Bull. Chem. Soc. Ethiop. **2023**, 37(2), 491-503.
© 2023 Chemical Society of Ethiopia and The Authors
DOI: https://dx.doi.org/10.4314/bcse.v37i2.17

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

SILVER NANOPARTICLE-MODIFIED GRAPHITE PENCIL ELECTRODE FOR SENSITIVE ELECTROCHEMICAL DETECTION OF CHLORIDE IONS IN PHARMACEUTICAL FORMULATIONS

Yousif Taha Maaroof[1,2*] and Kamal Mustafa Mahmoud[1]

[1]Department of Chemistry, College of Science, Salahaddin University-Erbil, Iraq
[2]Department of Petroleum Technology, Erbil Technology College, Erbil Polytechnic University, Iraq

(Received July 14, 2022; Revised August 16, 2022; Accepted October 22, 2022)

ABSTRACT. For the first time, silver nanoparticles (AgNPs) were fabricated with graphite pencil electrode (GPE) by immersing a bare hard black pencil (HB pencil) in $AgNO_3$ solution mixed with extract *Quercus infectoria* solution, followed by placing directly against to UV lamp (254 nm) and kept for 30 min. Silver modified-GPEs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectrometer (EDX). The silver nanoparticles fabricated with graphite pencil electrode (AgNPs–GPE) showed excellent selectivity to chloride ion, as well as excellent reproducibility, together with it has several advantages such as sensitivity, simplicity, low cost, green, and fast response. The maximum oxidation cyclic voltammogram current of the AgNPs-PGE was found at 160 mV. The linear range of chloride ions detection is between (0.8-52 mmol L^{-1}), and the limit of detection (LOD) of chloride ions is 0.041 mmol L^{-1}. Finally, the Silver fabrication electrode was used to determine the chloride ion concentration in drugs, such as phenylephrine, metformin, procaine, and dopamine formulated with hydrochloride, and satisfactory results were obtained.

KEY WORDS: Electrochemical sensor, Cyclic voltammetry, Pencil graphite electrode, Chloride ion

INTRODUCTION

Chloride ions at their different concentrations are wide distribution in world, such as medicine and health [1], building [2], clinical diagnosis [3], environmental monitoring [4, 5], industrial applications [6], and agricultural production [7]. Therefore, several traditional methods for detecting concentration of chloride ion in real samples were mentioned in the literature, namely titration [8], ion chromatography [9], colorimetry [10], fluorescence spectroscopy [11], and square wave voltammetry [12, 13]. Although these methods have many advantages, they also have many disadvantages such as pretreatment sample process is complex, using expensive equipment, more sample consumption, time consuming, and many other shortcoming [14]. The sensors have wide applications in various diverse areas such as, gas sensor for detecting NH_3 and HNO_3 [15], biosensor for detecting glucose [16], it is produces to different sets of requirements. Ion selective electrodes are most popular and commercially available methods for sensing different ions, including chloride [17-19]. Voltammetric methods using different working electrodes are often preferred for sets of applications in electrochemical methods, due to some advantages such as high sensitivity, fastness, simplicity, portability, as well as the possibility to analysis various turbid or coloured solutions [20, 21]. Recently, nanocomposite materials use with electrochemical sensing technology are mostly used to detect a broad range of organic, inorganic, and heavy-metal ions, which have excellent performance and increase sensitivity of electrochemical detection, because nanomaterials are prepared from the specific type of compounds, when prepared nano-compounds have large surface area, by increasing surface area per mass of a material, a greater amount of the material of sensor can come into contact with surrounding sample materials compare to bulk compounds. In addition, there are other advantages for nanocomposite materials

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*Corresponding author. E-mail: yousif.maaroof@epu.edu.iq such as convenience, and inexpensive cost in the field of substances detection [14]. Many researches have been used silver nanostructure materials in electrochemical detection of halide [22-24]. Furthermore, many researches have been focused on the fabrication of Ag films for electrochemical detection of halide [25, 26]. Voltammetric determination halides method consists of two peaks (oxidation and reduction peaks) of different silver halides, when silver substrate used as the sensing agent. As well as, silver electrochemical sensing have a selective and sensitive way for detection of halide ions, as reported in the previous work [23]. Moreover, silver reacts with halide ion, then the precipitation of silver halide is formed on the surface of working electrode. The redox reaction on the electrode surface is formed by reversible potentials of silver halides, which provide sensing for halides. The type of halide can be identified by potential, as well as the concentration can be determined by current of cyclic voltammetric method. Voltammetric methods are provides many advantages over conventional ion selective electrodes sensors for detection of halide such as selectivity because the surface of electrode is directly contacted with solution and without any diffusional barrier, an electrode affinity for halide ions are high, quickness and it can be applied as a microsensor fabrication [24]. The graphite pencil electrodes (GPEs) are a suitable tool for electrochemical applications. PGEs are disposable, renowned, easy to fabricate, reliable, simple, feasible, commercially available, inexpensive, and good electrode material. GPEs could be fabricated potentially substitute for other expensive electrode in electrochemical analysis such as, glassy carbon, boron-doped-diamond, and platinum electrodes [27]. Moreover, GPEs are ease to chemical modification, and surface renewal. The pencil graphite working electrodes are highly stable and reproducible electrodes, which dependent on the active surface of electrodes. In addition, they are used to electrochemical sensing of various species due to their lower background currents, which causes to significant lower detection limit and greater sensitivity. Before voltammetric measurements, the electrode surface should be polishing or pre-treatment of electrode by a weighing paper to a smooth finish before each use [28]. The GPEs were used as working electrode for the voltammetric analysis of various applications in sensing compounds, such as quantitative determination of total polyphenolic contents in tea samples based on caffeic acid voltammetric behaviour on a disposable pencil graphite electrode [20]. In this paper, silver nanoparticles-modified graphite pencil electrode (AgNPs-modified GPE) for detection of chloride, which were prepared using cap of *Quercus infectoria* as green reducing and stabilizing agent. The AgNPs-modified GPE was characterized morphology and structure by XRD, SEM, and EDX. The AgNPs-modified (GPEs) applied to electrochemical detection of chloride in dugs formulated with hydrochloride and it was characterized by cyclic voltammetry (CV).

EXPERIMENTAL

Reagents and apparatus

Silver nitrate ($AgNO_3$), disodium hydrogen phosphate (Na_2HPO_4), and sodium dihydrogen phosphate (NaH_2PO_4) were purchased from Sigma-Aldrich Co., Ltd. Potassium chloride (KCl) was purchased from Scharlau Co., Ltd. X-ray diffraction (XRD) measurements were carried out, using a PAN analytical X' pert PRO (Cu Kα = 1.5406 Å). Scanning electron microscopy (SEM) (Quanta 4500). The elemental analysis of the synthesized nanoparticles was analyzed by energy dispersive X-ray spectrometer (EDX) performed in SEM. Electrochemical measurements were conducted with potentiostat/galvanostat (Interface-1010E, USA). The three-electrode system are composed of fabricate the silver nanoparticles-modified graphite pencil electrode (HB pencil) working electrode, saturated calomel reference electrode, and platinum counter electrode.

Preparation of plant extract Quercus infectoria

The cap of *Quercus infectoria* was collected from Erbil Mountains during summer season. The caps were washed with running tap water and finally with distilled water to remove any surface contaminants. It was dried at room temperature and made into a fine powder. 5.0 g of cap of *Quercus infectoria* powder was added to 200 mL distilled water and heated at 70 °C for 2 hours. The mixture was filtered using Whatman No. 1 filter paper. The filtered extracts were then stored at 4 °C for further use.

Preparation of silver nanoparticles-modified graphite pencil electrode

4.0 mL extract solution of cap of *Quercus infectoria* and 2.0 mL of 1.0 M $AgNO_3$ were mixed thoroughly at room temperature in 10.0 mL test tube. Then, a bare GPE (HB pencil) was immersed into a 10.0 mL test tube. To fabricate silver nanoparticles-modified graphite pencil electrode (AgNPs-modified GPE), that test tube was placed directly against to UV lamp (254 nm) and kept for 30 min. The fabricate-GPE was removed and washed by gentle dipping into deionized water, then dried at 60 °C for 5 min in oven.

Preparation of real sample

Firstly 10 tablets of phenylephrine hydrochloride and metformin hydrochloride (each one contains 3.48 and 182 mg of chloride separately) weighed and grounded into a fine powder, respectively. Then selected amount of both powders were determined individually. The amount of powder was equivalent to one tablet in each measurement. The measured weight of both drugs mixed with 15 mL of deionized water individually. The insoluble part was filtered off on a Whatman No. 41 filter-paper, and filtrate part of phenylephrine hydrochloride was diluted to 25 mL by using volumetric flask (25 mL) and filtrate part of metformin hydrochloride was diluted to 100 mL by using volumetric flask (100 mL) with deionized water. As well as, 4 injections of procaine hydrochloride, (each one contains 0.65 mg of chloride ion) were diluted to 10 mL by using volumetric flask (10 mL) with deionized water. Finally, 3 injections of dopamine hydrochloride (each one contains 46.3 mg of chloride ion) were diluted to 100 mL by using volumetric flask (100 mL) with deionized water.

RESULTS AND DISCUSSION

Characterization

Figure 1A shows the surface morphology of bare pencil graphite before deposited Ag nanoparticles on it, while Figure 1B displays the surface morphology and structural characteristics of AgNPs-GPE using scanning electron microscopy (SEM). The surface morphology of Figure 1B appeared as a homogeneously coated of AgNPs on the surface of GPE and the surface of GPE became more roughness compared to SEM Figure 1A. In addition, Figure 1C shows mapping image on the surface of pencil graphite with AgNPs, which represent of the presence of C, O, and Ag main elements into composition of electrode, confirming that AgNps were successfully incorporated with GPE. Moreover, the energy dispersive X-ray spectrum in Figure 2A collected validated the chemical composition of the nanoparticles. The strong signal peak appears about 3.0 eV confirms the silver nanoparticles formation on the surface of GPE, as well as peaks of carbon, oxygen, silicon, gold and copper that can be seen at the surface of pencil. The gold signal in EDX analysis appeared due to using gold powder to get better SEM image of nanoparticles. Figure 2B shows the XRD patterns of the synthesized AgNPs from silver nitrate and *Quercus infectoria* extract as the capping and reducing agent which is in the range of 2θ from 20^o to 80^o observed five diffraction peaks at (2θ = 25.98◦, 42.00◦, 49.09◦, 54.00◦ and 72.58◦) could be assigned to (111), (020), (022), (131) and (222) respectively, which corresponding as centered cubic phase of silver nanoparticles (JCPDS No. 96-710-9247) [29]. The particle size of AgNPs were calculated according to the Scherrer formula, which average diameter about 27 nm.

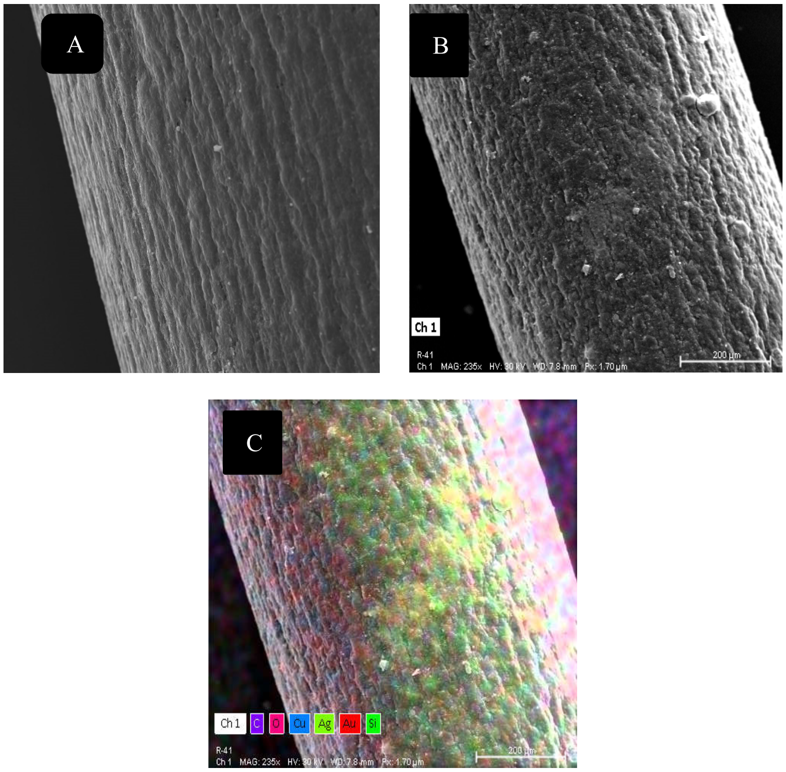


Figure 1. (A) SEM image of bare pencil graphite, (B) SEM micrograph of AgNPs-GPE magnified 235x and (C) corresponding mapping image of Ag in AgNPs-GPE.

Working electrode

Different working electrodes such as, glassy carbon, bare GPE, and AgNPs-GPE were tested under the same conditions using 15 mmol L^{-1} of KCl at a scan rate of 50 mV s^{-1}. The CVs shown in Figure 3, indicate that the background current of the AgNPs-GPE had the highest current curve comparing with both glassy carbon, and bare GPE. This referred to an excellent electrical property of AgNPs-GPE and rapid electron transfer between pencil graphite and silver nanoparticles compared to other electrodes. The maximum current of the AgNPs-GPE was found at 160 mV, which was sensitive to chloride ions. The mechanism to get cyclic wave was an oxidation-reduction reaction between chloride ions with silver atom which occupying the surface of pencil graphite to produce AgCl, as shown in this reaction: $Ag + Cl^- \rightarrow AgCl + e^-$ [30].

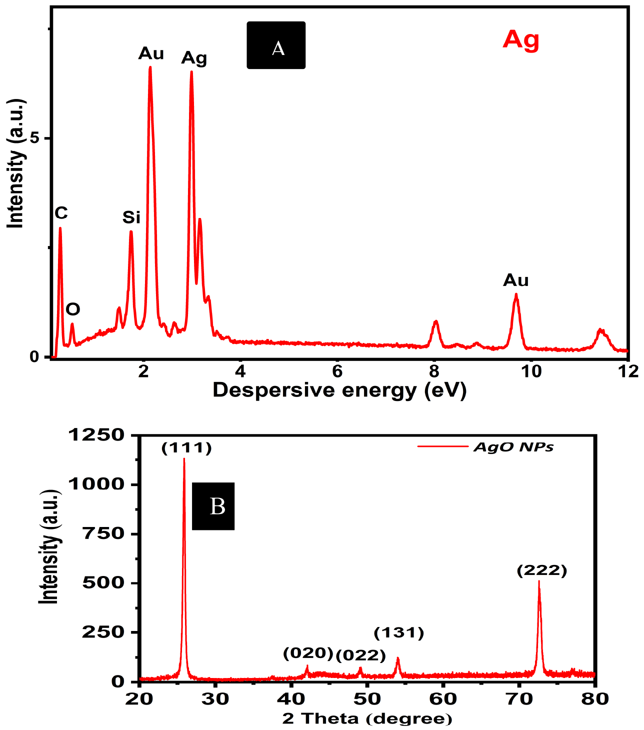


Figure 2. (A) Energy dispersive X-ray spectrum of the AgNPs-GPE and (B) XRD pattern of the silver nanoparticles as prepared.

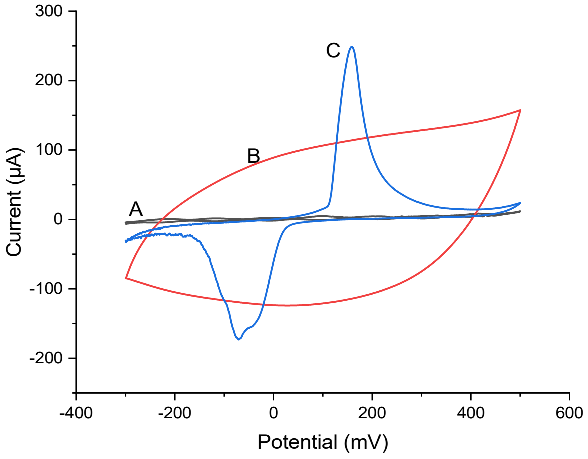
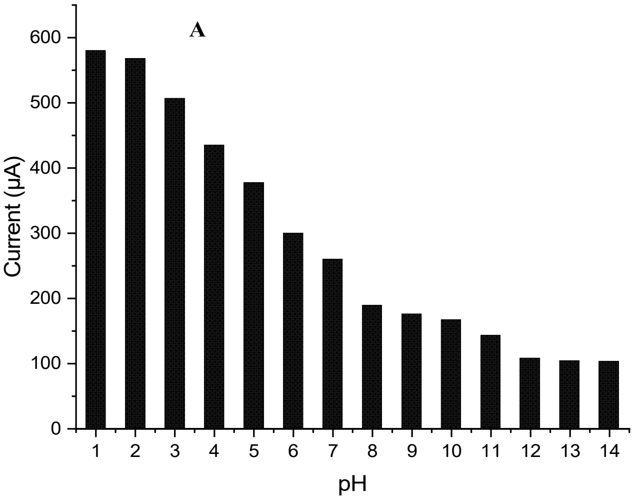


Figure 3. Cyclic voltammograms of A) bare-GPE, B) Glassy carbon, and C) AgNPs-GPE, in 15 mmol L^{-1} of potassium chloride at a scan rate of 50 mV s^{-1}.

Effect of pH

The cyclic voltammograms of oxidation current of the chloride ions (15 mmol L^{-1} KCl) on AgNPs-GPE were investigated at different pH range (1-14), as shown in Figure 4A. While the pH value increased from pH 7 to pH 14, the signal intensity of oxidation currents decreased. Although when the pH values decreased from pH 7 to acidic pH the signal intensity of oxidation current increased, but stability of oxidation current was lost which causes to poverty of the precision. The relative standard deviation (RSD) for eight cycles at pH 2 was 19.2% which shows instability of the measurements, as shown in Figure 4B. The pH 7 was chosen to balance the stability signal strength of the present work. In this work four different drugs were used, the pH 7 was selected to all samples, because, the oxidation current signal in pH 7 was stable.



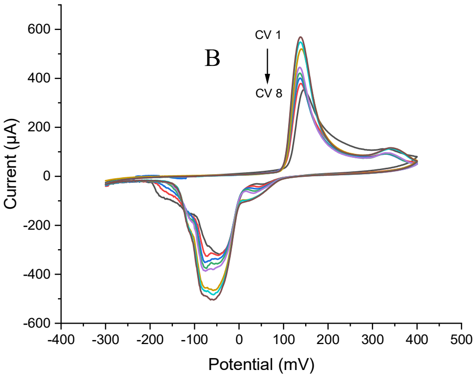


Figure 4. (A) The effect of pH on the oxidation current of AgNPs-GPE, in 15 mmol L^{-1} potassium chloride, at a scan rate of 50 mV s^{-1} and (B) Effect pH 2 on the stability of cyclic voltammograms AgNPs-GPE, in 15 mmol L^{-1} potassium chloride at a scan rate of 50 mV s^{-1}.

Effect of temperature

The oxidation peak currents of AgNPs-GPE were tested at different temperatures ranged from 10 °C to 50 °C. It was found that temperature does not have effect on the cyclic voltammograms of oxidation current for the chloride ions. Figure 5Figure shows this study, therefore, room temperature was recommended for further studies.

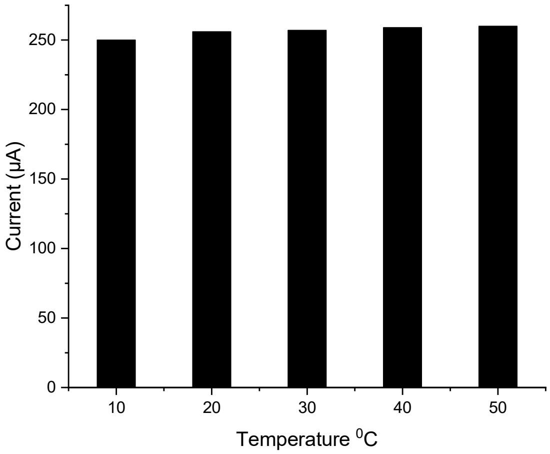
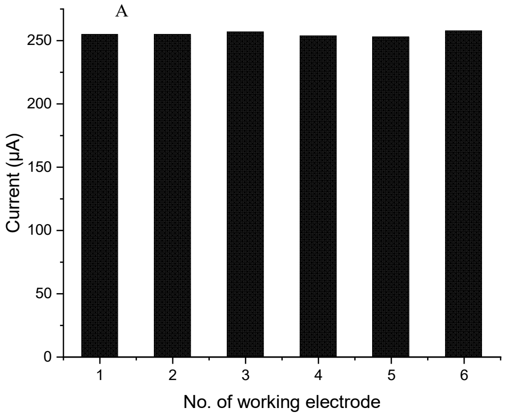


Figure 5. The effect of temperature on the oxidation current of AgNPs-GPE, in 15 mmol L^{-1} potassium chloride at pH 7, at a scan rate of 50 mV s^{-1}.

Repeatability and stability of electrode

The repeatability of proposed cyclic voltammetric platform was excellent for 15 mmol L^{-1} KCl. Figure 6A showed the oxidation peak currents for six different AgNPs-GPE which were tested under the same conditions, and the RSD was obtained about 0.74%. Furthermore, the stability of AgNPs-GPE was also studied when one AgNPs-GPE used for 30 days, as shown in Figure 6B. It showed that the prepared electrode had good stability, when change of analysis signal remained above 95% of the initial and it can be stored at room temperature for a long time without adding a stabilizer.



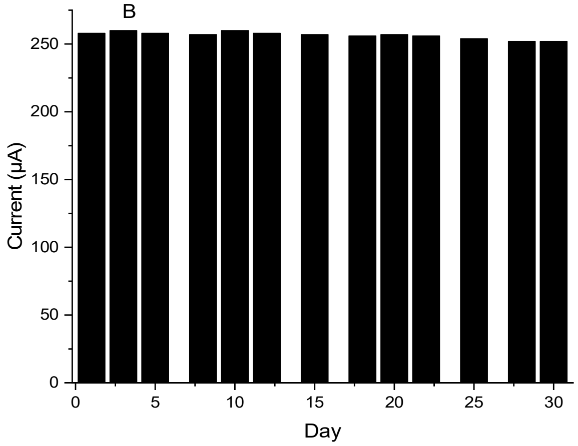


Figure 6. (A) The oxidation current of different AgNPs-GPE was tested for chloride ions (15 mmol L^{-1} potassium chloride) at a scan rate of 50 mV s^{-1} and (B) the oxidation current of the AgNPs-GPE tested for 30 days of chloride ions (15 mmol L^{-1} potassium chloride) at a scan rate of 50 mV s^{-1}.

Selectivity

Voltammetric detection at modified AgNPs-GPE provides sensitivity and selectivity to the analysis of chloride ion for a wide range of analytes. To improve the selectivity of this electrode, different cation, anions, and organic compounds were selected in this investigation, Figure 7A, B, and C) shown these studies. The same amount of chloride ion (15 m mol L^{-1}) was tested to each solutions mixed separately, the corresponding concentration of the cations were (K^+, NH_4^+, Na^+, Cu^{2+}, Ca^{2+}, Mg^{2+}, $Fe^{3+}$and Fe^{2+}), the anions were (CO_3^{2-}, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}), and organic compounds (fructose, maltose, glucose, paracetamol, and starch) the oxidation peak current basically consistent and the potentials ranging from −0.3 V to +0.5 V. The oxidation peak positions halogen element ions such as, fluoride, bromide and iodide do not overlap with oxidation peak of chloride ion [31], as shown in Figure 8. So the electrical analysis of chloride ions will not significantly interfere, therefore it is easy to distinguish [14]. The solubility product constant (K_{sp}) of silver halides such as, AgCl, AgBr, and AgI correlate with the oxidation potential peak of silver compound. Thermodynamically determines interaction tendency between the elements of halide anion with the surface silver atoms[23].The shift in the redox potentials of silver halides due to differences in the interaction tendency. The K_{sp} order of silver halides is Cl > Br > I in water. Until the K_{sp} decrease interaction tendency between the silver surface atoms and the halide anions is stronger, so bromide and iodide ions have stronger tendency than chloride ions to form silver halide compounds [25].

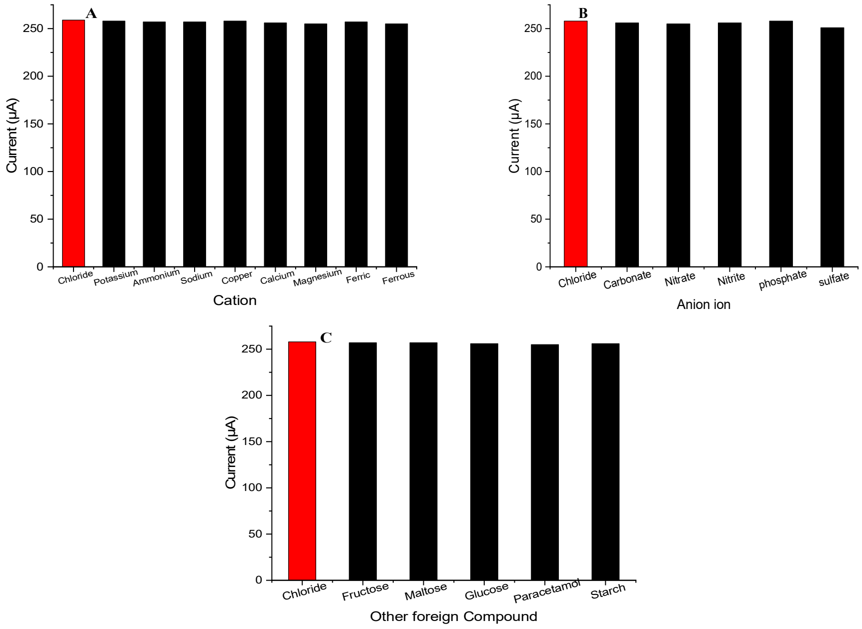


Figure 7. The oxidation current for cyclic voltammogram of AgNPs-GPE was tested to (A) different cations, (B) different anions, and (C) different organic compounds.

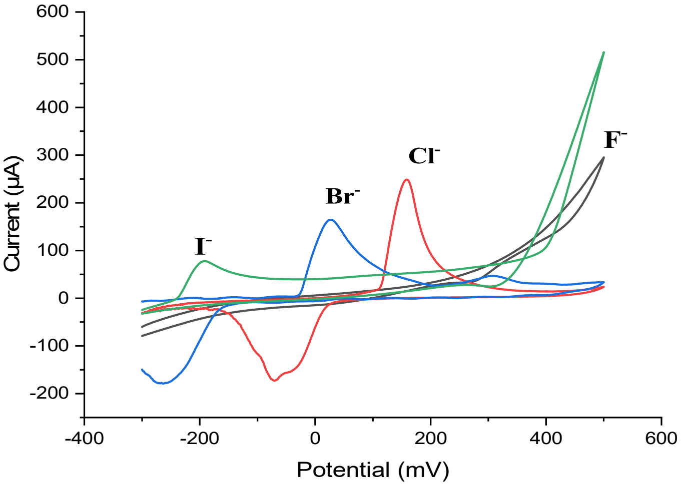


Figure 8. The cyclic voltammogram of AgNPs-GPE was tested in halogen anions (F^-, Cl^-, Br^-, and I^-) ions at 15 mmol L^{-1}, each halogen ions over the potentials ranging from −0.3 V to + 0.5 V.

Calibration curve

Under the optimum conditions, the AgNPs-GPE working electrode was applied with cyclic voltammetry to qualitative and quantitative determination of chloride ion in drugs formulated with hydrochloride, such as Phenylephrine, Metformin, Procaine, and Dopamine. The CV parameters are set according optimum conditions as follows: the scan voltage range was from −0.3 V to +0.5 V, scan rate at 50 mVs^{-1}, as well as 0.1 M of (pH = 7) phosphate buffer was used. The oxidation peak response of the AgNPs-GPE working electrode is directly proportional with concentration of chloride ion, as shown in Figure 9A and 9B. As a result, the linear range of the chloride ion is between (0.8-52 mmol L^{-1}) and LOD is about 0.041 mmol L^{-1}. One calibration curve was used because there was no shifting in the results of CV of the potassium chloride and drugs used in this study.

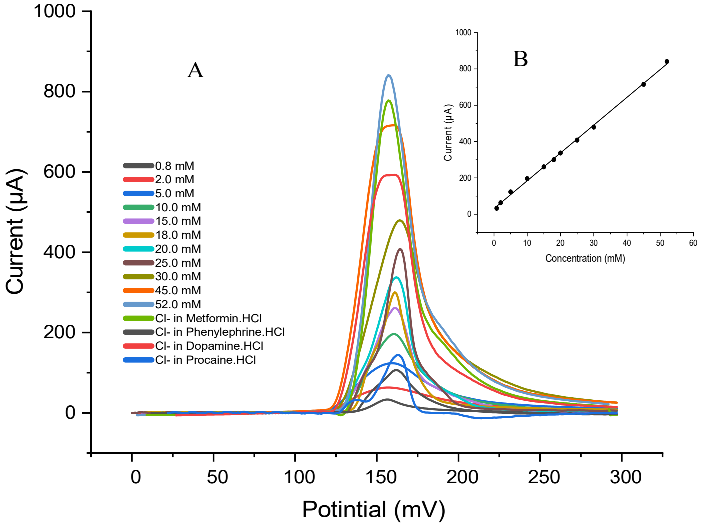


Figure 9. (A) The cyclic voltammogram of AgNPs-GPE for different concentrations of chloride ion: 0.8, 2, 5, 10, 15, 18, 20, 25, 30, 45, 52 mmol L^{-1} potassium chloride at a scan rate of 50 mV s^{-1} (pH = 7). (B) The calibration curve of Cl$^-$ in potassium chloride solution using AgNPs-GPE at mentioned concentrations in Figure 9A.

Analytical application for chloride real sample

Under the optimum conditions, the AgNPs-GPE sensor performance to quantitative determination of chloride ions in drugs formulated with hydrochloride. It was used to measure the chloride ion concentration in phenylephrine hydrochloride, metformin hydrochloride, procaine hydrochloride, and dopamine hydrochloride. Furthermore, the results of the proposed method compared with chloride ion selective electrode (Cl-ISE) method. Table 1 shows the accuracy and precision results, in which the error was between -1.19% and -5.15%. This indicates that the AgNPs-GPE can be used to detect the chloride ions in pharmaceutical formulations combined with hydrochloride. As well as, the relative standard deviation (RSD) for five determinations of chloride ions in drugs formulated with hydrochloride samples was between 0.387 and 2.673. Hence, the proposed method can be considered as a precise and reproducible method.

Table 1. Accuracy and precision data for the proposed method.

Drug sample	Drug content (mg)	Chloride ion content (mg)	Found (mg)		Error %	RSD
			Proposed method [a]	Cl-ISE		
Phenylephrine hydrochloride	20.0	3.48	3.334	3.51	-5.01	1.58
Metformin hydrochloride	850.0	182	179	182	-1.91	0.68
Procaine hydrochloride	5.00	0.65	0.626	0.66	-5.15	2.67
Dopamine hydrochloride	200.0	46.3	45.6	47.1	-3.16	0.387

[a] Average of five determinations.

CONCLUSION

In this research, AgNPs-GPE sensor was successfully prepared for the first time, when graphite pencil immersed into a mixture of $AgNO_3$ solution with the extract solution of cap of *Quercus infectoria* as green reducing and stabilizing agent and then directly placed against ultra violet light (254 nm). The average size of the Ag nanoparticles which deposed on the surface of GPE in AgNPs-GPE was about 27 nm. The AgNPs-modified GPE sensitivity was equal to 15.3 (µA/mM), which exhibited good sensitivity for detection of chloride ions as proved by the electrochemical CV curve. The prepared sensor used to determine four drugs which formulated with hydrochloride, such as phenylephrine hydrochloride, metformin hydrochloride, procaine hydrochloride, and dopamine hydrochloride. Furthermore, this technique can be used to detect bromide and chloride ions together. When pH of solution decreases the signal intensity increases, but stability of oxidation current was lost. So the pH 7 was chosen to balance the stability signal strength of the present work. The linear range of chloride ions detection was (0.8-52 mmol L^{-1}), and the LOD of chloride ions was 0.041 mmol L^{-1} in the scan range voltage of the working electrode −0.3V to +0.5V and the scan rate at 50 mVs^{-1}. AgNPs-GPE sensor has several advantages such as selectivity, sensitivity, simplicity, low cost, green, and fast response. Thus, this method can be used to determine chloride and bromide ions in different real samples.

ACKNOWLEDGEMENTS

The authors would like to thank the Scientific Research Centre in Erbil Polytechnic University for their facilities and help.

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