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Comparative study of lignocellulosic biomass and its components as electrode modifiers for detection of lead and copper ions

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Abstract Cellulose, xylan and lignin, as well as maize cell wall, were used as modifiers of carbon paste electrode. Comparative analysis of electrochemical performance of each modifier toward heavy metal detection was performed. A higher affinity of biomass constituents for lead ions than for copper ions influenced simultaneous detection of lead and copper ions. The new procedure for the simultaneous detection of lead and copper ions based on their co-adsorption was presented.

Keywords: cellulose, lignin, xylan, modified electrode, heavy metals detection

1. Introduction

The problem of water pollution with heavy metal ions and organic pollutants is ever-present. Industrial wastewaters often contain pollutants above permitted level even after required treatment. The aquatic systems are easily contaminated and prolonged exposure to even low doses of heavy metals leads to their accumulation in the human body causing severe health issues. Therefore, the detection and removal of pollutants are of great importance.

Modern electroanalytical methods can play an important role in the field of biological and environmental analysis. The advantages of these methods are low cost, high sensitivity, broad linear range and suitability for in situ measurements [1, 2]. They are especially convenient for large scale environmental monitoring of chemical carcinogens [3], pharmaceutical compounds [4- 6], and biological samples [8 - 9]. Beside detection application, electrocanalytical methods contribute to understanding of oxido-reduction mechanism of analyte. This knowledge enables insight of possible further impact on the environment or interaction with living cells [1]. Additionally, the electrochemical measurement can be performed in opaque media that makes them more convenient than spectroscopic and HPLC technique. The further improvement of

electrochemical methods and broadening of application scope greatly depends on properties of electrode material. New materials are constantly developing in order to obtain electrode material with low detection limit, high sensitivity, and selectivity. Another parameter in development engineering has lately been considered of importance – the usage of renewable sources. In that regard, materials with plant origin are the first choice. The lignocellulosic biomass has shown the potential as heavy metal adsorbent [10, 11]. These experiments also showed that the efficiency of biomass as adsorbent depended on their composition, i.e. the ratio of the constituents of lignocellulosic biomass: cellulose, lignin, and hemicelluloses. On the other hand, the electrode modified with cellulose [12-14] and lignin [15, 16] has already shown excellent properties as electrochemical sensors.

The objective of this paper was to compare the properties of individual constituents of lignocellulosic biomass with those of whole cell wall – the main part of biomass, as a modifier of carbon paste electrode. The electrodes modified with individual biopolymers or cell wall were tested for heavy metal ion determination. To our best knowledge comparative study of electrochemical properties of these biopolymers and cell wall has not be presented so far. Additionally, the procedure used in this paper offers a faster way for heavy metal detection avoiding long accumulation time.

2. Experimental

2.1 Sample preparation

Cellulose and xylan were of analytical grade and purchased from Sigma (Germany).

Lignin model compound was synthesized from its monomer coniferyl alcohol according to the procedure of Radotić et al. [17] and Radotić et al. [18]. Lignin is almost impossible to obtain

from biomass in an unaltered form due to its tight connections with the other cell wall polymers, but its model compound synthesized simulating natural conditions in the cell wall is a suitable substitute for the native lignin [19].

The cell walls were isolated from maize stems (*Zea mays* L.), as waste biomass, according to the procedure reported in Djikanović et al. [20]. In short, the stems were ground into a fine powder, and then subsequently extracted with 80 % methanol, 1 M NaCl, 0.5 % Triton X-100, distilled water, 100 % methanol, 100 % acetone, using a FastPrep-24 apparatus (MP Biomedicals, Santa Ana, CA, USA). Such obtained extractive-free cell wall material was dried at 60 ℃ for 1 h.

2.2   Sample characterization

Stem cell wall from maize, as a monocotyledonous plant, consists of 20-45 % cellulose, 20-45 % hemicelluloses, and 20 % lignin [21]. Characterization of the maize stem cell walls, i.e. presence of the constituent polymers by FTIR spectroscopy, was reported previously [19].

Cell wall fragments from maize stems were imaged using a Carl Zeiss LSM 410 laser scanning microscope (Carl Zeiss Jena, Jena, Germany), in transmission mode. The images were in resolution of 512 x 512 dots, covering the area of 64 x 64 μm. An isolated cell wall fragment from maize stems is shown in Figure 1.

Figure 1

The preserved cell wall structure is clearly seen.

2.3   Electrochemical test

Carbon black paste was prepared by hand mixing 0.5 g carbon black (CB) (Vulcan-XC 72R) with 0.5 g paraffin oil. The resulting paste was packed into the hollow (2 mm diameter) Teflon tube while the electrical contact was provided using copper wire and the obtained setup was used

as working electrode. Carbon pastes with the biopolymer samples as modifiers were prepared with CB/biopolymer ratio 5:1. The modified carbon paste electrodes were denoted as C-CPE for cellulose, X-CPE for xylan, L-CPE for lignin and CW-CPE for cell wall. The reference electrode was Ag/AgCl in 3 M KCl, while a platinum rod served as a counter electrode. The electrochemical measurements were performed using the Autolab electrochemical workstation (Autolab PGSTAT302N, Metrohm-Autolab BV, Netherlands). Impedance measurements were carried out at open circuit potential (OCP) using a 5 mV rms sinusoidal modulation in the 10 kHz–10 mHz frequency range. The 1 mM $K_4[Fe(CN)_6]$ in 0.2 M KCl was used as the electrolyte. Cyclic voltammetry was performed at a scan rate of 20 mVs^{-1} in the same electrolyte. Square wave voltammetry was used for investigation of the electrode response toward Pb^{2+} and Cu^{2+}. Two procedures were employed. The first procedure included the accumulation step of investigated ions on the electrodes from the magnetically stirred solution. After the accumulation, each electrode was rinsed with water and dried with paper. The electrode was then transferred in an electrochemical cell containing 1.0 M HCl that served as the stripping solution. After the reduction of accumulated metal ions at selected potential and for a defined interval, the determination of metal ions was performed by square wave voltammetry. The second procedure was performed without the accumulation step in the solution that contained metal ions.

2.4 Point of zero charge (PZC)

The point of zero charge - pH_{PZC} was obtained using the experimental method described by Čerović et al [22]. The 25.0 mg of sample was shaken in 50 ml of a 0.01 M NaCl solution for 24 h. The initial pH values ($pH_{initial}$) were adjusted in the pH range from 2 to 12 by adding appropriate amounts of 0.1 M HCl or 0.1 M NaOH solution. After 24 h the suspension was

centrifuged and the final pH values of supernatants were measured (pH_{final}). The point of zero charge was determined from the $pH_{initial}$ vs. pH_{final} diagram.

3. Results and Discussion

3.1 Electrochemical characterization of investigated samples

The cyclic voltammetry and electrochemical impedance spectroscopy in 1 mM potassium hexacyanoferrate (II) in 0.2 M KCl was used to test the electrochemical properties of biopolymer modified carbon paste electrode. The characteristic pair of peaks corresponding to the oxidation and the reduction peaks of $[Fe(CN)_6]^{3-/4-}$ featured in all recorded voltammograms (Fig. 2a).

Figure 2

The highest current response was recorded for C-CPE sample and the lowest for CW-CPE. The peak separation for anodic and cathodic scans provides a qualitative estimation of the electron transfer rate due to the redox process at the electrode surface. The lowest peak-to-peak separation was obtained for C-CPE indicating that the oxido-reduction rate for $[Fe(CN)_6]^{3-}/^{4-}$ couple was highest for C-CPE.

The electrochemical impedance measurements (EIS) were performed in the same solution (Fig. 2b) at the open circuit potential. The modified Randles equivalent circuit (inserted picture in Fig. 2b) was used to fit the obtained spectra. The circuit consists of internal resistance (Rs) in series with the parallel combination of the constant phase element (Q_2) representing double-layer capacitance and an impedance of a faradaic reaction (serial combination of charge transfer resistance (Rct) and constant phase element (Q_1) representing diffusion). The constant phase element represents a non-ideal capacitor. This element is often introduced in the equivalent electric circuit instead of ideal elements in order to better describe obtained results. Somewhat

depressed semi-circle and declined line at low frequencies indicated (a) deviation from ideal behavior. The impedance of the constant phase element is given as:

$$Z = \frac{1}{Y} = \frac{1}{(i\omega)^n Q} \qquad (1)$$

where Y is constant phase element admittance, i is the imaginary unit, ω is the angular frequency, n is constant phase element exponent which is associated with the system inhomogeneity and Q has the numerical value of the admittance $(1/\,|Z|)$ at $\omega = 1$ rad/s. The results obtained using fitting with this circuit are presented in Table 1.

Table 1

Nyquist plots consisted of a semicircle section at higher frequencies corresponding to the charge transfer limiting process and short linear section at low frequencies corresponding to the diffusion-limited process. Rct is determined by the(a) kinetically controlled electrochemical reaction of the redox probe at the electrode surface. The lowest charge transfer resistance was obtained for C-CPE.

Maze stem cell wall contains all three types of polymers, lignin being present in the lowest amount. Cellulose and hemicelluloses, with predominant xylan-type polymers, are more abundant and present in relatively equal amounts. Cellulose surface is positively charged at low pH values, the predominant acid group being carboxylic [23]. Xylan also contains carboxylic groups and thus positive surface charge, although its molecules are branched, while cellulose has a linear structure. Lignin contains C=O groups, as well as phenolic OH and alcoholic aliphatic OH, and methoxy groups. At low pH, it is less positively charged and has higher hydrophobicity. Its negative charge increases and hydrophobicity decreases with pH increase [24, 25]. These lignin properties may explain its high Rct values, while cellulose and xylan surface charge may

be responsible for their lower Rct. Cell wall's intermediate Rct value may be addressed to the fact that it contains these two types of polymers- polysaccharides and lignin, differing in their surface properties.

3.2 Electrochemical behavior of modified electrodes toward Pb^{2+} and Cu^{2+} ions

The electrochemical behavior of modified electrodes toward Pb^{2+} and Cu^{2+} ions was tested by square wave voltammetry (SWV). Two manners of detection were employed. The first manner involved the usual approach where the accumulation of analyte species was performed prior stripping step. The time of accumulation affects the resulting performance of the investigated electrodes by establishing the equilibrium of adsorbed ions at the electrode surface. The accumulation was performed from the solution containing 10 μM of Pb^{2+} and Cu^{2+} ions at pH 5.5. The well-defined peak of Pb^{2+} at -0.50 V vs. Ag/AgCl can be observed at SWV of all investigated electrodes (Fig. 3). At the foot of this peak at potential around -0.36 V poor resolved peak corresponding to copper ions could be seen. The characteristic peak of Cu^{2+} ion is usually recorded at potential around -0.1 V vs. Ag/AgCl. However, this peak was very low indicating high selectivity of all investigating samples toward lead ions. The well expressed peak of Cu^{2+} ions at -0.1 V was detected only in the absence of Pb^{2+} ions. The appearance of a peak at -0.36 V is previously noticed [26] and ascribed to the inter-metallic assemblies of the two metals during the accumulation step. The current response of different biopolymers reflects the availability of binding sites for investigated metal cations. Cellulose exhibited the highest current response among individual biomass constituents. However, the current response obtained for CW-CPE after accumulation time of 180 s was three times higher than cellulose response (Fig. 3).

Figure 3

These findings indicated that the accumulation of metal cation was not governed only by the number of binding sites in individual biomass constituent but also by their mutual interaction in the cell wall. According to FTIR results [19] maize cell wall showed a high percentage of intra-molecular hydrogen bonds indicating a high crystallinity of cellulose and a low percentage of inter-molecular hydrogen bonds indicative for weak interaction between cellulose and lignin. The crystalline form of cellulose has a lower number of OH^- groups that can bind metal cations, indicating that cellulose was not the main adsorption site in the cell wall. Similar results were obtained by Xiong et al. [27] for adsorption of cadmium in the rice cell wall. A possible application of CW-CPE for Pb^{2+} ions was tested.

To obtain the best results the parameters that affect the performance of SWV technique were tested: pH of accumulation, potential of reduction and time of reduction. The influence of pH of accumulation was tested in pH range 1.0 – 6.9. The highest current response was obtained for pH 4.9 what is in accordance with the previously published results [12]. The potential of reduction of accumulated ions was tested in the range -0.9 V to -1.2 V. The reduction performed at the potential of -1.0 V yielded the highest current. In a similar manner the duration of reduction at -1.0 V was tested in the range 5 – 30 s, and the best results were obtained for 20 s.

Therefore, further experiments were performed with accumulation step at pH 4.9 for 180 s, followed by transferring the electrode to stripping solution at pH 1.0 for reduction of accumulated ions at the potential of -1.0 V for 20 s. Finally, the determination of ions was performed by SWV immediately after the reduction step. The current response of CW-CPE toward Pb^{2+} (Fig. 4) was linear in the concentration range from 0.05 to 50 μM with two slopes: for the concentration range from 0.05 to 5 μM (Ip (μA) = 2.059 C(μM) + 0.287 (r = 0.991)) and from 10 to 50 μM (Ip (μA) = 0.334 C(μM) +12.777 (r = 0.994)).

Figure 4

However, the procedure that includes the accumulation step was not favorable for the simultaneous determination of Pb^{2+} and Cu^{2+} ions concentration. The problem arises from the affinity of functional biosorbent groups for metal cations. Previous research on affinity series of metal cations [28] showed that biosorbents have a higher affinity toward lead ions than for copper ions. Furthermore, the adsorption capacity of most of biosorbents is higher for lead ions than for copper ions [29]. Besides, research performed on cellulose/chitin beads [30] showed that selectivity was higher for lead in comparison to copper in low ion concentration solution.

Therefore, the second approach was implemented. The determination of Pb^{2+} and Cu^{2+} was performed without the previous accumulation step. The procedure included reduction of ions at the electrode surface under the optimized conditions in 0.1 M HCl, i.e. 40 s at the potential of -1.3 V. The effect of co-adsorption of copper ions in the presence of lead ions in the solution was used. The effect of increased adsorption of one pollutant in the presence of other was previously noted [31]. The results obtained for each modifier of carbon paste electrode are presented in Fig. 5-8.

Figure 5

Figure 6

Figure 7

Figure 8

Simultaneous determination of Pb^{2+} and Cu^{2+} was possible for the concentration up to 20 μM. For higher concentrations, the Cu^{2+} peak could not be resolved. Calibration plots of all electrodes except X-CPE showed two linear regions for the detection of Pb^{2+} ions. Calibration plots for

detection of Cu^{2+} ions showed only one linear region, except for L-CPE where two linear regions were observed. Linear regression parameters and concentration ranges are presented in Table 2.

Table 2

The best sensitivity for lead ion detection was obtained for the carbon paste electrode modified with cellulose. The highest sensitivity for copper ions detection was obtained for L-CPE for lower concentration range, but with the poor correlation coefficient. The further tests were performed with the C-CPE electrode.

The reproducibility of the C-CPE electrode was determined by measuring the current response of solution containing equal concentrations of Pb^{2+} and Cu^{2+} ions (10 μM). The relative standard deviation (RSD) of five independently prepared electrodes was 5.1 % for Pb^{2+} and 4.8 % for Cu^{2+}. The repeatability of one C-CPE electrode was determined in five successive measurements in the same solution and the RSD was found to be 3.4 % for Pb^{2+} and 2.8 % for Cu^{2+}. The influence of potential interference on the C-CPE electrode was studied from the solution that contained 10 μM of each Pb^{2+} and Cu^{2+}. The change of peak current up to 5 % was obtained for the 2-fold concentration of Ni^{2+}, Zn^{2+}, Co^{2+}, phenol, 4-NP, and 4-CP. The detection limit was estimated to be 0.01 μM for Pb^{2+} and 0.08 μM for Cu^{2+} (signal-to-noise ratio = 3). In order to test stability of electrode SWV were occasionally recorded on C-CPE. When not in use the electrode was protected with parafilm. Electrode retained ca. 80% of its activity after 1 week storage at room temperature.

The comparison of the analytical performance of C-CPE for electrochemical sensing of 4-CP and 4-NP with that of other modified electrodes reported in the literature is presented in Table 3.

Table 3

The investigated electrode showed a wide linear range with a good detection limit for simultaneous detection of Pb^{2+} and Cu^{2+}. The obtained features are comparable with some other sensors presented in literature. The main advantage of this sensor is that it is based on inexpensive, sustainable material without further modification,

3.3 Real sample

The analytical performance of C-CPE was tested using tap water. The pH value of the sample was adjusted to 1.0. The sample was spiked with known amounts of Pb^{2+} and Cu^{2+} and the obtained recovery values are presented in Table 4.

Table 4

The detection of copper was possible only after the addition of Pb^{2+} ions. The obtained results indicated that the tested electrode and proposed method can be used for the fast simultaneous analysis of Pb^{2+} and Cu^{2+} ions in the water.

3.4 Point of zero charge (PZC)

In order to better understand the process involved in the obtained results additional measurements were performed. The interaction of materials surface with charged species depends on electrostatic interactions. The charge of the material surface depends on the pH and influence interaction. The pH value at which the net charge of materials surface is zero is designated as point of zero charge (PZC). At $pH < pH_{PZC}$, the surface groups undergo protonation leading to positively charged surface, while at $pH > pH_{PZC}$ negatively charge surface is obtained through the process of deprotonation. The dependence of pH_f on pH_i in pH range 2-12 for all samples is presented in Fig. 9.

Figure 9

The pH$_{PZC}$ values of 6.1, 6.2, 5.3 and 5.3 were obtained for cellulose, xylan, cell wall and lignin respectively. The results imply that adsorption of cationic species should be performed at pH higher than pH$_{PZC}$. However, the optimization experiments for SWV showed that best results were obtained for pH 4.9. There are different groups present at the surface of investigated biopolymers. Cellulose and xylan are rich with carboxyl groups, while lignin contains carbonyl groups and phenolic and aliphatic hydroxyl groups. All these groups have distinct pKa values. The finding might imply that there are preferable adsorption sites that are already deprotonated at lower pH values such as carboxyl group.

In the second procedure adsorption of cations was governed by applied potential. Under applied negative potential local alkaline environment was created by electrolysis of water [36]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$
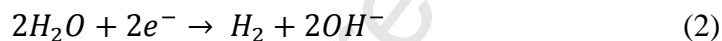
The local increase of pH would induce deprotonation of surface groups. Furthermore, deprotonation of acids immobilized on the can be induced by applied electric potential [37, 38]. In that manner appropriate adsorption sites would be formed for adsorption of metal cations. Biopolymers investigated in this work have variety surface groups arranged with different surface densities. The applied procedure would yield different local environment on the electrode surface.

Almost all calibration curves obtained in this work exhibited two linear domains. The linear region obtained for lower analyte concentration had high sensitivity and vice versa. The observed dependence was the consequence of different electrode activity in these two concentration regions that arise from ratio of available adsorption sites and concentration of analyte. Namely, at lower analyte concentration this ratio was high leading to high sensitivity, while at high concentration of analyte this ratio was lower.

Furthermore, almost all recorded SWV in this study showed peak potential shifting with the increase of concentration. According to literature data such behavior can be result of influence of ionic strength of solution [39], composition and concentration of supporting electrolyte [40] which influences metal cations interaction with water as well as interaction of deposited metal particles with each other and with electrode substrate [41].

The obtained results indicated that local electrode environment as well as mutual interaction of deposited particles significantly influenced the sensitivity of investigated electrode. The best sensitivity for simultaneous detection of lead and copper was obtained for cellulose modified electrode implying that obtained local environment was most favorable in that case.

4. Conclusion

The main aim of this paper was to investigate the effect of lignocellulosic biomass components as an electrode modifier. The analytical conditions affected the analytical performances of the carbon paste electrode modified with each of the investigated constituent of the maize cell wall as well as with complete cell wall. The electrode modified with cell wall showed the best performances under the analytical conditions that included accumulation step prior detection step. However, simultaneous detection of lead and copper ions was not possible under these conditions. The carbon paste electrode modified with cellulose showed the best performances for simultaneous detection of lead and copper ions using procedure without accumulation step and co-adsorption of lead and copper. It was demonstrated that materials from renewable sources provide a good alternative solution for lead and copper ion detection.

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Figure Captions

Figure 1: An isolated cell wall fragment from maize stems. The image was obtained by using a Carl Zeiss LSM 410 Microscope, in transmission mode.

Figure 2: Carbon paste electrodes modified with different biopolymer samples: a) Cyclic voltammograms recorded in 1 mM $K_4[Fe(CN)_6]$ + 0.2 M KCl at scan rate of 20 mV s-1; b) Nyquist plot recorded in same solution in OCP; inserted picture: the equivalent electric circuit used to fit EIS data.

Figure 3: SWV of carbon paste electrode modified with a) cellulose, b) xylan, c) cell wall and d) lignin recorded after different accumulation time.

Figure 4: a) SWV recorded at the CW-CPE for different concentrations of Pb2+ ion; b) calibration plot for determination of Pb^{2+} in the concentration range 0.05 – 50 μM.

Figure 5: a) SWV recorded on C-CPE from solution containing equimolar concentration of Pb^{2+} and Cu^{2+} ions in the concentration range 0.1 – 100 μM; b) and c) corresponding calibration plots for Pb^{2+} and Cu^{2+} ions.

Figure 6: a) SWV recorded on X-CPE from solution containing equimolar concentration of Pb^{2+} and Cu^{2+} ions in the concentration range 0.1 – 100 μM; b) and c) corresponding calibration plots for Pb^{2+} and Cu^{2+} ions.

Figure 7: a) SWV recorded on CW-CPE from solution containing equimolar concentration of Pb^{2+} and Cu^{2+} ions in the concentration range 0.1 – 100 μM; b) and c) corresponding calibration plots for Pb^{2+} and Cu^{2+} ions.

Figure 8: a) SWV recorded on L-CPE from solution containing equimolar concentration of Pb^{2+} and Cu^{2+} ions in the concentration range 0.1 – 100 μM; b) and c) corresponding calibration plots for Pb^{2+} and Cu^{2+} ions.

Figure 9: pH_f as a function of pH_i for investigated samples. Equilibration time was 24 h. Background electrolyte 0.01 M NaCl

Table 1: The parameters obtained by fitting Nyquist plot for data recorded in 1 mM $K_4[Fe(CN)_6]$ + 0.2 M KCl using electrodes modified with different clay samples

Electrode	R_{ct} (kΩ)	Y_1 (μSs^{n1})	n1	Y_2 (nSs^{n2})	n2
C-CPE	35	40.8	0.5	13.7	0.9
X-CPE	91	23.4	0.3	36.0	0.9
CW-CPE	171	19.8	0.3	39.6	0.9
L-CPE	286	32.0	0.6	24.5	0.9

R_{ct} – charge transfer resistance

Y - constant phase element admittance

n - constant phase element exponent

Table 2: Performances of diff erent modified electrode for detection of Pb^{2+} and Cu$^{2+.}$

Electrode	Pb		Cu	
	Concentration range (μM)	Linear regression	Concentration range (μM)	Linear regression
C-CPE	0.1-5	I(μA) = -0.004+0.894*C(μM); R=0.993	0.1-20	(μA) = 0.010+0.086*C(μM); R=0.998
	5-100	(μA) = 3.308+0.317*C(μM); R=0.998		
X-CPE	0.1-50	(μA) = -0.239+0.622*C(μM); R=0.998	0.1-20	(μA) = 0.011+0.079*C(μM); R=0.983
CW-CPE	0.1-2	(μA) = 0.046+0.664*C(μM); R=0.976	0.1-20	(μA) = 0.032+0.095*C(μM); R=0.979
	5-100	(μA) = 3.770+0.189*C(μM); R=0.999		
L-CPE	0.1-20	(μA) = -0.020+0.786*C(μM); R=0.996	0.1-2	(μA) = -0.129+0.598*C(μM); R=0.969
	20-100	(μA) = 10.175+0.266*C(μM); R=0.999	5-20	(μA) = 1.52+0.046*C(μM); R=0.992

Table 3: Comparison of the analytical performance at various electrodes in the determination of Pb^{2+} and Cu^{2+}.

Sample	Electrode	Method	Linear range (µM)	LOD (µM)	Ref. No.
Pb^{2+}	GCE/NFC	DPA	0.05-10	$0.5*10^{-3}$	[12]
	AuNPs/CNFs/GCE	SWA	0.1–1.0	0.1	[32]
	N@LEG/GCE	SWA	0.5–10, 10–380	0.16	[33]
	HAP-Nafion/GCE	DPA	0.1–10.0	0.049	[34]
	graphene-CeO2/GCE	DPA	0.2–2.5	0.00011	[35]
	C-CPE	SWV	0.1-5, 5-100	0.02	This work
	CW-CPE	SWV	0.05-5, 10-50		This work
Cu^{2+}	GCE/NFC	DPA	0.05-10	$0.5 *10^{-3}$	[12]
	AuNPs/CNFs/GCE	SWA	0.1–1.0	0.1	[32]
	HAP-Nafion/GCE	DPA	0.1–10.0	0.021	[34]
	graphene-CeO2/GCE	DPA	0.2–2.5	0.00016	[35]
	C-CPE	SWV	0.1-20	0.08	This work

Table 4: The determination of Pb^{2+} and Cu^{2+} in the tap water sample

Substance	Original (μM)	Added (μM)	Found (μM)	Recovery for Pb^{2+} (%, n=3)
Pb^{2+}	nd	1.00	1.04	104
	nd	2.00	1.98	99
Cu^{2+}	nd	1.00 Cu^{2+} and 1.00 Pb^{2+}	1.88 Cu^{2+} and 1.02 Pb^{2+}	102
	nd	2.00 Cu^{2+} and 1.00 Pb^{2+}	2.91 Cu^{2+} and 1.05 Pb^{2+}	105

Credit Author Statement
Ksenija Radotić: Conceptualization, Investigation, Writing
Daniela Djikanović: Resources, Investigation, Writing
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Nataša Jović-Jovičić: Investigation, Writing
Zorica Mojović: Conceptualization, Investigation, Writing, Supervision

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights
Biopolymers were used as modifier of carbon paste electrode.

Simultaneous detection of lead and copper ions was tested.

Biopolymer affinity for cations influenced simultaneous detection.

New procedure for simultaneous detection of lead and copper ions is presented.

The materials from renewable sources provide good alternative electrode materials.

10 μM
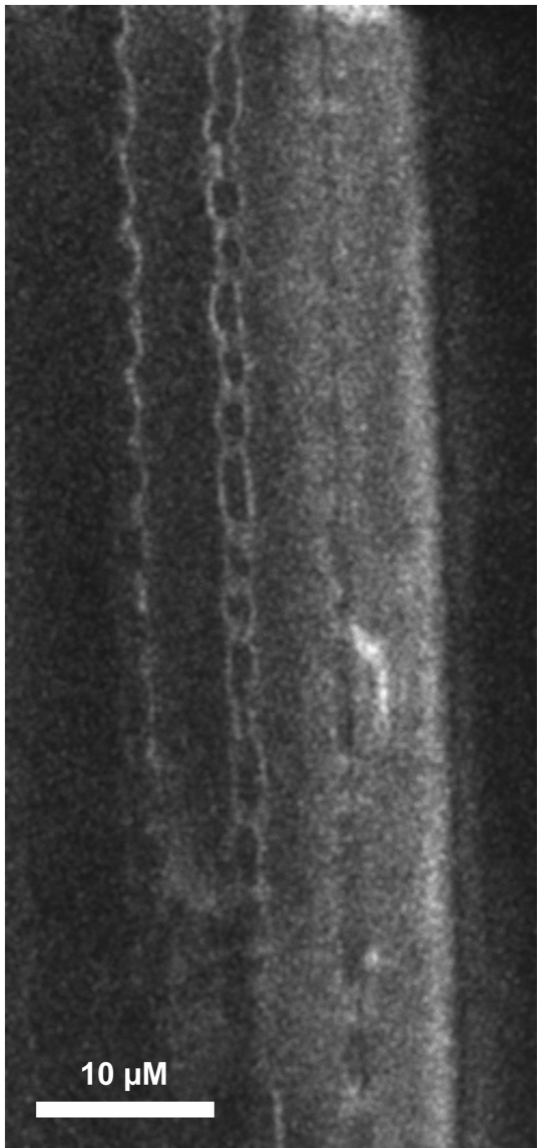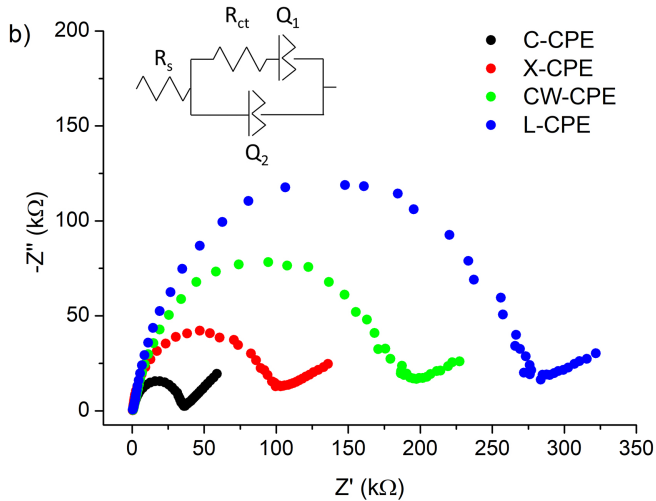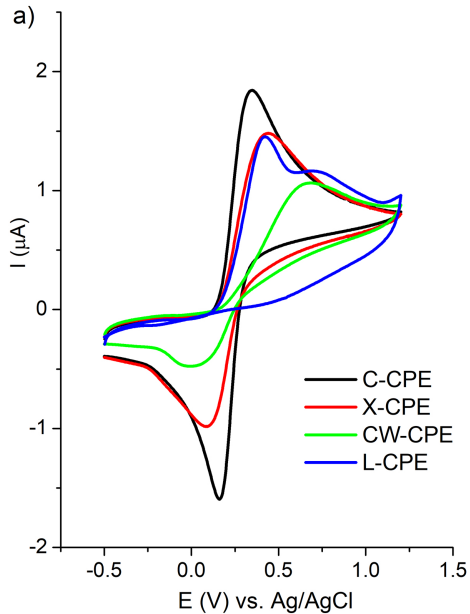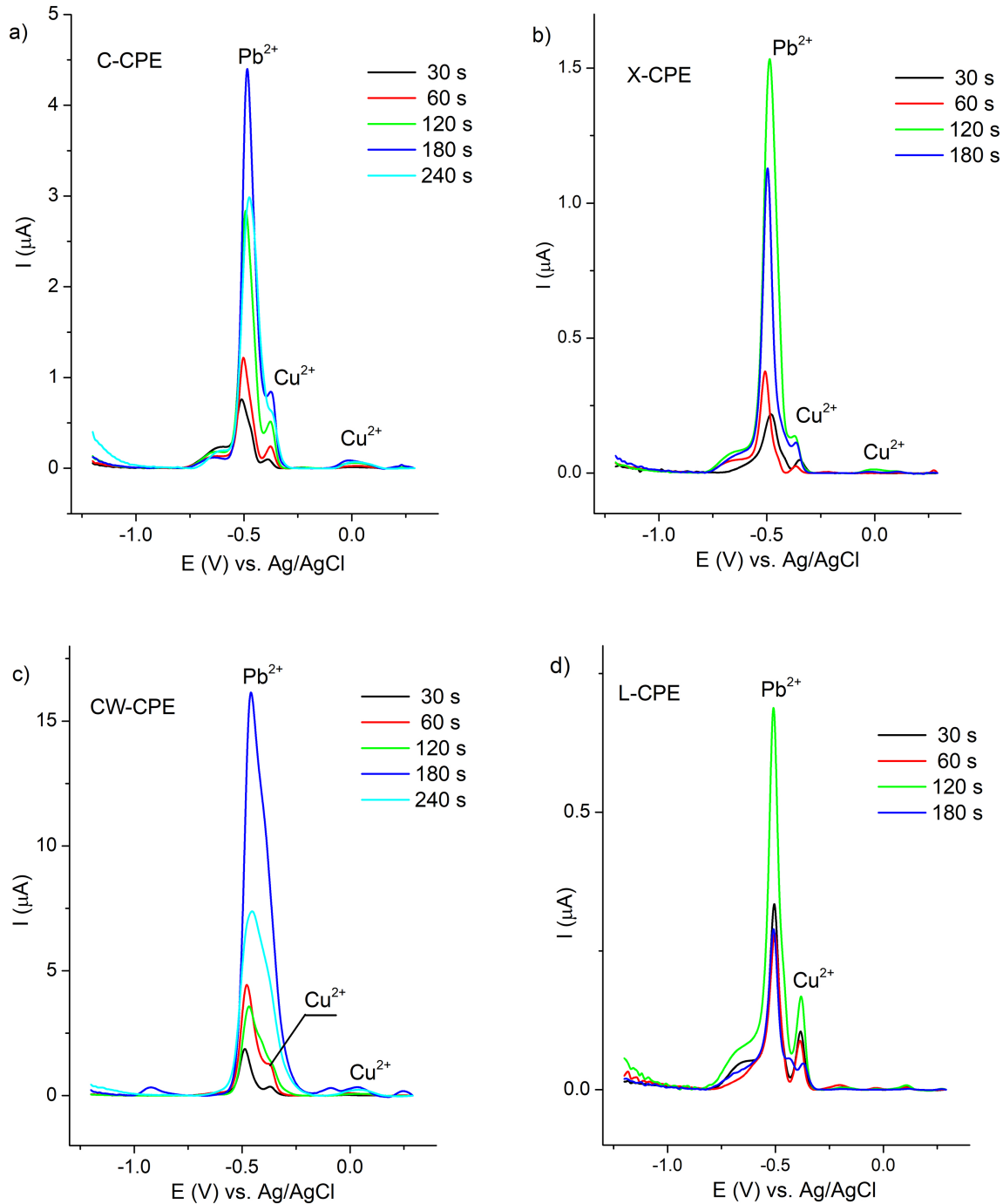
Figure 1

Figure 2

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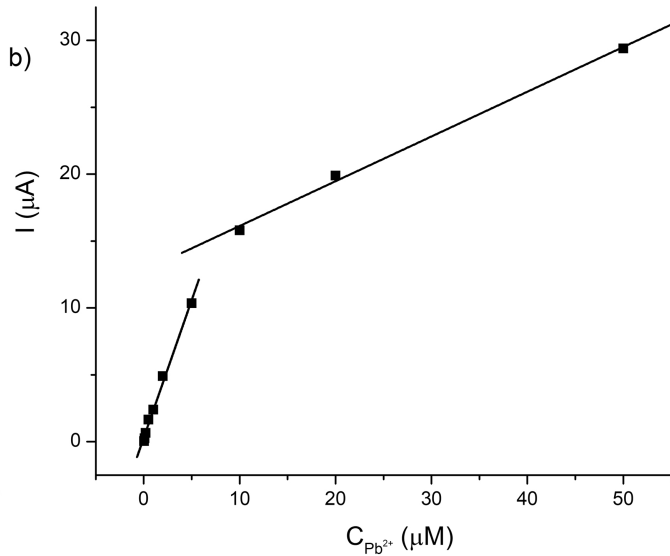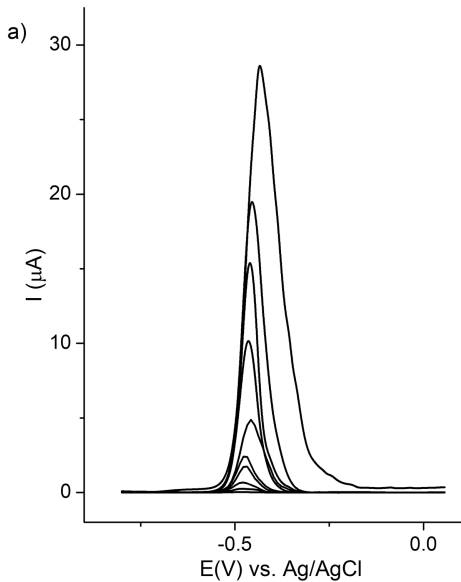
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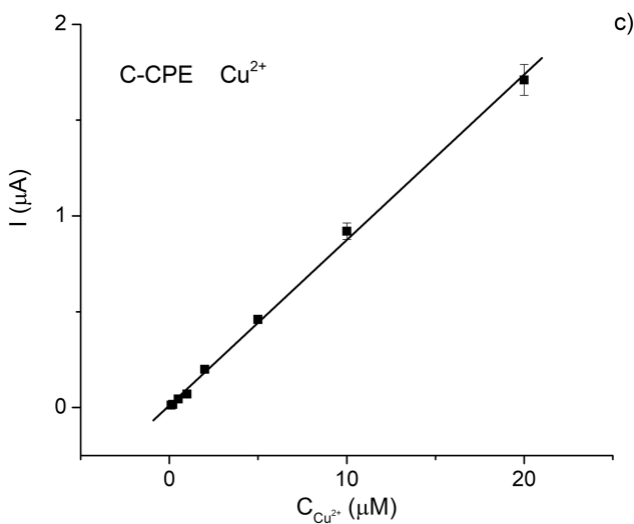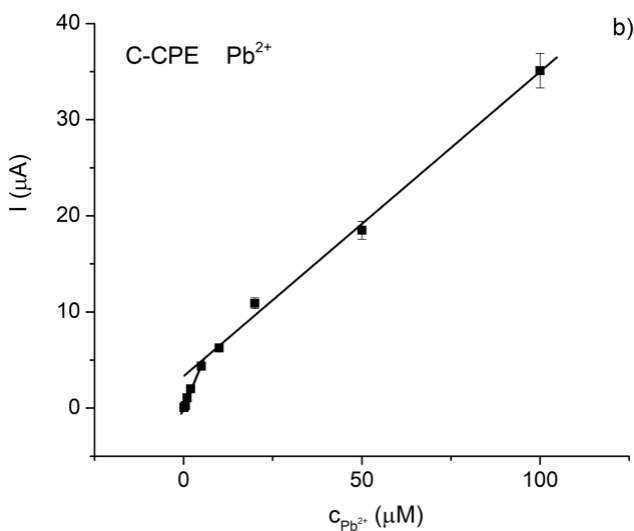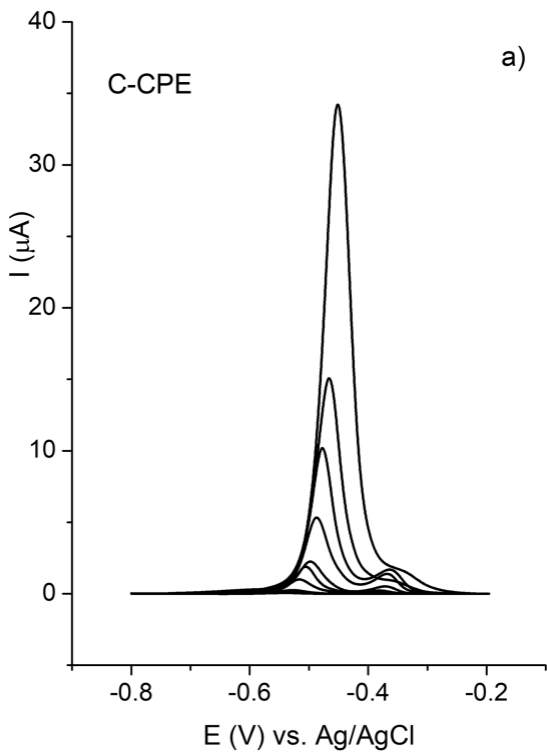
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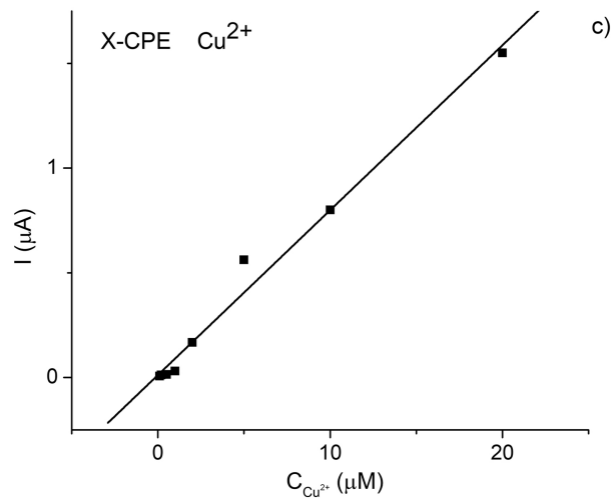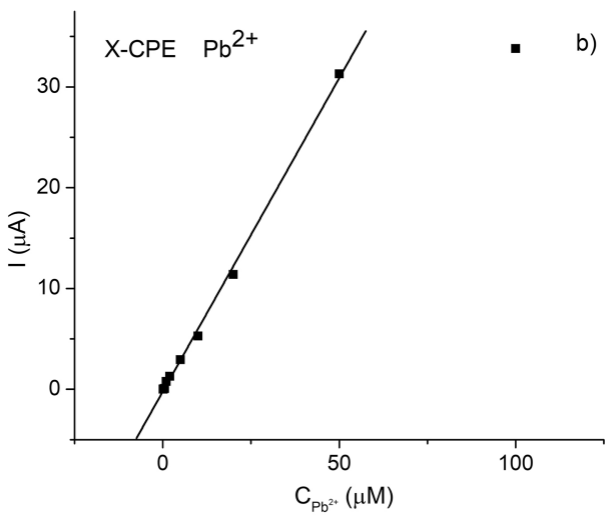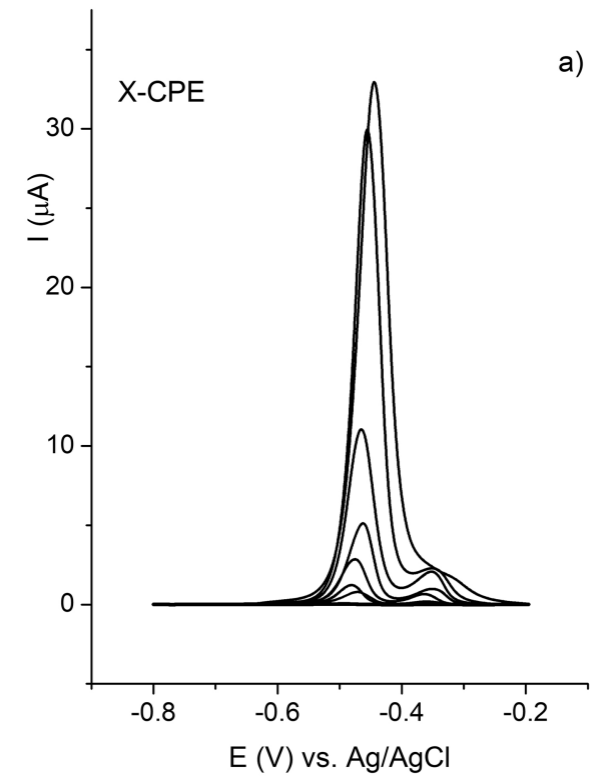
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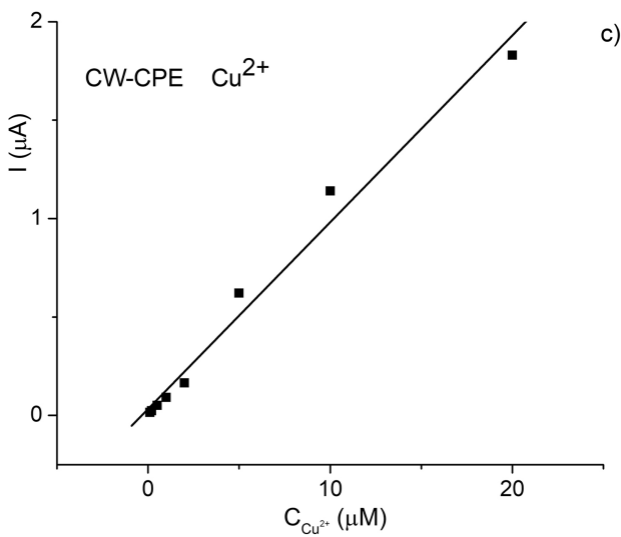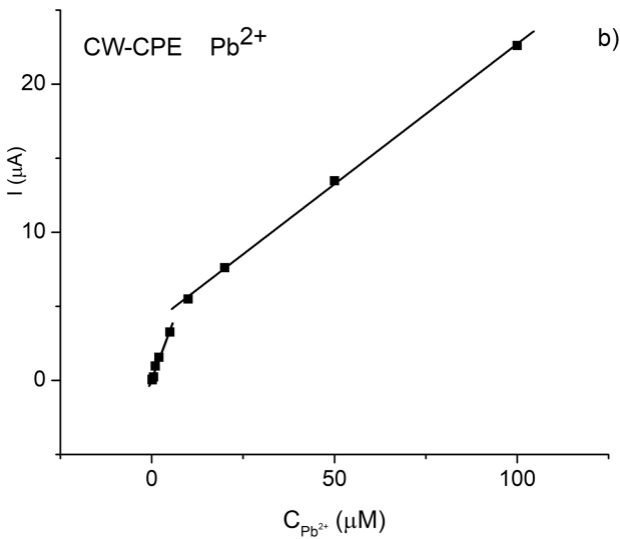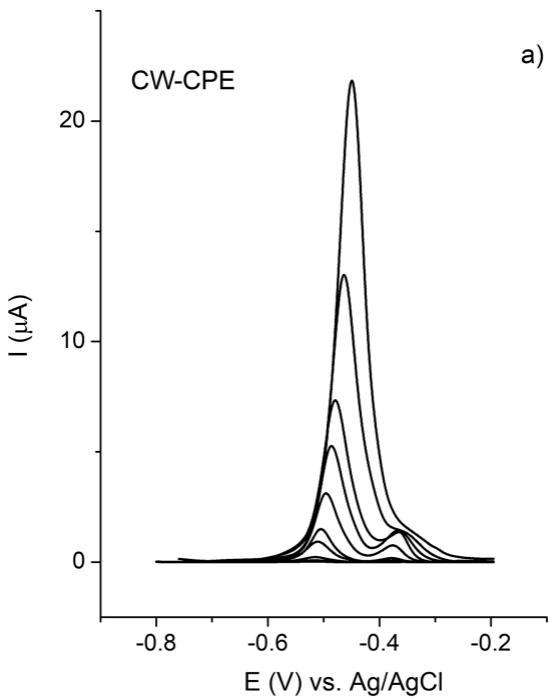
Figure 7

Figure 8

Figure 9