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Voltammetric determination of copper(II) ion using cyanex 921 modified pencil graphite electrodes

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In this study, polymer-based modified electrodes (PGE/PPy and PGE/PPy/Cyanex 921) based on pencil graphite electrodes (PGE) have been prepared for the determination of copper(II) ions. Parameters such as the number of cycles, scan rate, and solution pH have been optimized to prepare the electrodes. As a result of the analyses, the optimum number of cycles is determined to be 8 for the PGE/PPy and PGE/PPy/Cyanex 921 electrodes. The scan rate is 40 mV/s for PGE and 80 mV/s for PGE/PPy and PGE/PPy/Cyanex 921 electrodes. The pH value of the analysis medium is set to 2 for both the PGE and PGE/PPy electrodes and 3 for the PGE/PPy/Cyanex 921 electrode. The electrodes are prepared using the cyclic voltammetry (CV) technique. The performance of the electrodes in the determination of copper(II) ions was investigated using the differential pulse voltammetry (DPV) method. As a result of experiments with the electrodes, linearity is obtained in the ranges of 20–200 ppm (R^2=0.9991) for the PGE electrode, 20–150 ppm (R^2=0.9983) for the PGE/PPy electrode, and 20–140 ppm (R^2=0.9991) for the PGE/PPy/Cyanex 921 electrode. The limits of detection (LOD) for the PGE, PGE/PPy, and PGE/PPy/Cyanex 921 electrodes are found to be 3.60, 3.51, and 2.15 ppm, respectively (S/N=3). Interference effect experiments showed that the selectivity and sensitivity of the PGE/PPy/Cyanex 921 electrode for copper(II) are not significantly affected by the presence of interfering species. The developed electrodes are used to determine copper(II) ions added to water samples by the standard addition method, and the recovery values of the method were close to 100%.

Keywords: Cyanex 921, Copper (II), Modified electrode, Pencil graphite electrode, Voltammetry

Introduction

The determination and recovery of metal ions in aqueous solutions is of paramount importance for environmental protection, industrial waste management, and economic sustainability. In particular, the analysis of heavy metals such as copper (II) is critical due to their potential toxicity and environmental impact. While traditional techniques such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) are widely utilized for this purpose, their high operational costs, time-consuming sample preparation, and lack of portability limit their use for on-site monitoring. Consequently, there is an increasing demand for alternative techniques that are fast, low-cost, and highly sensitive. Electroanalytical methods, specifically differential pulse voltammetry (DPV) and cyclic voltammetry (CV), have come to theforefront as robust alternatives due to their practical and economic advantages.

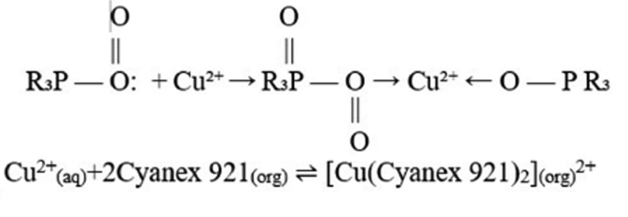
The performance of these electrochemical sensors is fundamentally dictated by the properties of the working electrode. While modified glassy carbon electrodes (GCE), gold electrodes (Au) and carbon paste electrodes (CPE) are common in literatüre[1], Pencil Graphite Electrodes (PGE) have emerged as a highly advantageous platform. PGEs offer a wide potential window, high sensitivity, and easy availability; furthermore, their low cost and single-use (disposable) nature effectively eliminate the risk of surface fouling and memory effects during environmental analysis. However, despite these benefits, bare PGEs often lack the necessary selectivity and sensitivity to detect trace metal ions in complex matrices, necessitating surface modification with functional materials[2,3].

For the selective separation of metal ions, organophosphorus compounds of the "Cyanex" series are highly powerful extractants. Studies on Cyanex compounds have been carried out using GC/MS, FTIR instruments[4], and liquid membranes[5-7] . Cyanex 272, 301, and 302 have been reported to provide high efficiency in copper determination and successful results in the production of uranyl (UO_2)-selective polymeric membrane electrodes[8].

A critical member of this series, Cyanex 921 (Trioctylphosphine oxide – TOPO), developed by Cytec, is an exceptionally durable reagent with 99% purity[9]. Organophosphorus extractants are widely used in solvent extraction processes for metal recovery from industrial and secondary resources, as well as in environmental remediation applications involving the removal of organic pollutants from aqueous systems[10].

Cyanex 921 interacts with Cu(II) ions through a non-ion-exchange, coordinative complexation mechanism, thanks to the strong electron-donating property of the phosphine oxide group (P=O) in its structure. In this interaction, the Cu^{2+} ion acts as a Lewis acid, while Cyanex 921 serves as the ligand, with coordination occurring via the lone electron pair on the phosphoryl oxygen. The resulting complex typically consists of the Cu(II) ion surrounded by one or two Cyanex 921 molecules, forming a structure soluble in the organic phase, which facilitates the transfer of the metal ion from the aqueous phase to the organic phase. Due to the non-proton-donating (non-ionic) nature of Cyanex 921, this complexation is minimally affected by pH changes and exhibits selective extraction behavior for Cu(II), especially in acidic environments[11-13]. The coordination complexation mechanism between Cyanex 921 and Cu(II) is shown in Scheme 1.

However, incorporating a selective ligand like Cyanex 921 onto an electrode surface requires a stable and conductive matrix to ensure high sensitivity. Polypyrrole (PPy), a prominent conductive polymer, addresses this need by providing a large surface area and excellent electron transfer properties. By forming a stable film on the electrode, PPy not only accelerates the electrochemical kinetics but also serves as an effective host for the immobilization of Cyanex 921. The synergy between the high metal-binding capacity of Cyanex 921 and the high conductivity of PPy is expected to significantly enhance the overall sensor performance.



$$R_3P - \overset{\overset{\displaystyle O}{\|}}{O}{:} + Cu^{2+} \rightarrow R_3P - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{O}} \rightarrow Cu^{2+} \leftarrow O - P\,R_3$$

$$Cu^{2+}{}_{(aq)} + 2\text{Cyanex } 921_{(org)} \rightleftharpoons [Cu(\text{Cyanex } 921)_2]_{(org)}^{2+}$$

Scheme 1 — Coordination complexation mechanism between Cyanex 921 and Cu(II)

A review of the literature reveals that, to our knowledge, no study has yet integrated the low-cost PGE platform with a polypyrrole and Cyanex 921 modification (PGE/PPy/Cyanex 921) for the determination of metal ions. This study aims to fill this gap by developing a unique electrochemical sensor that combines economic feasibility with high analytical performance. The characterization of the prepared electrodes was conducted using CV, while the quantitative determination of Cu(II) ions was performed using the DPV technique.

Experimental Section

Chemical Reagents

The chemical substances used in the experiments were of analytical grade. Pyrrole (Py), ortho-phosphoric acid (85%), acetonitrile (CH_3CN), lead(II) nitrate [$Pb(NO_3)_2$], and boric acid (H_3BO_3) were purchased from Merck. Lithium perchlorate ($LiClO_4$) and cadmium(II) nitrate pentahydrate [$Cd(NO_3)_2{\cdot}5H_2O$] were purchased from Sigma-Aldrich. Tetrabutylammonium perchlorate (TBAP) [$C_{16}H_{36}ClNO_4$] and silver nitrate ($AgNO_3$) were obtained from Fluka. Nickel(II) nitrate hexahydrate [$Ni(NO_3)_2{\cdot}6H_2O$] was obtained from Alfa Aesar, and acetic acid was obtained from Riedel-de Haën. Ultra-pure water was used in the preparation of all solutions.

Electrodes and Devices

Electrochemical measurements were performed using an Autolab/PGSTAT 302N Potentiostat-Galvanostat device equipped with NOVA 1.11 software (produced by Metrohm Autolab, Switzerland). All experiments were conducted in a three-electrode system. In this system, pencil graphite electrodes were used as the working electrode, an Ag/AgCl electrode as the reference electrode, and a Pt wire electrode as the counter electrode. The surface characterization of the electrodes was performed using a scanning electron microscope (SEM) (FEI Quanta FEG 250, USA). pH measurements of the solutions were conducted using a multi pH/ion meter (Mettler Toledo). All experiments were carried out at room temperature.

Preparation of electrode materials

Faber-Castell pencil leads (2B, 0.7 mm) were used as electrode materials due to their high carbon content and suitable conductivity properties. The pencil leads were cut to a length of 3 cm to obtain an appropriate size and were attached to a holder for use in the experiments. These bare pencil leads are defined as pencil graphite electrodes (PGE). The electrical conductivity of the PGE was achieved by soldering metal wires, which is crucial for the usability of the electrode. Removing impurities from the PGEs is a critical step for their performance. For this purpose, the electrodes were washed with pure water before analysis.

Preparation of the PGE/PPy electrode

Electrolyte solutions were prepared by dissolving 0.1 M pyrrole and 0.1 M tetrabutylammonium perchlorate (TBAP) in 15 mL of acetonitrile. The PGE, Ag/AgCl reference electrode, and platinum wire were immersed in the electrochemical cell solution. The electrode was prepared using the cyclic voltammetry (CV) method within the potential range of (–0.6) V to (+1.2) V at a scan rate of 80 mV/s and with 8-cycle voltage scanning.

Preparation of the PGE/PPy/Cyanex 921 electrode

Electrolyte solutions were prepared by dissolving 0.1 M pyrrole, 0.05 M Cyanex 921, and 0.1 M tetrabutylammonium perchlorate (TBAP) in 15 mL of acetonitrile. The PGE, Ag/AgCl reference electrode, and platinum wire were immersed in the electrochemical cell solution. The electrode was prepared using the cyclic voltammetry (CV) method within the potential range of (–0.6) V to (+1.2) V at a scan rate of 80 mV/s and with 8-cycle voltage scanning.

Conductive polymers such as polyaniline (PANI), polythiophene (PTh), and polypyrrole (PPy) are commonly used in the preparation of modified electrodes. Polypyrrole is one of the most preferred conductive polymers due to properties such as its ability to form stable films on various materials employing electrochemical polymerization, its high conductivity, ease of synthesis, high stability, stability in the oxidized state, and suitability for technological applications[14]. Polypyrrole is a conductive polymer easily synthesized by chemical or electrochemical methods. The high electrical conductivity and electrochemical redox activity of PPy make it a valuable material in many fields[15,16]. These properties enable PPy to play an important role in developing new-generation technologies in electronics, biomedicine, and energy storage.

Voltammetric measurements

The analysis phase was initiated after the optimization of pH and electrode preparation parameters. First, PGE/PPy and PGE/PPy/Cyanex 921 electrodes were prepared using the determined optimum values. Britton-Robinson buffer (BR) solution was prepared in water and contained 0.1 M $LiClO_4$, which was used as the analysis solution. Before starting the analysis, differential pulse voltammograms were recorded five times for each of the PGE, PGE/PPy, and PGE/PPy/Cyanex 921 electrodes within the potential range of (0) V to (1.4) V in the prepared solution to decrease their electroactivity. Different copper(II) concentrations in the 2–200 ppm range were applied in the second stage, and differential pulse voltammograms were recorded. The relationship between concentration and peak currents was then evaluated. The peak current values obtained from the voltammograms represent the average of three repeated measurements. A calibration curve was constructed for the analyzed copper(II) concentrations by taking the mean of the maximum peak current values obtained from the voltammograms.

Results and Discussion

Surface Characterization

SEM images were obtained using a FEI Qunta FEG 250 model scanning electron microscope to examine the surface morphology of the prepared electrodes. When the SEM images of the electrodes given in Fig. 1 are examined, it is observed that the surfaces of the modified electrodes are more porous compared to the bare pencil graphite electrode (Figs 2b & 2c). The

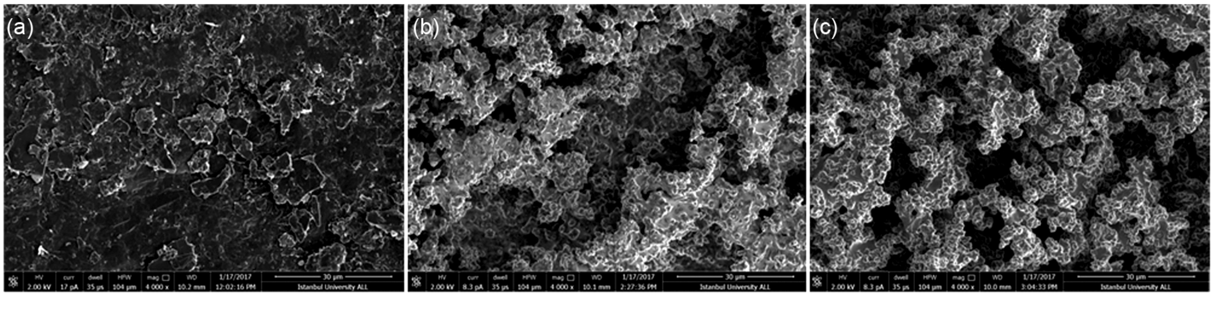


Fig. 1 — SEM images of the electrodes: (a) PGE, (b) PGE/PPy electrode and (c) PGE/PPy/Cyanex 921 electrode

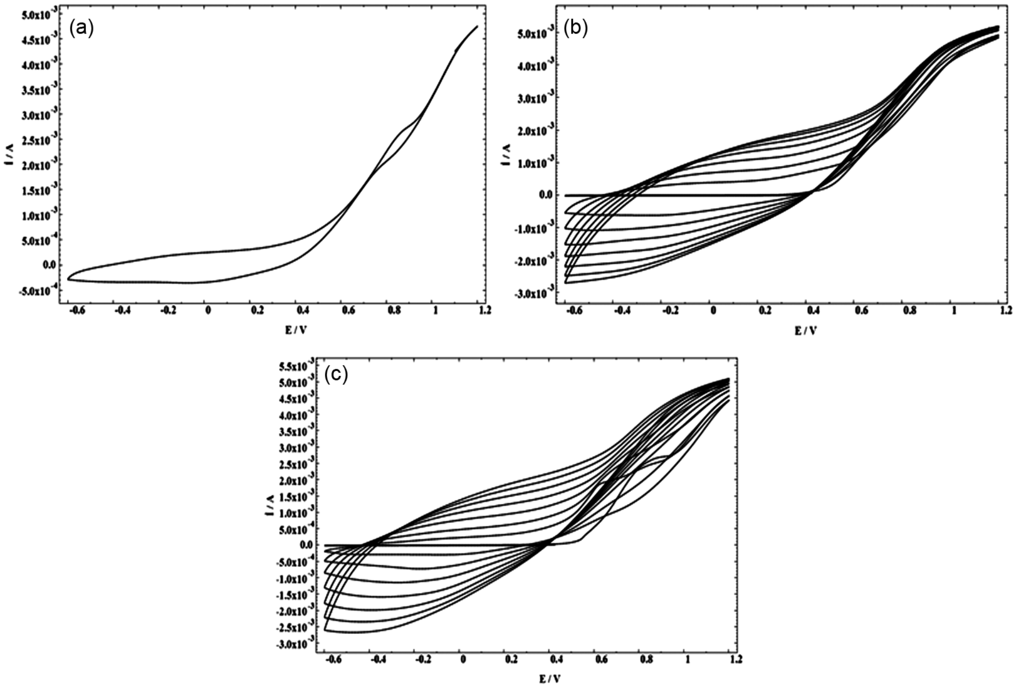


Fig. 2 — CV voltammograms of the electrodes: (a) PGE/PPy (1 cycle), (b) PGE/PPy (8 cycles) and (c) PGE/PPy/Cyanex 921 (8 cycles)

difference in the SEM image of the PGE/PPy/Cyanex 921 modified electrode from those of the bare pencil graphite electrode (PGE) (Fig. 2a) and the polypyrrole electrode (PGE/PPy) suggests that the Cyanex 921 compound is incorporated into the structure during the polymerization process. Upon examination of the images, it is seen that the surfaces of the modified electrodes contain more tightly packed crystalline structures than the PGE surface. These SEM images confirm that the modification process has been successfully completed.

CV measurements of the electrodes

When a potential scan was applied anodically between (–0.6) V and (+1.2) V at a scan rate of 80 mV/s in an acetonitrile solution containing 0.1 M pyrrole and 0.1 M TBAP supporting electrolyte using the PGE, an irreversible peak corresponding to the oxidation of pyrrole was observed around (+0.8) V (Fig. 2b).

To form a polypyrrole film layer on the surface of the PGE, an 8-cycle potential scan was applied between (–0.6) V and (+1.2) V at a scan rate of 80 mV/s in the polymerization solution containing 0.1 M pyrrole. In this way, the PGE/PPy electrode was prepared. The polypyrrole film's reduction and oxidation peak currents increase as the film layer grows, while the oxidation peak corresponding to pyrrole disappears (Fig. 2c).

The PGE/PPy/Cyanex 921 modified electrode was prepared by applying an 8-cycle potential scan between (–0.6) V and (+1.2) V at a scan rate of 80 mV/s in an acetonitrile solution containing 0.1 M pyrrole monomer, 0.05 M Cyanex 921, and 0.1 M TBAP supporting electrolyte. After the application, it was observed that a film layer had formed on the surface of the pencil graphite electrode. The peak currents corresponding to polypyrrole were observed to increase gradually. The difference between the 8-cycle voltammogram of the PGE/PPy/Cyanex 921 modified electrode and that of the PGE/PPy electrode emphasizes that a different electrode was prepared by incorporating the Cyanex 921 compound into the structure.

Optimization of electrode preparation parameters

Before proceeding to the optimization of the electrode preparation parameters, to reduce the electroactivity of the polypyrrole films on PGE/PPy and PGE/PPy/Cyanex 921 electrodes, differential pulse voltammograms were recorded five times within the potential range of (0) V to (1.4) V for each electrode in a 0.1 M $LiClO_4$ solution prior to the addition of copper(II) solution. This procedure was also performed to maintain identical conditions for the PGE electrode. In this process, performed in the absence of copper(II) ions, it was observed that the oxidation peak for the electrodes gradually decreased.

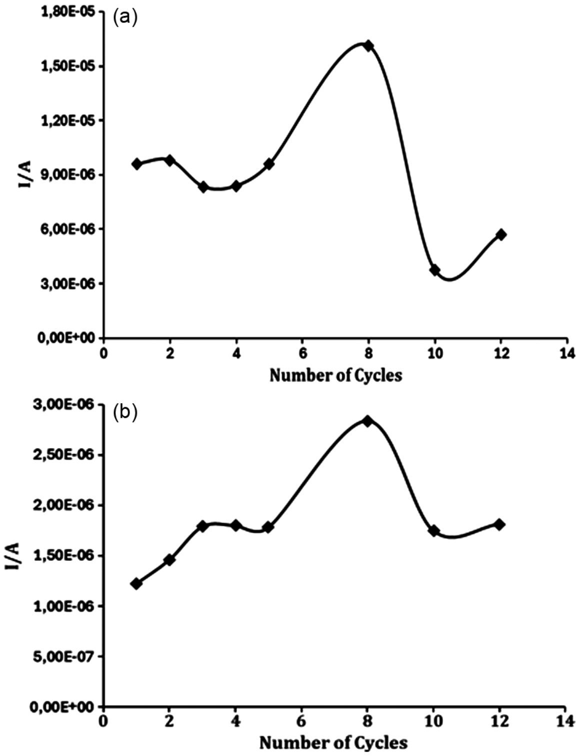


Fig. 3 — Effect of the number of cycles on the response of the electrodes (a) PGE/PPy and (b) PGE/PPy/Cyanex 921

Effect of number of cycles on electrode response

The optimum number of cycles affects the effectiveness of the formed polymeric layer. This polymeric layer is responsible for the detection and recognition properties of the electrode. The number of cycles applied during the electropolymerization process influences the sensor's measurement sensitivity and linearity[17].

The electrodes were prepared by performing electropolymerization at different numbers of cycles (1, 2, 3, 4, 5, 8, 10, 12) in the potential range of (–0.6) V to (+1.2) V and at a scan rate of 80 mV/s using the CV method to determine the optimum number of cycles of the electropolymerization process.

DPV analyses were carried out with PGE/PPy and PGE/PPy/Cyanex 921 modified electrodes in a 0.1 M $LiClO_4$ solution containing 128 ppm copper(II) to determine the optimum number of cycles. The maximum current values obtained for eight different cycle numbers are presented in the graphs (Fig. 3). For both electrodes, the optimum number of cycles, where the maximum current observed was determined to be 8. A review of studies on the electrochemical behavior of polypyrrole also shows that similar results have been obtained for the number of cycles[18].

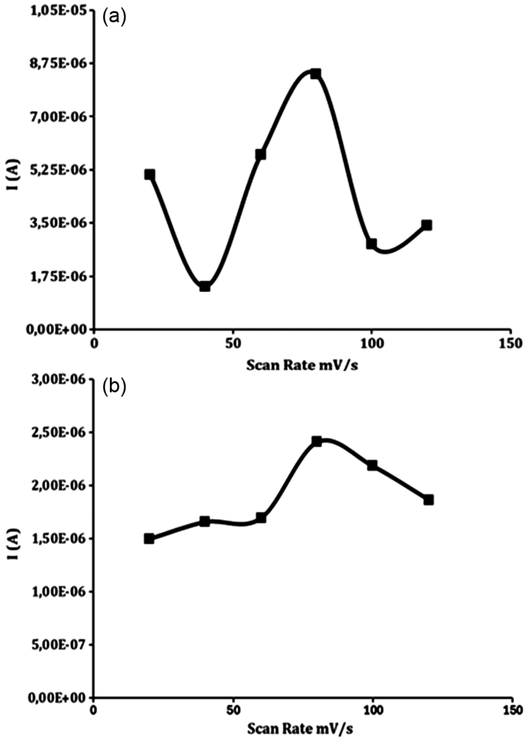


Fig. 4 — Effect of scan rate on the response of the electrodes (a) PGE/PPy and (b) PGE/PPy/Cyanex 921

Effect of scan rate on electrode response

For the optimization of the scan rate, electropolymerization was carried out using the CV method within the potential range of (–0.6) V to (+1.2) V at scan rates ranging from 20 mV/s to 120 mV/s, in 20 mV/s increments, and electrodes with 8 cycles were prepared.

DPV analyses were performed with PGE/PPy and PGE/PPy/Cyanex 921 modified electrodes prepared at different scan rates in a 0.1 M $LiClO_4$ solution containing 128 ppm copper(II) to determine the optimum scan rate. The relationship between the maximum current values obtained with the modified electrodes and the scan rate is shown in Fig. 4. The optimum scan rate was accepted as 80 mV/s, at which the maximum peak current value was obtained for the PGE/PPy electrode.

Similarly, the highest peak current value for the PGE/PPy/Cyanex 921 modified electrode was also observed at a scan rate of 80 mV/s. When the results obtained from the scan rate analyses are examined, it is seen that they are concordant with the literature[18].

Effect of pH on electrode response

After optimizing the electrode preparation parameters, the modified electrodes were prepared

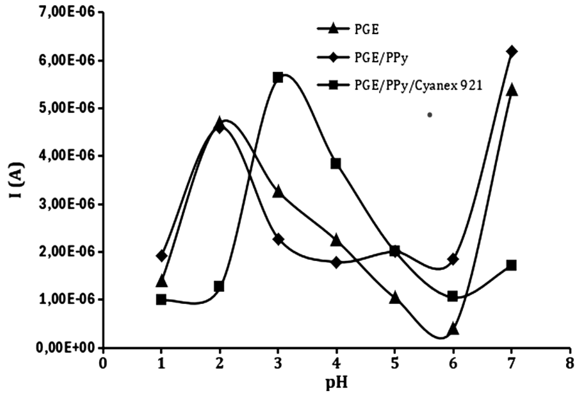


Fig. 5 — Effect of analysis medium pH on the performance of the electrodes

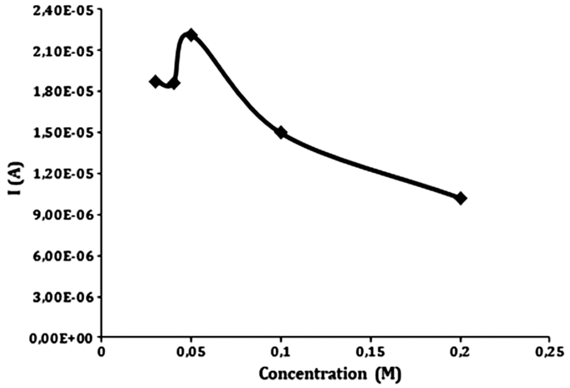


Fig. 6 — Effect of modifier concentration on electrode response

under these optimum conditions. For the analyses, a Britton-Robinson (BR) buffer solution was prepared in an aqueous medium with a pH range of 1.0–7.0, and 0.1 M $LiClO_4$ supporting electrolyte was added. In the presence of 128 ppm copper(II) ions, analyses were carried out using the DPV method. The maximum peak current values obtained from the measurements performed at different pH values for PGE and PGE/PPy electrodes are presented in Fig. 5. Although maximum current values were observed at pH 7 for both PGE and PGE/PPy, precipitation occurred in the solution at this pH; therefore, pH 2, where the second highest current values were obtained, was selected as the optimum pH for both electrodes. For the PGE/PPy/Cyanex 921 electrode, pH optimization showed that the maximum current value was obtained at pH 3, according to the applied potential.

Effect of cyanex 921 concentration on electrode response

PGE/PPy/Cyanex 921 electrodes containing different concentrations of the Cyanex 921 (0.03 M, 0.05 M, 0.1 M, 0.2 M) were prepared to determine the optimum concentration of the Cyanex 921 modifier added to the solution prepared for the polymerization process. DPV analysis was performed in a BR buffer solution containing 128 ppm copper(II) ions and 0.1 M $LiClO_4$, and the maximum peak current values were examined. As a result of the analysis, it was observed that the maximum current value was obtained when the concentration of Cyanex 921 was 0.05 M (Fig. 6).

Analysis of copper(II) ion by differential pulse voltammetry (DPV)

The electrochemical determination of copper(II) was performed by adding 2–200 ppm copper(II) ions to a BR buffer solution at the optimum pH containing 0.1 M $LiClO_4$ supporting electrolyte, using PGE and the modified electrodes prepared under optimum conditions, and employing the DPV method. Measurements for each electrode were repeated at least three times. Fig. 7 shows the DPV voltammograms obtained in the concentration range of 2–200 ppm using the electrodes, and Figure 8 shows the calibration graphs plotted with the maximum peak current values.

When the maximum peak current values obtained with the electrodes in Fig. 8 (a, b, and c) are plotted against copper(II) concentrations, linearity is observed in the range of 20–200 ppm for the PGE electrode, 20–150 ppm for the PGE/PPy electrode, and 20–140 ppm for the PGE/PPy/Cyanex 921 electrode. The R^2 values were determined to be 0.9991, 0.9983, and 0.9991, respectively.

As a result of the DPV analysis performed in the 2–200 ppm copper(II) concentration range with the electrodes, the limit of detection (LOD) and limit of quantification (LOQ) were calculated based on the linear relationship between the maximum peak current values and concentration (S/N=3) (Table 1).

The voltammograms obtained from DPV analysis using PGE, PGE/PPy, and PGE/PPy/Cyanex 921 electrodes in a 128 ppm copper(II) solution are compared in Fig. 8. Comparison of DPVs obtained with the electrodes in 128 ppm copper(II) solution is shown in Fig. 9. From this figure, it is observed that the current response of the PGE/PPy/Cyanex 921 electrode to copper(II) ions is higher than the current responses obtained with PGE and PGE/PPy electrodes. This result demonstrates that the Cyanex 921 compound has a catalytic effect on the electrode surface in the electrochemical determination of copper(II) ions, increasing the peak current value and thus enhancing the selectivity of the electrode

Table 1 — Calculated R², LOD, and LOQ values of the electrodes

Electrodes	R^2	LOD (ppm)	LOQ (ppm)
PGE	0.9991	3.60	11.98
PGE/PPy	0.9983	3.51	11.68
PGE/PPy/Cyanex 921	0.9991	2.15	7.15

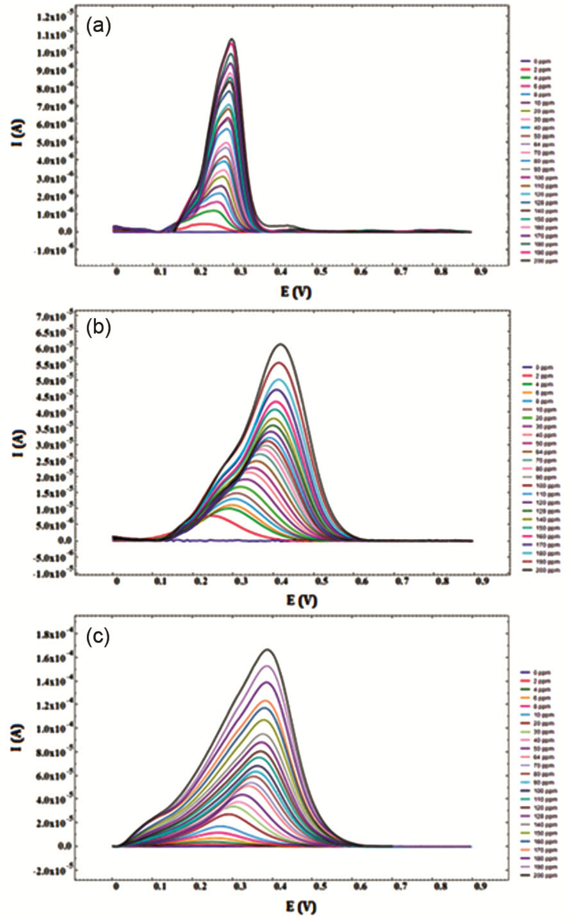


Fig. 7 — Differential pulse voltammograms of (a) PGE, (b) PGE/PPy, and (c) PGE/PPy/Cyanex-921 electrodes for 2–200 ppm copper(II) solution

for copper(II) ions. This finding indicates that modification with the Cyanex 921 compound is favorable in copper(II) ion analysis.

Effect of interfering species on electrode response

The electrochemical responses of the developed sensors to copper(II) ions were investigated in the presence of different metals in the analytical environment (Table 2). For this purpose, PGE, PGE/PPy, and PGE/PPy/Cyanex 921 electrodes prepared under optimum conditions were used in a solution containing 160 ppm copper(II) ions, to which cadmium(II), nickel(II), lead(II), and zinc(II) ions

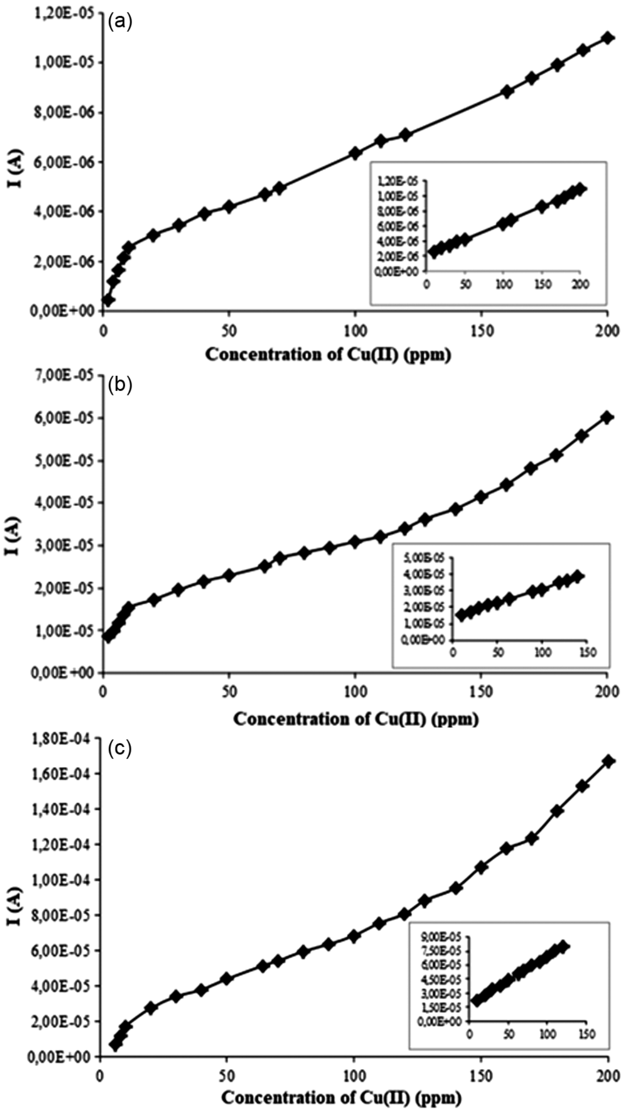


Fig. 8 — Graph of current values obtained by DPV for copper(II) concentrations ranging from 2–200 ppm using (a) PGE, (b) PGE/PPy and (c) PGE/PPy/Cyanex 921 electrodes

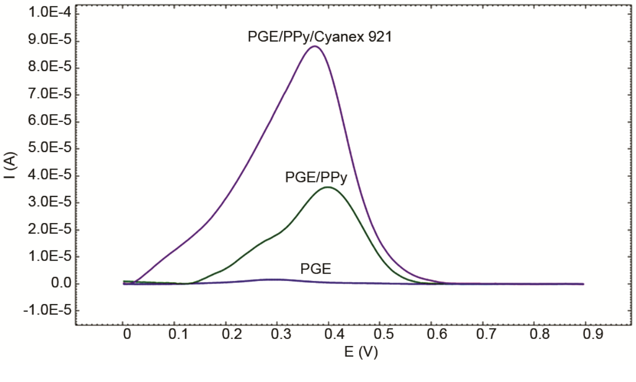


Fig. 9 — Comparison of differential pulse voltammograms obtained with the electrodes in a 128 ppm copper(II) solution

Table 2 — Effect of potentially interfering species at various concentrations on the DPV response of the electrodes in the presence of 160 ppm copper(II) ions

Interfering species	Concentration values of interfering species (ppm)	Change in current values (μA)		
		PGE	PGE/PPy	PGE/PPy/ Cyanex921
Cd(II)	10	3.86	10.86	3.67
	20	4.53	12.25	5.39
	30	6.05	13.45	8.03
	40	7.19	14.95	11.89
	50	8.77	17.05	14.72
Ni(II)	10	12.04	8.75	3.92
	20	12.92	10.46	5.97
	30	13.73	11.16	7.53
	40	13.84	12.39	8.65
	50	14.16	12.73	8.93
Pb(II)	10	9.53	1.00	1.15
	20	9.75	2.62	2.79
	30	11.01	3.84	4.08
	40	11.45	5.69	5.37
	50	14.02	7.81	7.51
Zn(II)	10	10.84	11.71	-
	20	11.25	13.52	-
	30	11.44	15.25	-
	40	11.76	16.98	-
	50	12.13	17.25	-

were added in increasing concentrations (ranging from 0 to 50 ppm in 10 ppm increments). Since it was thought that these ions could cause interference, the effects of cadmium(II), nickel(II), lead(II), and zinc(II) ions on the response of PEG, PEG/PPy, and PEG/PPy/Cyanex 921 electrodes toward copper(II) ions were investigated by DPV analysis.

Stability of the electrodes

The stability of the developed sensors was found to be high due to the stable surface provided by electrode modification. Pencil graphite electrodes modified with polypyrrole (PPy) and Cyanex 921 produced reproducible signals in short-term measurements, with minimal signal variation observed during voltammetric scans performed on the same day. Electrochemical tests revealed that the sensor performance did not exhibit significant deterioration over numerous repeated measurements. These results demonstrate that the modified electrodes are both physically and chemically stable and can be used as reliable sensors for the analysis of environmental or industrial samples.

Table 3 — Copper(II) concentrations (added and determined) in the water sample using the PGE/PPy/Cyanex 921 electrode

Added Cu(II) concentration (ppm)	Determined Cu(II) concentration (ppm)	% Recovery
64.00	63.19	98.74
128.00	129.00	100.78

Determination of copper(II) ion in water sample with PGE/PPy/Cyanex 921 electrode

A water sample was prepared by adding copper(II) ions within the calibration curve range using the standard addition method, and DPV measurements were carried out with the PGE/PPy/Cyanex 921 electrode prepared under optimum conditions. The copper(II) concentration was determined using the calibration equation with the maximum peak current values obtained from DPV measurements, and recovery values were calculated (Table 3).

Discussion

In this study, a pencil graphite electrode (PGE), a polypyrrole (PPy)-modified PGE, and a PGE modified with a commercial modifier, Cyanex 921, were employed for the electrochemical determination of copper(II) ions. A review of the literature indicates that gold, graphite, glassy carbon, and carbon paste electrodes have been widely used for the electrochemical determination of copper(II) ions[18-28]. However, the fact that pencil graphite electrodes have not previously been used for this purpose enhances the originality of this study and its contribution to literature.

With respect to Cyanex compounds used for modification purposes (Cyanex 272, Cyanex 301, and Cyanex 302), the literature reports only a limited number of studies, primarily focused on the fabrication of polymeric membrane electrodes selective for the uranyl (UO_2^{2+}) ion[9,34]. The absence of prior reports on the use of Cyanex 921 in a similar application further demonstrates the originality and methodological novelty of the present study. The low cost, ease of availability, electrochemical inertness, and disposable nature of pencil graphite electrodes are the main reasons for their selection in this work.

The surface morphology of the electrodes was examined using SEM, confirming that the modification process was successfully achieved. Parameters affecting the electrochemical response of each electrode such as the number of cycles, scan rate, solution pH, and modifier concentration were optimized using CV. After determining the optimum conditions, the carbon-based pencil graphite electrode surfaces were modified with polypyrrole and Cyanex 921.

According to the CV results obtained during the electropolymerization of polypyrrole, the oxidation peak was observed at 0.80 V and the reduction peak at −0.40 V. Upon the incorporation of Cyanex 921, the oxidation peak shifted to 0.60 V and the reduction peak to −0.50 V, indicating that Cyanex 921 molecules were successfully embedded within the polypyrrole polymer matrix and that changes occurred in the electronic structure of the polymer. This methodology is consistent with previous electrochemical studies employing modified pencil graphite electrodes[29] and is supported by reported findings indicating that modified PGEs enhance analyte sensitivity[31-33]. Furthermore, similar electrode modification strategies have been shown to be effective for different analytes when using modified pencil graphite electrodes[30].

The PGE, PGE/PPy, and PGE/PPy/Cyanex 921 electrodes prepared under optimal conditions were used for the determination of copper(II) ions by differential pulse voltammetry (DPV). Under optimal conditions (8 cycles, 80 mV/s, pH 3.0, and 0.05 M Cyanex 921), the electrochemical response was found to increase significantly, and this enhancement was shown to result not only from the increased surface area but also from the improved electron transfer kinetics[35]. This improvement is attributed to the synergistic effect of the conductive polypyrrole matrix and the selective coordination ability of Cyanex 921 toward Cu(II) ions. The peak current values in the obtained voltammograms allow a comparative evaluation of the electrodes' sensitivity toward copper(II) ions (Table 4). The results indicate that the peak current of the PGE/PPy/Cyanex 921 electrode is significantly higher than those of the other electrodes, with low %RSD values. These findings confirm that Cyanex 921 catalyzes the reduction and oxidation processes of Cu(II) ions on the electrode surface, thereby enhancing both sensitivity and selectivity.

When the effects of different metal ions were examined, it was determined that the PGE/PPy/ Cyanex 921 electrode was less affected by other metals with respect to the copper(II) signal (Table 2). The pencil graphite electrodes modified with PPy and Cyanex 921 produced reproducible signals in short-term measurements, with minimal signal variation observed during voltammetric scans performed on the same day (Table 5). These results indicate that the electrodes are both physically and chemically stable and can be reliably used as sensors for the analysis of environmental or industrial samples. Overall, the findings demonstrate that the developed electrode exhibits high selectivity and sensitivity toward copper(II) ions even in the presence of other metal ions. In addition, the high recovery values obtained using the standard addition method in real water samples indicate the reliability of the method and its potential for environmental applications (Table 3).

Table 4 — Peak currents and %RSD values obtained for 128 ppm copper(II) with PGE/PPy, PGE/PPy/Cyanex 921 electrodes, and PGE

Electrode	Peak Current (mA)	%RSD
PGE	0.0083	1.77
PGE/PPy	0.0363	1.78
PGE/PPy/Cyanex 921	0.0856	0.26

Table 5 — Signal variation of the electrodes during voltammetric scans conducted on the same day

	Current Value (mA)					
Number of analyzes	1	2	3	4	5	Average (±SD)
PGE/PPy	0.030	0.031	0.029	0.031	0.029	3.04 (±0.07)
PGE/PPy/Cyanex 921	0.036	0.036	0.036	0.036	0.037	3.63 (±0.04)

The results obtained in this study clearly show that pencil graphite electrodes can serve as low-cost, rapidly prepared sensor platforms capable of achieving high sensitivity and selectivity through surface modification. The modified PGEs demonstrate methodological applicability not only for the determination of copper(II) ions but also for other electrochemical determinations reported in the literature, such as vanillin[29] and vitamin B6[30]. This highlights the contribution of the present work to the fields of analytical chemistry and environmental analysis, as well as the potential applicability of the electrodes developed for different analytes.

The low %RSD values (Table 5) indicate the high analytical stability and repeatability of the developed electrode. Considering that surface instability and signal drift between measurements have been reported as major disadvantages of polymer-modified electrodes in the literature, the Cyanex 921–containing system can be considered to largely overcome this limitation. This behaviour may be attributed to the homogeneous dispersion of Cyanex 921 within the PPy matrix and the formation of strong complexation sites on the electrode surface.

The significantly higher electrochemical response of the PGE/PPy/Cyanex 921 electrode toward copper(II) ions compared to the bare PGE and the PPy-modified electrode indicates that the modification is not limited to an increase in surface area but also positively affects the kinetics of the electrochemical reactions. It is proposed that the sulfur- and phosphorus-containing functional groups of Cyanex 921 form selective coordination complexes with copper(II) ions, facilitating electron transfer and thereby enhancing the peak current. This mechanism is consistent with previous studies reporting the high affinity of phosphorus- and thiol-based extractants for copper(II) ions[34].

The linear calibration curves obtained for copper(II) ions in the concentration range of 2–200 ppm (Figs 8–9) demonstrate that the developed electrode is suitable for quantitative analysis over a wide concentration range. Although this range was defined in line with the objectives of the TUBITAK 114Y585 project, the calculated LOD and LOQ values suggest that the electrode may also be applicable at lower concentrations. Nevertheless, it should be noted that an additional preconcentration step or further surface modifications may be required for ultra-trace (ppb-level) determinations.

Selectivity studies revealed that the PGE/PPy/Cyanex 921 electrode largely preserved the copper(II) ion signal in the presence of other metal ions. Experiments conducted at a fixed copper(II) ion concentration of 160 ppm showed that the effects of interfering metal ions on the peak current were limited, further supporting the preferential complexation tendency of Cyanex 921 toward copper(II) ions. This characteristic represents a significant advantage for the analysis of multicomponent environmental water samples. However, the potential interference of metal ions with similar coordination behavior, such as Hg(II) or Ag(I), at higher concentrations should be investigated in more detail in future studies.

The high recovery values obtained from standard addition experiments performed on real water samples (Table 4) demonstrate the accuracy of the method and its robustness against matrix effects. However, the use of a limited number of real samples may be considered a limitation in terms of the generalizability of the method to different environmental matrices, such as wastewater, groundwater, or seawater.

Conclusion

Overall, the PGE/PPy/Cyanex 921 electrode offers several important advantages, including low cost, simple and rapid preparation, high repeatability, and short analysis time when combined with the DPV technique. These features position the developed sensor as a competitive alternative to existing electrochemical copper(II) sensors. The innovative aspect of this study lies in the effective use of Cyanex 921 as a modifier in a polymer-modified electrode system, providing a selective sensing platform for copper(II) ions. Future studies focusing on long-term stability, lower concentration ranges, and performance evaluation in different environmental matrices will further expand the applicability of the proposed method.

Conflict of interest

The authors declare that they have no conflict of interest.

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