: 157-166 (2016).
- [11] Heatherley S.V., Hayward R.C., Seers H.E., Rogers P.J., [Cognitive and Psychomotor Performance, Mood and Pressor Effects of Caffeine after 4, 6, and 8 h Caffeine Abstinence](#), *Psychopharmacology*, **178**: 461-470 (2005).
- [12] Al-Faris N. A., Emirates J., [Assessment of Intake of Caffeine in Random Population in Riyadh and its Levels in some Food by HPLC](#), *Food Agric.*, **21**: 21-31 (2009).
- [13] Ichikawa K., wada T., Nishihara T., Tsuji M., Mori A., Yokohama F., Hasegawa D., Kawamoto K., Tanakaya M., Katyama Y., Sakuragi S., Ito H., [A Case of Life-Threatening Supraventricular Tachycardia Storm Associated With Theophylline Toxicity](#), *J. Cardiol. Cases*, **15**: 125-128 (2017).
- [14] Hector C.G., Alejandro C.O., Arsenio M.P., [Determination of Theophylline in Blood Serum by UV Spectrophotometry and Partial Least-Squares \(PLS-1\) Calibration](#), *Anal. Chim. Acta*, **384**: 95- 103 (1999).
- [15] Jafari M. T., Rezaei B., Javaheri M., [A New Method Based on Electrospray Ionisation Ion Mobility Spectrometry \(ESI-IMS\) for Simultaneous Determination of Caffeine and Theophylline](#), *Food Chemistry*, **126** (4): 1964- 1970 (2011).
- [16] Srdjenovic B., Djordjevic-Milic V., Grujic N., Injac R., Lepojevic Z., [Simultaneous HPLC Determination of Caffeine, Theobromine, and Theophylline in Food, Drinks, and Herbal Products](#), *J. Chromatogr. Sci.*, **46**: 144- 149 (2008).
- [17] Wentao B.; Kyung H. R., [Comparison of Different Silica-Based Imidazolium Stationary Phases for LC in Separation of Alkaloids](#), *Chromatographia*, **71**: 25-30 (2010).
- [18] Chavez J.L., Lyon W., Kelley-Loughnane N., Stone M.O., [Theophylline Detection Using an Aptamer and DNA-Gold Nanoparticle Conjugates](#), *Biosens. Bioelectron.*, **26**: 23 -28 (2010).
- [19] Garcinuno R. M., Fernandez P., Perez-conde C., Gutierrez A. M., Camara C., [Development of a Fluoroimmunosensor for Theophylline Using Immobilised Antibody](#), *Talanta*, **52**: 825- 832 (2000).
- [20] Alizadeh M., Ghahramani E., Zarrabi M., Hashemi S., [Efficient De-Colorization of Methylene Blue by Electro-Coagulation Method: Comparison of Iron and Aluminum Electrode](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **34**(1): 39-47 (2015).
- [21] El-Hallag I.S., El-Mossalamy E.H., Asiri A.M., [Electrochemical Investigation of Antibacterial Laser Dye Compound in 1,2-Dichloroethane at a Platinum Electrode](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **31**(3): 9-18 (2012).
- [22] Akvan F., Neshati J., Mofidi J., [An Electrochemical Measurement for Evaluating the Cathodic Disbondment of Buried Pipeline Coatings Under Cathodic Protection](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **34**(2): 83-91 (2015).
- [23] Gupta V.K., Ganjali M.R., Norouzi P., Khani H., Nayak A., Agarwal S., [Electrochemical Analysis of Some Toxic Metals Ion-Selective Electrodes](#), *Critical Reviews in Analytical Chemistry*, **41**: 282-313 (2011).
- [24] Gupta V.K., Mergu N., Kumawat L.K., Singh A.K., [Selective Naked-Eye Detection of Magnesium\(II\) Ions Using a Coumarin-Derived Fluorescent Probe](#), *Sensors and Actuators B*, (2014).
- [25] Ashrafi A. M., Mustakeem M., David N., [Study the Transport Properties of Anion and Cation Exchange Membranes toward Various Ions Using Chronopotentiometry](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**(2): 81-87 (2017).
- [26] Sadeghi B., Sarraf-Mamoory R., Shahverdi H. R., [The Effect of LiFePO<sub>4</sub> Coating on Electrochemical Performance of LiMn<sub>2</sub>O<sub>4</sub> Cathode Material](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **31**(4): 29-33 (2012).
- [27] Fouladgar M., Ahmadzadeh S., [Application of a Nanostructured Sensor Based on NiO Nanoparticles Modified Carbon Paste Electrode for Determination of Methyl dopa in the Presence of Folic Acid](#), *Applied Surface Science*, **379**: 150- 155 (2016).
- [28] Prakash S., Chakrabarty T., Singh A.K., Shahi V.K., [Polymer Thin Films Embedded With Metal Nanoparticles for Electrochemical Biosensors Applications](#), *Biosensors and Bioelectronics*, **41**: 43-53 (2013).

- [29] Wang Y., Huang B., Dai W., Ye J., Xu B., Sensitive Determination of Capsaicin on Ag/Ag<sub>2</sub>O Nanoparticles/Reduced Graphene Oxide Modified Screen-Printed Electrode, *Journal of Analytical Chemistry*, **776**: 93- 100 (2016).
- [30] Kumar M., Swamy B. E. K., Role of Heat on the Development of Electrochemical Sensors on Bare and Modified Co<sub>3</sub>O<sub>4</sub>/CuO Composite Nanopowder Carbon Paste Electrodes, *Materials Science and Engineering C*, **58**: 142-152 (2016).
- [31] Gholivand M.B., Malekzadeh G., Derakhshan A.A., Boehmite Nanoparticles Modified Carbon Paste Electrode for Determination of Piroxicam, *Sensors and Actuators B*, **201**: 378- 386 (2014).
- [32] Mashhadizadeh M. H., Akbarian M., Voltammetric Determination of Some Anti- Malarial Drugs Using a Carbon Paste Electrode Modified With Cu(OH)<sub>2</sub> Nano-Wire, *Talanta*, **78**: 1440 – 1445 (2009).
- [33] Kalambate P. K., Rawool C. R., Karna S. P., Srivastava A. K., Highly Sensitive and Selective Determination of Methylethylgometriner Maleate Using Carbon Nanofibers/Silver Nanoparticles Composite Modified Carbon Paste Electrode, *Materials Science and Engineering C*, **69**: 453 -461 (2016).
- [34] Ojani R., Raof J., Ebrahimi M., A Cyclic Voltammetric Study of the Aqueous Electrochemistry of Some Anthraquinone Derivatives on Carbon Paste Electrode, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **20**(2): 75-81 (2001).
- [35] Vitras K., Svancara I., Metelka R., J., Carbon Paste Electrodes in Electroanalytical Chemistry, *Serb. Chem. Soc.*, **74** (10): 1021 – 1033 (2009).
- [36] Lindquist J., Carbon Paste Electrode With a Wide Anodic Potential Range, *Anal. Chem.*, **45**(6): 1006-1008 (1973).
- [37] Apetrei C., Apetrei I. M., Saja J. A. D., Rodriguez-Mendez M. L., Carbon Paste Electrode Made from Different Carbonaceous Materials: Application in the Study of Antioxidants, *Sensors*, **11**: 1328-1344 (2011).
- [38] Amani Z., Nezamzadeh-Ejehieh A., A Novel Non-Enzymatic Glucose Sensor Based on the Modification of Carbon Paste Electrode with CuO Nanoflower: Designing the Experiments by Response Surface Methodology(RSM), *J. Colloid Interface Sci.*, **504**: 186 – 196 (2017).
- [39] Darroudi A., Eshghi H., Rezaeian S., Chamsaz M., Bakavoli M., Haghbeen K., Hosseiny A., A Novel Carbon Paste Electrode for Potentiometric Determination of Vanadyl Ion, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **34**(4): 89-96 (2015).
- [40] Gupta V.K., Karimi-Maleh H., Sadegh R., Simultaneous Determination of Hydroxylamine, Phenol and Sulfite in Water and Waste Water Samples Using a Voltammetric Nanosensor, *Int. J. Electrochem. Sci.*, **10**: 303-316 (2015).
- [41] Taei M., Abedi F., New Modified Multiwalled Carbon Nanotubes Paste Electrode for Electrocatalytic Oxidation and Determination of Warfarin in Biological and Pharmaceutical Samples, *Chinese Journal of Catalysis*, **37**: 436-445 (2016).
- [42] Karimi-Maleh H., Tahernejad-Javazmi F., Atar N., Yola M. L., Gupta V. N., Ensafi A.A., A Novel DNA Biosensor Based on a Pencil Graphite Electrode Modified with Poly Pyrrole/Functionalized Multi-Walled Carbon Nanotubes for Determination of 6-Mercaptopurine Anti Cancer Drug, *Ind. Eng. Chem. Res.*, **54**: 3634-3639 (2015).
- [43] Song Y., Zhang X., Yang S., Wei X., Sun Z., Electrocatalytic Performance for Methanol Oxidation on Nanoporous Pd/NiO Composite Prepared by One- Step Dealloying, *Fuel*, **181**: 269 – 276 (2016).
- [44] Habibi B., Ghaderi S., Electrooxidation of Formic Acid and Formaldehyde on the Fe<sub>3</sub>O<sub>4</sub>@Pt Core-Shell Nanoparticles/Carbon-Ceramic Electrode, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **35**(4): 99-112 (2016).
- [45] Yola M.L., Gupta V.K., Eren T., Sen A.E., Atar N., A Novel Electro Analytical Nanosensor Based on Graphene Oxide/Silver Nanoparticles for Simultaneous Determination of Quercetin and Morin, *Electrochimica Acta*, **120**: 204-211 (2014).
- [46] Gupta V. K., Karimi-Maleh H., Sadegh R., Simultaneous Determination of Hydroxylamine, Phenol and Sulfite in Water and Waste Water Samples Using a Voltammetric Nanosensor, *Int. J. Electrochem. Sci.*, **10**: 303-316 (2015).
- [47] Foroughi F., Rahsepar M., Hadianfard M. J., Kim H., Facile Synthesis and Electrochemical Performance of Graphene-Modified Cu<sub>2</sub>O Nanocomposite for Use in Enzyme-Free Glucose Biosensor, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **39**(2): 1-10 (2018).

- [48] Raof J., Zabihi M. S., Hosseini S. R., Sohrabi M. R., [Electro-Catalytic Oxidation of Methanol at Ni\(OH\)<sub>2</sub> Nanoparticles-Poly\(O-Anisidine\)/Triton X-100 Film onto Phosphotungstic Acid-Modified Carbon Paste Electrode](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **38**(2): 37-48 (2019).
- [49] Mazloum-Ardakani M., Rajabi H., Beitollahi H., Mirjalili B. B. F., Akbari A., Taghavinia N., [Voltammetric Determination of Dopamine at the Surface of TiO<sub>2</sub> Nanoparticles Modified Carbon Paste Electrode](#), *Int. J. Electrochem. Sci.*, **5**: 147- 157 (2010).
- [50] Behara D. K., Palukuru P. S., Devangam V. P., [N,S-Codoped TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> Heterostructure Assemblies for Electrochemical Degradation of Crystal Violet Dye](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **39**(2): 169-177 (2020).
- [51] Zhao Q., Wang J., Huang X., Yao Y., Zhang W., Shao L., [Copper-Enriched Palladium-Copper Alloy Nanoparticles for Effective Electrochemical Formic Acid Oxidation](#), *Electrochemistry Communications*, **69**: 55 -58 (2016).
- [52] Srivastava S. K., Gupta V. K., Jain S., [Determination of Lead Using a Poly\( Vinyl Chloride\)- Based Crown Ether Membrane](#), *Analyst*, **120**: 495-498 (1995).
- [53] Gupta V. K., Singh L. P., Singh R., Upadhyay N., Kaur S. P., Sethi B., [A Novel Copper\(II\) Selective Sensor Based on Dimethyl 4,4' \(O-Phenylene\) Bis \(3-Thioallo Phanate\) in PVC Matrix](#), *Journal of Molecular Liquids*, **174**: 11-16 (2012).
- [54] Gupta V.K., Kumar S., Singh R., Singh L. P., Shoor S.K., Sethi B., [Cadmium\(II\) Ion Sensing Through P-Tert-Butyl Calix\[6\] Arene Based Potentiometric Sensor](#), *Journal of Molecular Liquids*, **195**: 65-68 (2014).
- [55] Gupta K.V., Sethi B., Sharma R.A., Agarwal S., Bharti A., [Mercury Selective Potentiometric Sensor Based on Low Rim Functionalized Thiocalix \[4\]-Arene As a Cationic Receptor](#), *Journal of Molecular Liquids*, **177**: 114-118 (2013).
- [56] Andrews E., Katla S., Kumar C., Patterson M., Sprunger P., [Electrocatalytic Reduction of CO<sub>2</sub> at Au Nanoparticles Electrodes: Effects of Interfacial Chemistry on Reduction Behavior](#), *Journal of Electrochemical Society*, **162**(12): F1373- F1378 (2015).
- [57] Chaturvedi S., Dave P.N., Shah N.K., [Applications of Nano-Catalyst in New Era](#), *Journal of Saudi Chemical Society*, **16**: 307-325 (2012).
- [58] Yang Y.J., Li W., [High Sensitive Determination of Theophylline Based on Manganese Oxide Nanoparticles/Multiwalled Carbon Nanotube Nanocomposite Modified Electrode](#), *Ionics*, **21**: 1121- 1128 (2015).
- [59] Wang H.B., Zhang H.D., Zhang Y.H., Chen H., Xu L.L., Huang K.J., Liu Y.M., [Tungsten Disulfide Nano-Flower/Silver Nanoparticles Composites Based Electrochemical Sensor for Theophylline Determination](#), *Journal of the Electrochemical Society*, **162**(7): B 173-B 179 (2015).
- [60] Tajik S., Taher M. A., Beitollahi H., [Application of a New Ferrocene-Derivative Modified-Graphene Paste Electrode for Simultaneous Determination of Isoproterenol, Acetaminophen and Theophylline](#), *Sensors and Actuators B*, **197**: 228 - 236 (2014).
- [61] Guney S., Cebeci F. C., [Selective Electrochemical Sensor for Theophylline Based on an Electrode Modified With Imprinted Sol-Gel Film Immobilized on Carbon Nanoparticle Layer](#), *Sensors and Actuators B: Chemical*, **208**: 307-314 (2015).
- [62] Gao Y., Wang H., Gua L., [Simultaneous Determination of Theophylline and Caffeine by Large Mesoporous Carbon/Nafion Modified Electrode](#), *Journal of Electroanalytical Chemistry*, **706**: 7-12 (2013).
- [63] Yang G., Zhao F., Zeng B., [Facile Fabrication of a Novel Anisotropic Gold Nanoparticle-Chitosan-Ionic Liquid/Graphene Modified Electrode for the Determination of Theophylline and Caffeine](#), *Talanta*, **127**: 116-122 (2014).
- [64] Jafari M., Irankhah A., Mahmodzadeh M., Hoshyar N., [Effect of Pt on Zn-Free Cu-Al Catalysts for Methanol Steam Reforming to Produce Hydrogen](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **37**(4): 93-100 (2018).
- [65] Haley H., "High-Valent Copper Catalysis", *Chem. 535 Seminar*, 6 December 2012.
- [66] Luo J., Jiang S., Zhang H., Jiang J., Liu X., [A Novel Non-Enzymatic Glucose Sensor Based on Cu Nanoparticle Modified Graphene Sheets Electrode](#), *Analytica Chimica Acta*, **709**: 47- 53 (2012).

- [67] Heli H., Hajjizadeh M., Jabbari A., Moosavi-Movahedi A.A., [Copper Nanoparticles-Modified Carbon Paste Transducer as a Biosensor for Determination of Acetylcholine](#), *Biosens Bioelectron*, **24**: 2328-2333 (2009).
- [68] Nagashree K. L., Ahmed M. F., [Electrocatalytic Oxidation of Methanol on Cu-Modified Polyaniline-Electrode in Alkaline Medium](#), *J. Appl. Electrochem.*, **39**: 403-410 (2009).
- [69] Heli H., Zarghan M., Jabbari A., Parsaei A. J., [Electrocatalytic Oxidation of the Antiviral Drug Acyclovir on a Copper Nanoparticles-Modified Carbon Paste Electrode](#), *Solid State Electrochem.*, **14**: 787- 795 (2010).
- [70] Suseelamma A., Raja K., Reddy K. H., [Synthesis Characterization, DNA Binding and Nuclease Activity of Cobalt\(II\) Complexes of Isonicotinoyl Hydrazones](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **37**(4): 63-74 (2018).
- [71] Bahrami Adeb N., Mohammadi N., Khorramjah F., [Synthesis and Characterization of a Novel Nanoporous Composite Based on Elemental Sulfur and Graphitic Mesoporous Carbon](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **35**(4): 1-9 (2016).
- [72] Abbaszadeh A., Safari N., Amani V., Notash B., Raei F., Eftekhari F., [Mononuclear and Dinuclear Copper\(II\) Complexes Containing N, O and S Donor Ligands: Synthesis, Characterization, Crystal Structure Determination and Antimicrobial Activity of \[Cu\(phen\)\(tda\).2H<sub>2</sub>O\] and \[\(phen\)<sub>2</sub>Cu\(\(-tda\)Cu\(phen\)\)\(ClO<sub>4</sub>\)<sub>2</sub>.1.5H<sub>2</sub>O\]](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **33**(4): 1-13 (2014).
- [73] Rezvani A.R., Hadadzadeh H., [The Electrochemical and Spectroscopic Studies of trans-\[Lco\(\(DO\)\(DOH\)pn\)L'\] Complexes](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **21**(1): 21-27 (2002).
- [74] Safavi A., Shams E., [Electrochemical Investigation of Mo\(VI\)-MTB-ClO<sub>3</sub><sup>-</sup> System in Phosphate Buffer](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **20**(2): 96-101 (2001).
- [75] Nematollahi D., Rahimi J., Hesari M., Hamzehloei A., [Electrochemical Study of Iodide in the Presence of 2-Thioarbituric Acid- Catalytic Determination of 2-Thioarbituric Acid](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **20**(2): 90-95 (2001).
- [76] Golabi S. M., Fazli M., Rastegar-Mirzaei Y., [Electrochemical Behaviour of Nifedipine and Nitrendipine in Chloroform and Chloroform-Isopropanol Mixture](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **17**(1): 21-28 (1998).
- [77] Tavakolyanpoour F., Vaqif Husain S., Rastegar M.H., Saber Tehrani M., Abroomand Azar P., [Electrochemical Oxidation of Flavonoids and Interaction With DNA on the Surface of Supramolecular Ionic Liquid Grafted on Graphene Modified Glassy Carbon Electrode](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **37**(3): 117-125 (2018).
- [78] Naddaf E., Abedi M. R., Zabihi M. S., Imani A., [Electrocatalytic Oxidation of Ethanol and Ethylene Glycol onto Poly \(O-Anisidine\)-Nickel Composite Electrode](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**(1): 59-70 (2017).
- [79] Khanna P.K., Gaikwad S., Adhyapak P.V., Singh N., Marimuthu R., [Synthesis and Characterization of Copper Nanoparticles](#), *Materials Letters*, **61**: 4711-4714 (2007).
- [80] Wu S., Chen D., [Synthesis of High-Concentration Cu Nanoparticles in Aqueous CTAB Solutions](#), *Journal of Colloid and Interface Science*, **273**: 165-169 (2004).
- [81] Rezaei B., Damiri S., [Voltammetric Behavior of Multi-Walled Carbon Nanotubes Modified Electrode-Hexacyanoferrate\(II\) Electrocatalyst System as a Sensor for Determination of Captopril](#), *Sensors and Actuators B*, **134**: 324- 331 (2008).
- [82] Hegde R.N., Hosamani R. R., Nandibewoor S. T., [Electrochemical Oxidation and Determination of Theophylline at a Carbon Paste Electrode Using Cetyltrimethyl Ammonium Bromide as Enhancing Agent](#), *Anal. Lett.*, **42**: 2665-2682 (2009).
- [83] Khouchaf A., Takky D., Chbihi M. E. M., Benmokhtar S., [Electrocatalytic Oxidation of Methanol on Glassy Carbon Electrode Modified by Metal Ions \(Copper and Nickel\) Dispersed into Polyaniline Film](#), *Journal of Materials Science and Chemical Engineering*, **4**: 97 -105 (2016).
- [84] Miller B., [Split-Ring Disk Study of the Anodic Processes at a Copper Electrode in Alkaline Solution](#), *J. Electrochem. Soc.*, **116** (12): 1675 -1680 (1969).

- [85] Miller J.C., Miller J.N., "Statistics for Analytical Chemistry", Ellis Harwood, New York, (1994).
- [86] Hajjizadeh M., Jabbari A., Heli H., Moosavi-Movahedi A.A., [Electro-Oxidation and Determination of Mefenamic Acid and Indomethacin on a Copper Electrode](#), *Chem. Anal.*, **53**: 429 -444 (2008).
- [87] Heli H., Hajjizadeh M., Jabbari A., Moosavi-Movahedi A.A., [Fine Steps of Electrocatalytic Oxidation and Sensitive Determination of Some Amino Acids on Copper Nanoparticles](#), *Anal. Biochem.*, **388**: 81 -90 (2009).
- [88] Maleki A., Nematollahi D., [Mechanism Diversity in Anodic Oxidation of N,N-Dimethyl-p-Phenylene-Diamine by Varying pH](#), *Journal of Electroanalytical Chemistry*, **704**: 75-79 (2013).
- [89] Khan R., Ahmad R., Rai P., Jang L.W., Yun J.H., Yu Y.T., [Glucose-Assisted Synthesis of Cu<sub>2</sub>O Shuriken-Like Nanostructures and Their Application as Nonenzymatic Glucose Biosensors](#), *Sensors and Actuators B*, **203**: 471-476 (2014).
- [90] Farghali O., Mohamed N., [Voltammetric Determination of Azithromycin at the Carbon Paste Electrode](#), *Talanta*, **62**: 531- 538 (2004).