

Preparation of pyridoxine-based polyurethane modified sensors and their use in simultaneous determination of Cu(II) – Co(II) ions

Ebru Kuyumcu Savan^{a,*}, Dilek Kazıcı^a, İmren Özcan^b, Songül Bayram^b, Süleyman Köytepe^b

^a Division of Analytical Chemistry, Department of Basic Pharmaceutical Sciences, Faculty of Pharmacy, İnönü University, 44280, Malatya, Turkey

^b Chemistry Department, Faculty of Arts and Science, İnönü University, Malatya, 44280, Turkey

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ABSTRACT

In this study, pyridoxine-based polyurethane-modified electrodes were prepared to simultaneously and sensitively measure copper (Cu(II)) and cobalt (Co(II)) ions in complex matrix samples. For the production of the electrodes, firstly, the synthesis of pyridoxine-based polyurethane structures was carried out. In these syntheses, the polymer structure was diversified by using different isocyanates. Polyethyleneglycol-200 (PEG), pyridoxine (B6), and β -cyclodextrin (β -CD) groups were used as the source of polyol. The synthesized polyurethane structures were characterized by different instrumental techniques and used in gold electrode surface modification. Modified sensor surfaces were examined by scanning electron microscopy and atomic force microscopy techniques. The prepared modified sensors were used for the simultaneous detection of Cu(II) and Co(II) ions using the differential pulse voltammetry technique. The limit of detection (LOD), limit of quantitation (LOQ), and R^2 values for Cu(II) ions were calculated as 8.81 μ M, 29.4 μ M, and 0.993, respectively. LOD, LOQ, and R^2 values for Co(II) ions were calculated as 9.84 μ M, 32.8 μ M, and 0.9935, respectively. For repeatability, the relative standard deviation (RSD %) of the prepared simultaneous sensors was determined as 1.54 and 1.71 for Cu(II) and Co(II), respectively. As a result, Cu(II) and Co(II) ions were measured independently and simultaneously with high sensitivity. According to these results, it is predicted that pyridoxine-based polyurethane-modified sensors may be suitable for the simultaneous detection of Cu(II) and Co(II) in medical, food, and agricultural samples.

1. Introduction

Today's technology is constantly developing new methods for monitoring and evaluating environmental impacts, and reducing environmental pollution levels [1]. Increasing human population and consequently increasing industrial production lead to an increase in environmental pollution at a signaling level [1–3]. Especially organic pollutants as well as heavy metal pollutants cause environmental problems. Heavy metals such as Zn, Co, Ni, Cu, and Cd pose a great threat to the environment [4–6]. Therefore, warnings and inspections by important health organizations are increasing for the monitoring and detection of such heavy metal ions. Instrumental techniques are becoming increasingly important to carry out these inspections faster and to monitor heavy metal contaminants [7,8]. In the analytical detection and monitoring of heavy metals, devices such as UV, AAS, AES, ICP, XPS, and XRD are widely used, which require high cost and competent users [9–19]. In addition, depending on the amount of heavy metal level in the sample, techniques such as SEM-EDX,

electrogravimetry, and ion chromatography can be used in some cases [20–22]. However, these types of detection methods have some disadvantages as they require high-cost devices and long analysis preparation processes [23–27]. In particular, prolonging the analysis process in monitoring heavy metal pollutants in environmental samples is undesirable. For this reason, faster, more practical, and low-cost analysis methods are being researched. Electrochemical techniques and sensors with similar advantages are widely tested for this purpose in the literature [27–29].

Electrochemical sensors are sensor systems that do not require a pre-processing step and can measure accurately, sensitively, and quickly. It is widely used especially in the monitoring of environmental effects, in biomedical applications, agriculture and medicine, and in the follow-up of important components in food samples [30–33]. Different electrode modification techniques have been developed to eliminate the interfering species in the measurement systems in this area. For example, modification with polymeric film structures, separation of potentials of interfering species with electrocatalysis applications, and the use of

* Corresponding author.

E-mail address: ebru.savan@inonu.edu.tr (E. Kuyumcu Savan).

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electrode modifications containing nano-structures are some of them [34,35]. In some applications, applications such as molecular imprinting technique or supporting the electrode surface with active sensing molecules come to the fore, especially in samples with complex matrices [36].

In this study, which was carried out for this purpose, pyridoxine-based polyurethane-modified sensors were prepared, which can make accurate and sensitive measurements and at the same time respond very quickly. A mixture of pyridoxine, β -CD, PEG, and different diisocyanates were polymerized, and pyridoxine-based polyurethane structures were prepared. PEG units provide the solubility, processability, and flexibility of the resulting polyurethane structure. While β -CD structures enable the accumulation of analyte structures on the electrode surface, pyridoxine groups ensure the binding of Co(II) and Cu(II) ions on the electrode surface. The structure and morphology of the prepared sensors were determined by FTIR, SEM, and AFM. The high affinity of pyridoxine groups against Cu(II) and Co(II) these ions were utilized at the fabricated electrodes. Electrochemical measurements were investigated in detail for Cu(II) and Co(II) ions with the DPV. As a result, selective high-sensitivity polymeric sensors for Cu(II) and Co(II) ions were obtained thanks to pyridoxine-based structures. It has been determined that pyridoxine-based polyurethane-modified sensors can be used for rapid monitoring, and detection of Cu(II) and Co(II) ions in blood, urine, saliva, plant, food, and environmental samples.

2. Materials and methods

2.1. Reagents

Pyridoxine (B_6), β -cyclodextrin, and polyethyleneglycol-200 were used as polyol sources in the synthesis of pyridoxine-based polyurethanes. Hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI), and 1,4-phenylene diisocyanate (PDI) used as diisocyanate were obtained from Sigma Aldrich Chemical Company. Tetrahydrofuran (THF) and dimethylformamide (DMF) were obtained from Akros. $CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$ used as stock solutions were obtained from Merck and Riedel-deHaën brands, respectively, and they were of analytical grade. Other chemicals used for the experiment are Merck and Sigma Aldrich and are of analytical purity. The stock solutions of $CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$ and the other solutions were prepared daily with ultrapure water. The concentration of the stock solutions was prepared to be 10 mM. Nitrogen gas was passed through all solutions for 2 min before the voltammetric study was performed.

2.2. Equipment

In the characterization of the polyurethane structures, firstly, Fourier-transform infrared spectroscopy (FTIR) analyses were performed to confirm the chemical structure. PerkinElmer spectrum two model FTIR spectrophotometer was used for these analyses. Analyses were performed with a sensitivity of 4 cm^{-1} in the range of 400–4000 cm^{-1} . In FTIR analysis, measurements were taken in atr mode. Shimadzu TGA-50 and Shimadzu DSC-60 model devices were used to characterize the thermal properties of the obtained sensors. Thermogravimetric analysis (TGA) was performed at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and in a static air atmosphere. A heating rate of $5\text{ }^\circ\text{C}/\text{min}$ was used for differential scanning calorimetry (DSC) analysis. 5 mg of sample was analyzed in the range of 300–300 $^\circ\text{C}$ under an atmosphere of air against reference Al_2O_3 .

SEM and AFM were used together to define the prepared modified sensor surfaces and unmodified gold (Au) electrode surfaces. LEVO EVO 40 SEM analyzer was used for SEM analysis. Samples to be measured were coated with 20 nm gold-palladium with Baltech brand sputter before analysis. Parking system XE100 AFM device was used in AFM analysis. AFM Analyses were performed in noncontact mode. After the analysis, surface roughness values and topography results were

obtained.

Electrochemical analyses were performed with Gamry Interface 1010B (Gamry, USA) potentiostat and triple electrode system (BASi C3 Cell Stand). In the triple electrode system, Ag/AgCl (aqueous medium) was used as the reference electrode, platinum wire was used as the auxiliary electrode, and Au electrode was used as the working electrode. DPV technique was used for the quantitative determination of Cu(II) and Co(II) ions, and CV and electrochemical impedance spectroscopy (EIS) were used for the characterization of the modified electrode. The response time measurements of the modified electrode were carried out under room conditions using BAS (Bioanalytical Systems, Inc.) cell stand and BAS-100 electrochemical potentiostat. Ultrapure water used in all solutions prepared for the experiment was obtained from Milli Q (Millipore, 18.2 M Ω cm, Merck).

2.3. Synthesis of pyridoxine based polyurethane structures

Within the scope of the study, structural diversification of the polyurethane structures to be used for electrode surface modification was achieved by using three different diisocyanate groups. The solution polymerization technique was used in polymer synthesis and the obtained polymers were coated on the electrode surfaces to form a film. During the synthesis of polyurethanes, using the monomer ratios given in Table S1, three different polymeric structures belonging to the polymer codes given in Table S1 were obtained.

In the general synthesis procedure, the triple polyol mixture containing the pyridoxine, β -CD, and PEG structure was dissolved in 20 mL of THF/DMF (9/1) mixture in a 50 mL tank. The equimolar diisocyanate structure was added to this mixture at room temperature and under an Argon atmosphere. It was refluxed at $90\text{ }^\circ\text{C}$ for 6 h after the pre-reaction process under Argon atmosphere for 30 min. After this reflux period, the polyurethane structure was precipitated by the addition of methanol and dried in a vacuum oven at $50\text{ }^\circ\text{C}$ for 24 h. Completion of polymerization reactions was monitored by FTIR analyses. It was understood that the polymerization was completed when the isocyanate peak disappeared at 2265 cm^{-1} . Obtained polymeric structures were examined by FTIR and thermal analysis techniques.

2.4. Preparation of modified sensors

Before the modified sensor was prepared, and after the electrochemical measurements, the Au electrode was polished with 1.0, 0.3, and 0.05 μm alumina powders on cleaning pads and passed through distilled water. Modified sensors were produced by dropping PEG-200/MDI/B6, PEG-200/HDI/B6, and PEG-200/PDI/B6 polymers onto the Au electrode surface at determined film thicknesses and then drying at room temperature for 24h (Fig. S1). The best response was measured on the new generation modified sensor (PEG-200/HDI/B6/Au), produced by dropping 2 μL of PEG-200/HDI/B6 polymer onto the Au electrode surface.

2.5. Characterization of pyridoxine based polyurethane structures

In the study, three different polyurethane structures (PEG-200/MDI/B6, PEG-200/HDI/B6, and PEG-200/PDI/B6) were synthesized. In particular, pyridoxine-based polyurethane structures were prepared for the modification of Au electrode surfaces. The chemical structure of the obtained polyurethanes was confirmed by FTIR spectra (Fig. S2). Firstly, no free isocyanate peak was seen at approximately 2260 cm^{-1} in the FTIR spectra given in Fig. S2. The absence of a free isocyanate peak indicates that the polymerization reaction is completed. In addition, in the FTIR spectra of the polymers, the urethane bond carbonyl peak is observed at approximately 1750 cm^{-1} , the urethane bond C–N peak is observed at approximately 1440 cm^{-1} , and the N–H peak is observed at approximately 1540 cm^{-1} . The presence of these peaks in the spectrum indicates that the desired urethane bond has been formed. In addition,

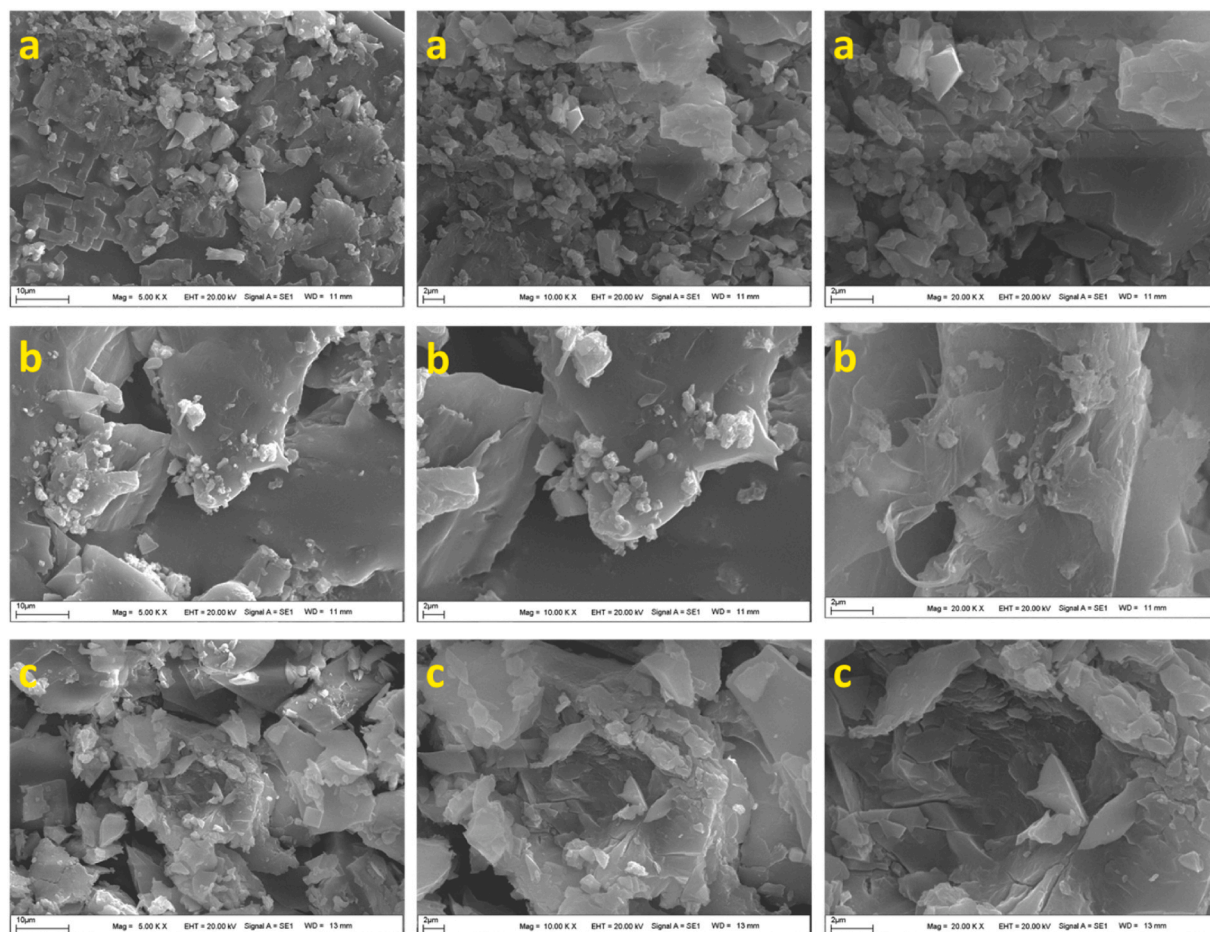


Fig. 1. SEM images of the polymers PEG-200/HDI/B6 (a), PEG-200/PDI/B6 (b), and PEG-200/MDI/B6 (c).

hydrogen bond stretching vibrations of the N–H structure in the range of $3000\text{--}3300\text{ cm}^{-1}$ and H-bond stretching vibrations of OH groups in the range of $3300\text{--}3600\text{ cm}^{-1}$ are observed in polyurethane structures. Asymmetric and symmetric stretching vibrations of aliphatic C–H groups are seen in the range of $2850\text{--}2950\text{ cm}^{-1}$. In addition, the C–O–C stretching vibration in the β -CD groups in the polymer structure is seen around 1091 cm^{-1} , and the C–O stretching vibration is seen around 1060 cm^{-1} . Due to the main chain structure, C–C stretching vibration is seen around 1380 cm^{-1} . Aliphatic C–H out-of-plane bending peak was detected around 650 cm^{-1} . Additionally, a C=N peak originating from the pyridoxine structure is observed at 1650 cm^{-1} . As a result, FTIR spectra of the polymers confirm that the desired polyurethane structure has been obtained. In addition, the polyurethane structures obtained within the scope of the study must be sterilizable for the sensors to be used in biomedical applications. For this reason, the thermal properties of the obtained structures were examined. TGA and DSC analyses were performed in the analysis of thermal properties. In TGA analyses (Fig. S3), four main mass losses were detected in the polyurethane structures. The first mass loss is at approximately 120°C and is the mass loss due to structural moisture. The second mass loss is a mass loss caused by the dispersion of the hard segments in the polyurethane structure and is observed at approximately $200^\circ\text{C}\text{--}300^\circ\text{C}$. The third mass loss is observed between 300°C and 450°C and is due to the degradation of the soft segments. The final mass loss is due to thermal degradation of the polymeric structure. It is seen between 450°C and 600°C .

The glass transition temperature (T_g) of polymeric structures was determined on the DSC thermograms given in Fig. S4. Glass transition temperatures of 112.2°C , 119.8°C , and 180.1°C were measured for

three different polyurethane structures, respectively.

SEM images of Au electrode surfaces modified with synthesized polyurethane structures are shown in Fig. 1. In the relevant SEM images, it is seen that the surface morphologies have changed to a certain extent compared to the unmodified Au electrode surface. In particular, the uncoated electrode surface appears quite flat and smooth. On the coated electrode surface, it has been determined that the surface has a more fractal and cavity structure. This increasing fractal structure in the modified sensor leads to an increase in the surface area of the electrode and an increase in the electrode surface sensitivity.

2.6. Surface and morphological characterization of PEG-200/HDI/B6 modified sensor

Within the scope of the study, PEG 200, Pyridoxine, and β -cyclodextrin mixture with different diisocyanate structures was polymerized. Three different polyurethane structures obtained as a result of syntheses using three different isocyanate structures were defined as PEG-200/MDI/B6, PEG-200/HDI/B6, and PEG-200/PDI/B6. Obtained polyurethane structures were used in the modification of the Au electrode. Modified sensors were used for the simultaneous detection of Co(II) and Cu(II) ions after dropping onto the Au electrode surface using a pyridoxine-based polyurethane structure selected from PEG-200/MDI/B6, PEG-200/HDI/B6, and PEG-200/PDI/B6.

SEM analyses were performed to show the surface structure of the bare electrode before and after modification. SEM images of the surfaces of the bare Au electrode and PEG-200/HDI/B6 modified sensor (b) structures are given in Fig. S5. In these images, the surface of the bare electrode is quite flat and smooth, while the modified sensor has a high

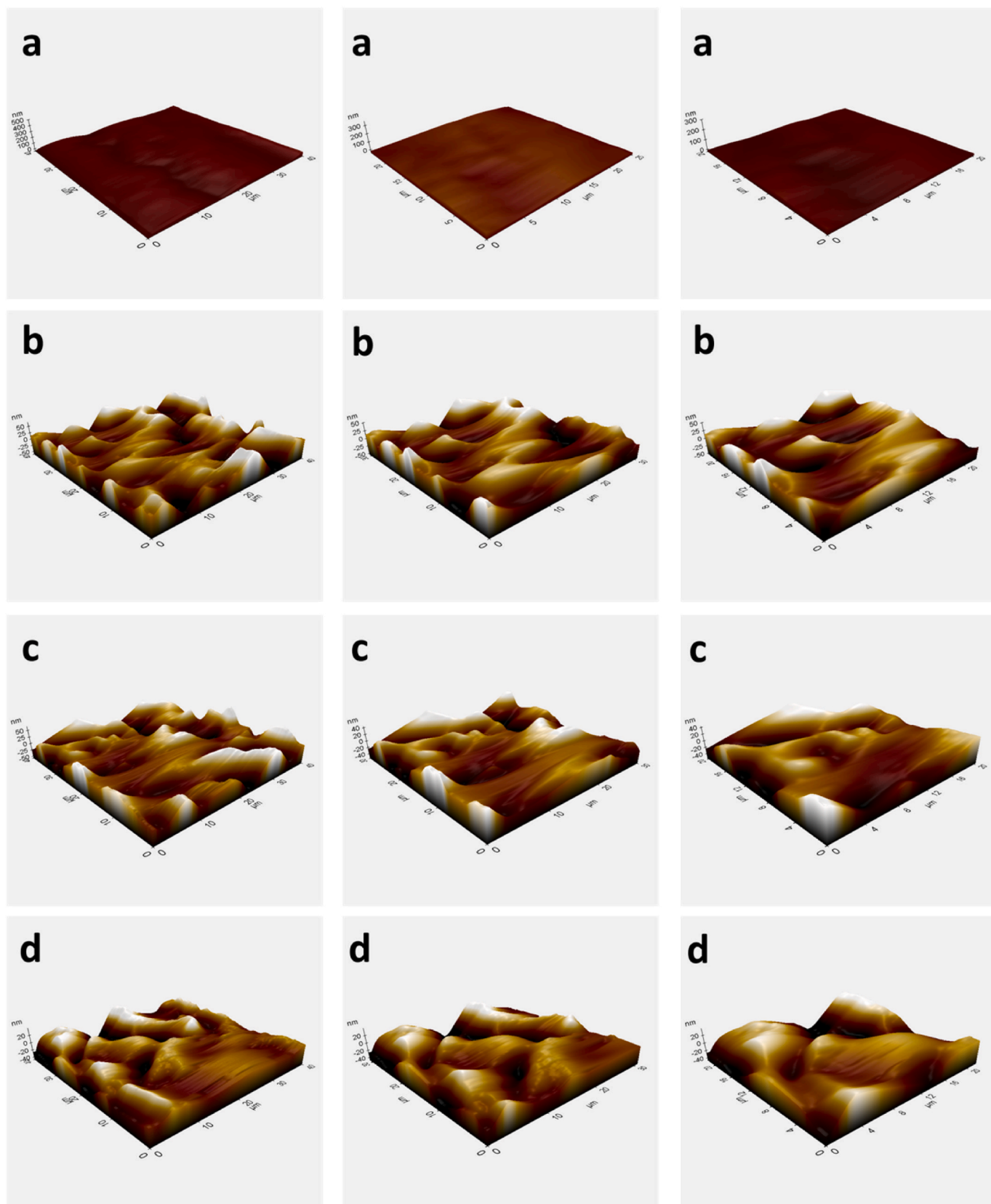


Fig. 2. AFM images of bare Au electrode (a), PEG-200/HDI/B6 (b), PEG-200/PDI/B6 (c), and PEG-200/MDI/B6 (d) modified sensors.

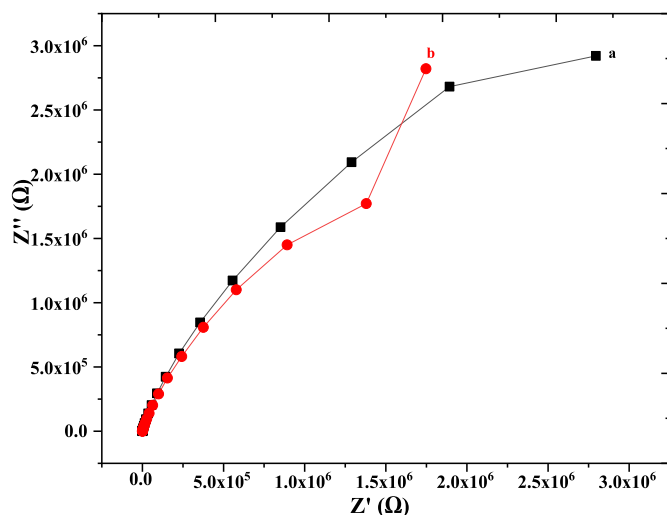


Fig. 3. EIS responses of 5 mM $K_4Fe(CN)_6$ in 0.1 M KCl solution, PEG-200/HDI/B6/Au modified sensor (a) and bare Au electrode (b).

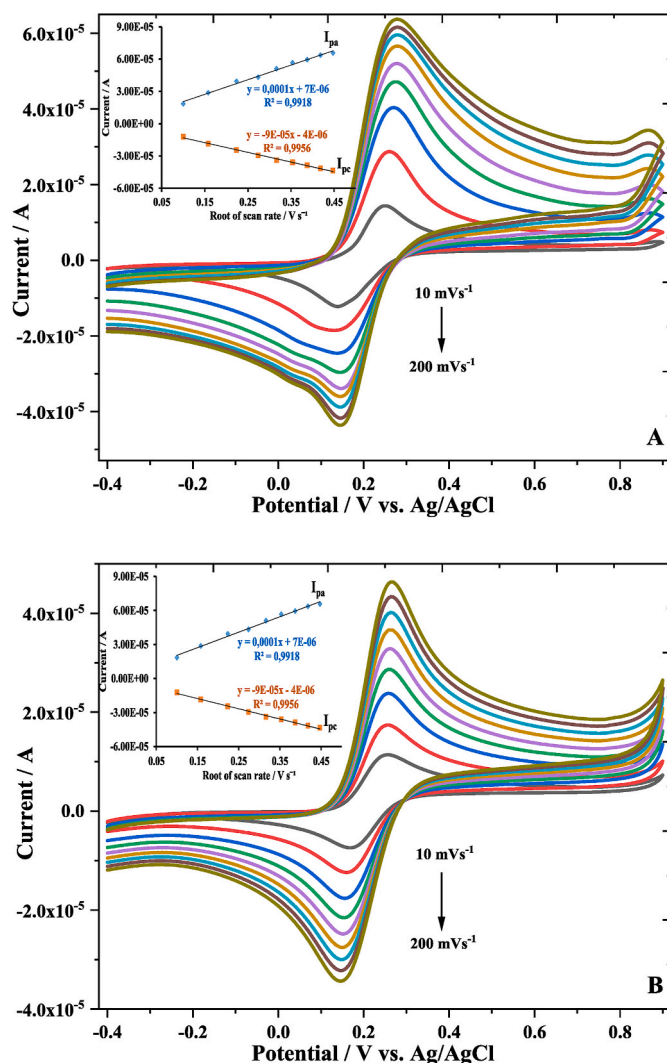


Fig. 4. A. CV responses of PEG-200/HDI/B6/Au modified sensor and B. Au electrode at increasing scan rates in a solution of 5 mM $K_4Fe(CN)_6$ in 0.1 M KCl. Inset; It shows linear curves between the square root of the scanning rates and corresponding current values.

cavity and fractal structure.

AFM analyses were performed, and electrode surface roughness was measured to confirm this change in the surface. The AFM analysis results given in Fig. 2 are presented in comparison with the Au electrode surface. According to these results, a significant surface roughness and surface area increase on the electrode surface can be seen with the pyridoxine-based polyurethane coatings applied on the surface of the modified sensors (Fig. S6). Accordingly, it is an expected prediction that the obtained modified sensors will be more sensitive to analytes.

2.7. Electrochemical characterization of PEG-200/HDI/B6 modified sensor

Since EIS is a very powerful technique to obtain information about the charge transfer properties of the electrodes, this technique was used to investigate the interface properties of the electrodes. 5.0 mM $[Fe(CN)_6]^{3-/4-}$ solution was used as redox probe. The bare Au electrode and the PEG-200HDI/B6/Au modified sensor were electrochemically characterized by CV and EIS. These methods are basic techniques about the conductivity of the electrode surface as well as explaining the mechanisms involved in the processes of electron and charge transfer resistance.

Nyquist curves of the PEG-200/HDI/B6/Au modified sensor and bare Au electrode were compared (Fig. 3). When Fig. 3 is examined, the charge transfer resistance (CTR) was calculated as 39.46 Ω and 36.99 Ω for the modified sensor and bare Au electrode, respectively. According to this value, it is seen that the bare Au electrode has a lower resistance than the modified sensor. Since electron conduction is easy on the bare Au electrode surface, the lowest Rct value was obtained as expected. This shows that the bare Au electrode carries out the electron transfer more easily than the modified sensor since there is no complicating factor.

To explain the electron transfer rate of the electrodes, CV responses at increasing scanning rates were investigated for the modified sensor and bare Au electrode in a solution of 5 mM $K_4Fe(CN)_6$ in 0.1 M KCl (Fig. S7). the peak current of the PEG-200/HDI/B6/Au modified sensor was measured to be higher than the peak current of the bare Au electrode when the data obtained was examined. The peak-to-peak separation (ΔE_p) values for the bare Au electrode and the PEG-200/HDI/B6/Au modified sensor were calculated as 105 mV and 130 mV, respectively.

The CV responses at increasing scan rates in Fig. 4 were used to evaluate the electroactive surface areas of the bare Au electrode and the PEG-200/HDI/B6/Au modified sensor since the charge transfer resistance is related to the electroactive surface of the electrode. The active surface area was calculated from the Randles Sevcik equation (Eq. 1) by using the slope values in the graph of the relationship between I_p values and the square root of increasing scanning speeds ($v^{1/2}$).

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

I_p in the equation is the peak current (Ampere), n is the number of electrons given and received, A is the surface area of the electrode (cm^2), D is the diffusion coefficient ($cm^2 s^{-1}$, $7.6 \times 10^{-6} cm^2 s^{-1}$), C is the redox probe represents the concentration of $K_4Fe(CN)_6$ in the KCl electrolyte (mol/cm^3) and v represents the scanning rate (V/s). The surface areas of the bare Au electrode and PEG-200/HDI/B6/Au modified sensor were calculated as 0.0367 cm^2 and 0.0270 cm^2 , respectively.

2.8. Film thickness

The polymer film and its thickness that would provide the best response were investigated. For this purpose, modified sensors were fabricated by dropping the synthesized PEG-200/MDI/B6, PEG-200/HDI/B6, and PEG-200/PDI/B6 polymers separately onto the Au electrode surface (in different volumes; 2, 4, 6, 8, and 10 μL). It was

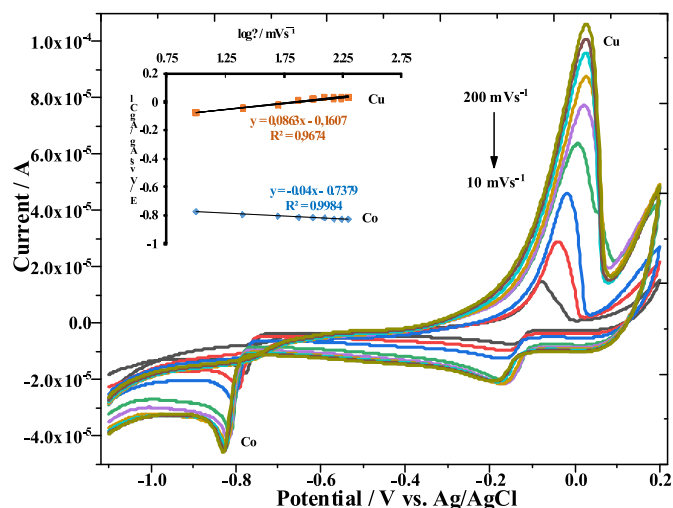


Fig. 5. CV responses of 2.22 mM Cu(II) and Co(II) ions on the PEG-200/HDI/B6/Au modified sensor surface at different scanning speeds. Inset: The linear relationship between potential and logarithm of scan rate.

produced by drying at room temperature. In the first stage, voltammetric measurements were carried out using the SWV technique at the fabricated modified sensors for 0.66 mM Cu(II) ion prepared in 0.1 M KCl support electrolyte solution (Fig. S8). When Fig. S8D is examined, it is seen that the best response for the Cu(II) ion was obtained at the sensor obtained with PEG-200/HDI/B6 polymer with a film thickness of 2 μ L.

After optimization of the polymer composite, the support electrolyte

medium and polymer film thickness were investigated where the highest peak current response could be obtained for the simultaneous electrochemical oxidation of Cu(II) and Co(II) ions at the modified sensor (PEG-200/HDI/B6/Au), that the best peak current response was observed. DPV responses were investigated for the simultaneous detection of 3.8 mM Co(II) and 1.9 mM Cu(II) ions in 0.1 M NaCl at the PEG-200/HDI/B6/Au modified sensors prepared by different thicknesses (2, 4, 6, 8, and 10 μ L) (Fig. S9). When the obtained voltammograms were examined, the best discrimination and highest peak current for the simultaneous determination of 3.8 mM Co(II) and 1.9 mM Cu(II) ions were obtained at the modified sensor produced with 2 μ L PEG-200/HDI/B6. As a result of this optimization, the modified sensor obtained with this thickness was used in all subsequent studies.

In the next stage, to determine the support electrolyte medium, DPV responses of 1.9 mM Cu(II) and Co(II) ions were investigated in Na₂SO₄, KCl, LiClO₄, NaClO₄, and NaCl electrolytes with 0.1 M concentrations at the PEG-200/HDI/B6/Au modified sensor (Fig. S10). As a result of the optimization, it was observed that there was no significant change in the oxidation peak current in all electrolyte solutions for 1.9 mM Co(II) ion. The highest peak current was obtained in 0.1 M LiClO₄ electrolyte solution for 1.9 mM Cu(II) ion, and 0.1 M LiClO₄ was used as the supporting electrolyte solution in subsequent studies.

2.9. Voltammetric behavior of Cu(II) and Co(II) ions

The effect of the scanning rate was investigated to gain insight into the electrochemical redox mechanism procedure and to identify whether the electrochemical process occurs under diffusion or adsorption control mechanism. To elucidate the electrochemical behavior of

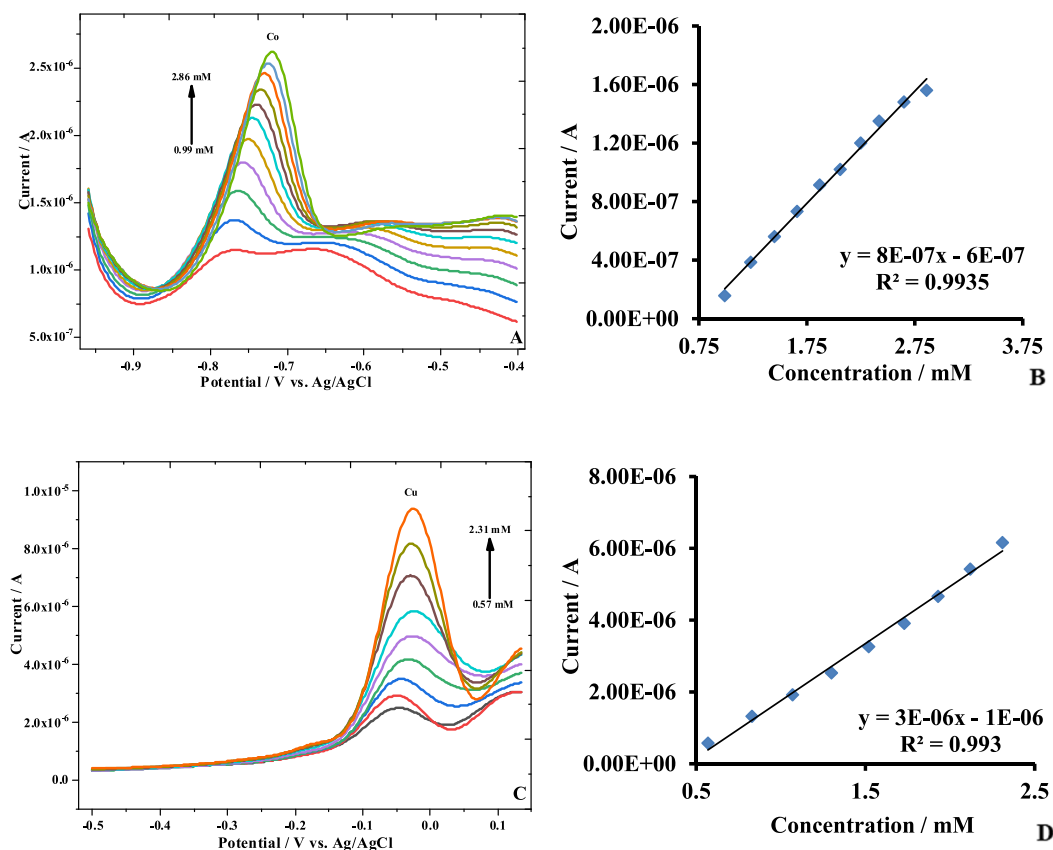


Fig. 6. A. DPV results of increasing concentrations of Co(II) ion (0.99, 1.23, 1.45, 1.66, 1.87, 2.06, 2.25, 2.42, 2.65, 2.86 mM) in 0.1 M LiClO₄ supporting electrolyte solution at the PEG-200/HDI/B6/Au modified sensor. B. Calibration curve of Co(II) ion in the linear range. C. DPV results of increasing concentrations of Cu(II) ion (0.57, 0.83, 5.66, 1.07, 1.3, 1.52, 1.73, 1.93, 2.12, 2.31 mM in 0.1 M LiClO₄ supporting electrolyte solution) at the PEG-200/HDI/B6/Au modified sensor. D. Calibration curve of Cu(II) ion in the linear range.

Table 1

Regression data of the calibration line for Co(II) and Cu(II) at PEG-200/HDI/B6/Au modified sensor.

	Cu	Co
Calibration graph equation	$I_p(A) = 3.10 \times 10^{-6}C - 1.10 \times 10^{-6}$	$I_p(A) = 8.10 \times 10^{-7}C - 6.10 \times 10^{-7}$
Linearity range (mM)	0.57–2.31	0.99–2.86
SD of slope	1.01×10^{-7}	2.19×10^{-8}
SD of intercept	1.61×10^{-7}	4.44×10^{-8}
Correlation coefficient (R^2)	0.9931	0.9935
LOD (μM)	8.81	9.84
LOQ (μM)	29.4	32.8
Repeatability of peak current (RSD %) ^a	1.54	1.71

^a Each value is the mean of three experiments.

2.22 mM Cu(II) and Co(II) ions at optimum conditions, the CV behavior was examined at increasing scanning rates (10, 25, 50, 75, 100, 125, 150, 175, and 200 mVs^{-1}) at the modified sensor in 0.1 M $LiClO_4$ solution (Fig. 5). When the obtained voltammogram results were examined, it was observed that the peak currents of both Cu(II) and Co(II) ions increased as the scanning speed increased. While the cathodic reduction peak was observed at an average of 813 mV for the Co(II) ion, the anodic oxidation peak was detected at an average of 22 mV for the Cu(II) ion. Additionally, it was observed that the peak potential of the Cu(II) ion shifted to positive, while the peak potential of the Co(II) ion shifted to negative. It is known that the slope of the linear curve for diffusion-controlled systems is 0.5, and for adsorption-controlled systems, the slope of the curve is 1.0. Therefore, to describe the process of Co(II) and Cu(II) ions at the PEG-200/HDI/B6/Au modified sensor, the linear relationship between I_p (A) and the square root of the scanning speed ($\nu^{1/2}$) was examined in Fig. S11A. $I_{pCo}(A) = -2 \times 10^{-6} \nu^{1/2} (Vs^{-1}) - 1 \times 10^{-5}$ ($R^2 = 0.9722$) and $I_{pCu}(A) = -7 \times 10^{-6} \nu^{1/2} (Vs^{-1}) - 1 \times 10^{-5}$ ($R^2 = 0.9888$) equations were obtained for Co(II) and Cu(II), respectively. According to the linear equations of $I_p - \nu^{1/2}$, the electrooxidation process of Co(II) and Cu(II) ions was diffusion-controlled in the PEG-200/HDI/B6/Au modified sensor. As a result of examining the linear relationships between $\log I_p$ and $\log \nu$, $\log I_{pCo}(A) = 0.2691 \log \nu (mVs^{-1}) - 5.1299$ ($R^2 = 0.9729$) and $\log I_{pCu}(A) = 0.5996 \log \nu (mVs^{-1}) - 5.4085$ ($R^2 = 0.9953$) equations were obtained. The slope values of the linear relationship between $\log I_p$ and $\log \nu$ were close to the theoretical value of 0.50, clearly confirming the diffusion-controlled mechanism.

The Laviron equation was used to obtain information about the electrons involved in the oxidation of Co(II) and Cu(II) ions on the electrode surface. According to the Laviron equation, the number of electrons is calculated from the slope of the E_p versus $\log \nu$ graph (Laviron, 1979). The equations for the oxidation peak of Co(II) ion ($E_{pCo}(V) = -0.0400 \log \nu (mVs^{-1}) - 0.7379$ ($R^2 = 0.9984$)), and for the oxidation peak of Cu(II) ion ($E_{pCu}(V) = -0.0863 \log \nu (mVs^{-1}) - 0.1607$ ($R^2 = 0.9674$)) were obtained from Fig. S11E. The number of electrons was calculated as 3 and 1 for Co(II) and Cu(II), respectively. Based on these data, it can be said that three and one electrons, play a role in the oxidation of Co(II) and Cu(II) ions on the PEG-200/HDI/B6/Au modified sensor surface, respectively.

2.10. Analytical parameters

While evaluating the analytical performance of the PEG-200/HDI/B6/Au modified sensor for Co(II) and Cu(II) ions, DPV, a fast and sensitive electrochemical technique, was applied in 0.1 M $LiClO_4$ supporting electrolyte solution. In the first stage, Co(II) and Cu(II) ions were measured voltammetrically under optimized conditions and increasing concentrations separately (Fig. 6). Under optimum conditions, the corresponding features of the linear regression analysis were calculated for both ions (Table 1). When Fig. 6 is examined, it is seen that the peak currents increase linearly in the concentration range of 0.99–2.86 mM

for Co(II) ions and the concentration range of 0.57–2.31 mM for Cu(II) ions. The regression equation for the Co(II) ion is $I = 8 \times 10^{-7}C - 6 \times 10^{-7}$ ($R^2 = 0.9935$) and the regression equation for the Cu(II) ion is $I = 3 \times 10^{-6}C - 10^{-6}$ ($R^2 = 0.9931$) exhibited linear response at the PEG-200/HDI/B6/Au modified sensor. Other important validation data, including sensitivity, LOD, LOQ, and linearity range, were calculated and summarized in Table 1. For Co(II) and Cu(II) ions in the specified concentration range, LOD was calculated using equations $3 \times SD/m$ and LOQ, $10 \times SD/m$. Here "SD" is the standard deviation of the experiment repeated ten times and "m" is the slope of the calibration graph. The LOD value for the Co(II) ion was calculated as 9.84 μM , the LOQ value as 32.8 μM , the LOD value for the Cu(II) ion as 8.81 μM and the LOQ value as 29.4 μM . The sensitivity of the modified sensor for Co(II) and Cu(II) was calculated as 0.0218 and 0.0817, respectively. The precision (repeatability) of the technique was evaluated in RSD% and the results were reported in Table 1. As a result of the measurements at the PEG-200/HDI/B6/Au modified sensor, the RSD% results of the repeatability peak current for Co(II) and Cu(II) ions were calculated as 1.71 and 1.54, respectively. Based on these results, it can be seen that the developed sensor shows excellent sensitivity.

Additionally, DPV responses at the PEG-200/HDI/B6/Au modified sensor were examined for increasing concentrations of Cu(II) (1.26, 1.56, 1.71, 1.84, and 1.98 mM) in the presence of 3.15 mM Co(II) (Fig. S12). Co(II) and Cu(II) ions were stable in the presence of each other and exhibited excellent voltammetric response.

The response time of the obtained PEG-200/HDI/B6/Au modified sensor for Cu(II) and Co(II) ions was examined with the Time base technique. For this, each ion was added consecutively four times and the response times of the PEG-200/HDI/B6/Au modified sensor were monitored. The results obtained for four different responses are given in Fig. S13. According to these results, the response time of the PEG-200/HDI/B6/Au modified sensor for the Cu(II) ion was 4.2 s, while the response time for the Co(II) ion was determined as 3.5 s.

Heavy metal ions have significant toxic effects on the environment and human life. For this reason, many sensors have been developed to detect such ions quickly and simultaneously. Efforts are being made to develop sensors with different structures, especially for the determination of Hg, Cd, Co, Ni and Cu ions, which have high toxic effects. Studies are constantly continuing, especially for the determination of lower metal ion levels, the development of structures with lower response times, and the development of sensing analysis methods that can determine multiple toxic ion types at the same time. Ion chromatography for the simultaneous detection of heavy metal ions, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrophotometry (although analysis methods such as FAAS) and atomic absorption spectroscopy (AAS) are widely used, these techniques involve time-consuming sample preparation steps, require expensive equipment and require specialized personnel [37–39]. For this reason, voltammetric techniques that can provide fast, cheap, practical, and reliable results are widely studied today [40,41]. A platinum electrode (Pt) was modified with poly(3,4-ethylenedioxythiophene) and N α , N α -bis-(carboxymethyl)-L-lysine hydrate (NTA lysine) PEDOT/NTA for the detection of Hg^{2+} , Zn^{2+} , and Pb^{2+} ions by Alshawi et al. [42]. Linear responses to Hg^{2+} , Pb^{2+} , and Zn^{2+} ions were obtained at this electrode in the concentration range of 5–100 μgL^{-1} . The limits of detection (LODs) of Hg^{2+} , Pb^{2+} , and Zn^{2+} ions were 1.73, 2.33, and 1.99 μgL^{-1} , respectively. In another study, Tapia and colleagues managed to determine both Pb(II) and Cd(II) ion concentrations in the range 0.2–25.0 μgL^{-1} using a bismutene-modified screen-printed electrode [43]. Thanh et al. developed a bismuth film-modified electrode structure for the simultaneous determination of Zn(II), Cd(II), Pb(II), and Cu(II) ions [44]. Especially today, nanoparticle-doped sensors are widely used to develop LODs, high sensitivity, and fast sensors [38]. However, in such sensors, the search for effective sensors with different polymeric films

Table 2

Comparison of some studies carried out for the determination of Cu(II) and Co (II).

Interfering Ions	Linear Range	LOD	Detection Method	Reference
Cu (II)	4.0–9.6 μM	–	Spectrophotometric	[45]
Co(II)	8.0–80.0 μM	–	Spectrophotometric	[45]
Cu (II)	5–10 μM	4.63 μM	Fluorescent Detection	[46]
Cu (II)	1–10 μM	0.773 μM	Fluorescent Detection	[47]
Cu (II)	1–10 μM	0.49 μM	Fluorescent Detection	[48]
Cu (II)	9–265 ng mL^{-1}	7.5 ng mL^{-1}	Ion Chromatography	[37]
Co (II)	0.03–70 ng mL^{-1}	0.01 ng mL^{-1}	Ion Chromatography	[37]
Cu (II)	2–4 μM	1.4 μM	DPV	[49]
Co (II)	10–30 mM	2.3 mM	CV	[50]
Cu (II)	0.57–2.31 mM	8.81 mM	DPV	Present Work
Co (II)	0.99–2.86 mM	9.84 mM		

continues due to reasons such as nanoparticle leaching from the electrode surface over time, the electrode surface not being easily cleaned, and agglomeration problem in nanoparticles. In this context, within the scope of the study, pyridoxine and β -Cd based polymeric structures were prepared and used to detect Cd(II) and Cu(II) ions simultaneously.

In Table 2, the analytical parameters of the modified PEG-200/HDI/B6/Au are compared with some heavy metal ion detection methods in the literature. The PEG-200/HDI/B6/Au electrode prepared according to this table detects Co(II) and Cu(II) ions simultaneously in a very wide measurement range. In addition, the determination time is shorter than many techniques such as ICP-MS, ICP-OES and AAS, which have a sample preparation step. Thus, modified sensor that can be used practically for a long time can make accurate, sensitive, and precise measurements, and can also respond very quickly has been prepared.

3. Conclusions

In this study, an effective sensor structure was prepared by modifying the Au electrode surface with a pyridoxine-based polyurethane film structure for the simultaneous detection of Co(II) and Cu(II) ions. PU film structure was preferred to increase the electrode surface area, to remove potentially interfering species from the electrode surface and to provide analyte affinity. β -CD and vitamin B6 groups were used together to increase the accumulation of Co(II) and Cu(II) ions on the electrode surface, especially within the PU structure. The synthesized PU structures were structurally identified by FTIR spectroscopy. Thermal properties and surface morphology of PU structures were examined using thermal analysis techniques and SEM analyses. The structurally, thermally and morphologically optimum film (PEG-200/HDI/B6) structure was used for Au electrode surface modification. The obtained modified electrode (PEG-200/HDI/B6/Au) structure was used to detect Co(II) and Cu(II) ions simultaneously with the DPV technique. Under optimal detection conditions, the PEG-200/HDI/B6/Au electrode exhibited a relatively wide LDR (0.57–2.31 μM), low LOD (8.81 mM), and LOQ (29.4 mM) for Cu(II) ions. The modified PEG-200/HDI/B6/Au electrode exhibited LDR (0.99–2.86 μM), low LOD (9.84 mM), and LOQ (32.8 mM) for Co(II) ions. Moreover, the PEG-200/HDI/B6/Au electrode exhibited outstanding reproducibility, low determination time, and high stability ability. According to these results, it is predicted that the designed new generation pyridoxine-based sensor can be used for rapid monitoring and detection of Cu(II) and Co(II) ions in blood, urine, plant samples, food samples and many environmental samples. In this way, field and instantaneous measurements can be taken quickly, reliably and practically with the prepared modified electrodes.

CRedit authorship contribution statement

Ebru Kuyumcu Savan: Writing – review & editing, Writing – original draft, Supervision, Methodology, Data curation, Conceptualization. **Dilek Kazıcı:** Visualization, Validation, Investigation, Data curation. **İmren Özcan:** Investigation. **Songül Bayram:** Investigation. **Süleyman Köytepe:** Writing – original draft, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The PCT application for this study and the designed sensor material were entered into the TURKPATENT records on 14/12/2023 with the application number PCT/TR2023/051546, and were transferred to the international stage.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2024.126520>.

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