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Iron nanoparticles and nanowires as modifiers of carbon paste electrodes for the detection of traces of copper, lead, and zinc ions in water

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ABSTRACT

This work describes the application of nano-iron modified carbon paste electrodes (CPEs) for the detection of copper, lead, and zinc ions in aqueous solutions. The CPEs were manufactured by mixing commercial graphite powder with mineral oil and two types of iron nanomaterials, namely iron nanoparticles (Fe-NPs) and iron nanowires (Fe-NWs) whose preparation processes and properties were also presented herein. Preliminary electrochemical results showed that the CPEs modified with Fe-NWs (10% relative to the graphite) possessed a larger electrochemically active surface area in a comparison with unmodified electrodes and those modified with Fe-NPs. The current responses of investigated electrodes depended on the type of metal ion and its concentration. Contrary to previous literature reports on the modification of CPEs, higher current responses and lower detection limits were found for electrodes prepared with Fe-NWs. This indicates that the Fe-NWs constitute a promising modifier of CPEs for sensor application.

Keywords: Carbon paste electrode; Iron nanoparticles; Iron nanowires; Magnetic-field-induced synthesis; Metal ion detection

1. Introduction

Heavy metals occur naturally in the environment and are of anthropogenic origin. Moreover, the increasing emission of metals through human activity into the environment, which constitutes a great danger is a worrying trend, because they are non-degradable and do not decompose [1]. Due to the high mobility of their salts, migration into the subsoil and groundwater as well as to drinking water sources is rather quick [2]. Furthermore, their good solubility in water enables consumption by living organisms and then passed on to the alimentary chain and life cycle [3,4]. These hazardous and bio-accumulative environmental pollutants could be the cause of various health problems and pathologies, including cancer, liver damage, Wilson disease, insomnia, depression, lethargy, neurological signs and increased thirst, fetal brain damage, kidney diseases, autoimmunity, etc. [5,6]. Lead is extremely toxic even at low concentrations. Zinc and copper are essential elements necessary for most organisms but overexposure

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to them can also be life-threatening [5,6]. Therefore, it is absolutely necessary to constantly monitor the concentration of these metals [1–3,5,7].

The protection and conservation of water resources as well as access to good quality water are one of the cornerstones of environmental protection (US EPA Integrated Risk Information System – Program Outlook Update, 2020; Guidelines for Drinking-water Quality, WHO, 2011 Geneva). According to the European directive "Water Frame Directive" (WFD) (European Directive 2000/60/EC), environmental monitoring of heavy metals is of critical importance for both ecological assessments and public health. The WFD aims to limit the concentration in surface waters of 41 dangerous chemical substances (including heavy metals) which pose a particular risk to the environment and to human health. The directive points out in particular, the four most dangerous heavy metals (Hg, Cd, Pb, and Ni) and establishes their maximum authorized as well as annual average concentration values in surface waters. Therefore, the development of *in situ*, real-time, and highly-sensitive technique for effective monitoring (inexpensive widespread testing of water for metals) and environmental management is urgently needed [8–10].

The detection of heavy metal ions can be carried out by applying several spectroscopic techniques (e.g., atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES), X-ray fluorescence technique, neutron activation analysis), and electrochemical techniques (e.g., square wave anodic stripping voltammetry (SWASV), differential pulse anodic stripping voltammetry (DPASV), adsorptive stripping voltammetry (AdsSV), differential pulse voltammetry (DPV) [4,5,7,10]. The main advantages of the first group are their universality, suitability for a large range of elements, sensitivity, and low limit of detection (LOD). They are however time-consuming and require the expensive consumables and competent operators to perform a multi-stage sample preparation and complicated analytical procedures which are not suitable for sites and environmental measurements [8,9,11]. On the other hand, the electrochemical methods constitute an alternative option for the spectroscopic techniques due to their simplicity, high speed, low costs, the user-friendly, excellent limit of detection, high sensitivity, capacity for multi-elemental determination, and lack of reagents. Moreover, they are well-suited for miniaturization and automatic *in situ* measurements with minimal sample changes [3,5–11]. However, these techniques could also be improved in terms of their sensitivity, LODs, and automation. Therefore, there are many investigations that aim to develop new materials for the production of electrodes [9–11].

One of the most attractive electrochemical sensors is a group that uses carbon paste electrodes (CPEs). These electrodes can be easily manufactured and at the same time, their surface regeneration is very simple. They also possess good mechanical stability, low Ohmic resistance, chemical inertness, steady and reproductive response [7,10,11].

Over 60 years have passed since the first publication of work on the carbon paste electrode (CPE) invented by Adams [12,13]. Electrodes consisting of a paste of graphite powder and paraffin/mineral oil still play an important role in electroanalysis [14,15]. Over the years, CPEs have been the subject of a large number of research works. Their application has been growing systematically, among others in environmental analysis. These electrodes are subjected to various modifications. One of the possible ways is the addition of another component to the standard CPE composite [7,10,11,16–19]. For instance, this can be carbon or any inorganic nanomaterial, which serves as a modifier. Carbon nanotubes [18–21], graphene [22–25], and mesoporous silica materials [26–28] seem to be particularly promising in this role. In some published works, the influence of one of the mentioned above modifiers is usually studied. Metallic nanostructures have relatively rarely been used as CPE modifiers. The main aim of this study, therefore, was the application and comparison of two types of nano-iron materials (nanoparticles and nanowires) as modifiers of CPE electrodes for the detection of copper, lead, and zinc ions in water.

2. Experimental

2.1. Materials and methods

All the chemical reactants were analytical grade and used directly without further purification or modification. The iron nanoparticles and iron nanowires were synthesized and washed with the use of the following chemicals: iron(III) chloride hexahydrate ($FeCl_3·6H_2O$; 98%, Carl Roth GmbH, Germany), sodium borohydride ($NaBH_4$; 97%, Carl Roth GmbH, Germany), ethanol (99.8%, Avantor Performance Materials Poland), and acetone (99.5%, Carl Roth GmbH, Germany). Argon (>99%) was supplied from the BialGaz Company (Poland). The graphite powder (diameter < 20 μm) and the high purity mineral oil (Nujol) used in the preparation of the carbon paste were obtained from Sigma-Aldrich (United States of America).

The electrochemical measurements were carried out with potassium chloride (99.5%), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III) (99%) and copper(II) nitrate ($Cu(NO_3)_2$; 99%), lead(II) nitrate ($Pb(NO_3)_2$; 99%) and zinc nitrate ($Zn(NO_3)_2$; 99%) obtained from Avantor Performance Materials (Poland).

2.2. Preparation of iron nanoparticles and iron nanowires

The iron nanoparticles (Fe-NPs) and iron nanowires (Fe-NWs) were prepared according to previously established and reported processes [29–31] illustrated in the chemical reaction presented below in Eq. (1).

$$FeCl_3·6H_2O + 3\ NaBH_4 + 3\ H_2O \rightarrow Fe_{(s)} + 3\ B(OH)_3 + 3\ NaCl + 10.5\ H_{2(g)} \quad (1)$$

$$Fe^{3+} + 3\ NaBH_4 + 9\ H_2O \rightarrow Fe_{(s)} + 3\ B(OH)_3 + 3\ Na^+ + 10.5\ H_{2(g)} \quad (2)$$

In a typical synthesis, 300 mL of 0.09 M aqueous solution of $FeCl_3·6H_2O$ and 175 mL of 1 M aqueous solution of $NaBH_4$ were used for the reaction. Furthermore, the process was performed under constant argon flow with or without an external magnetic field (~0.05 T) generated by two parallel neodymium magnets. This led to the formation of either Fe-NPs or Fe-NWs. After the process, the as-prepared iron nanomaterials were washed three times with ethanol and then three times with acetone in order to remove any by-products. Finally, the product was dried in a vacuum dryer at 50°C for 2 h. The materials obtained in this way were applied as modifiers for the CPE.

2.3. CPE preparation

The unmodified CPE was prepared by mixing graphite with mineral oil (Nujol) in a ratio of 70%:30% (m/m) using an agate mortar and pestle until a homogenous paste was obtained. The mixture was kept at room temperature for appropriate time, and then the paste was packed into the Teflon electrode holder cavity (2.5 mm diameter and 3.5 mm in depth) and polished with a filter paper. The modified CPE was prepared by mixing the graphite powder (90%, m/m) and Fe-NPs or Fe-NWs (10%, m/m) using a mortar and pestle and a subsequent addition of mineral oil. A homogenized paste consisted of solid and liquid components in m/m ratio of about 70:30.

2.4. Characterization of CPE and modifiers

2.4.1. Chemical and physical properties

The morphology and structural properties of the materials used in the production of CPEs were determined by means of a Hitachi SU8020 (Japan) scanning electron microscopy (SEM) and a Bruker D2 phaser X-ray diffractometer (United States of America) (XRD) equipped with a Cu X-ray lamp. Furthermore, the texture of the Fe-NPs, Fe-NWs, and graphite powder was measured on the basis of low temperature nitrogen adsorption–desorption isotherms on a TriStar II 3020 adsorption analyzer (Micromeritics, United States).

2.4.2. Electrochemical investigations

All the cyclic voltammetry (CV) measurements were performed with an analytical system potentiostat/galvanostat AutoLab, PGSTAT 20 (EcoChemie, Netherlands) supported by GPES 4.9 software. A conventional three-electrode cell (20 mL) comprising of modified or unmodified CPE as working electrode, a platinum wire as a counter electrode, and a saturated calomel electrode as a reference electrode were used. All measurements were carried out at room temperature. The solutions were purged of dissolved oxygen (with use nitrogen) before carrying out voltammetric analysis.

Firstly, the electrochemical characterization of the unmodified as well as modified CPE (containing 10% of modifier – Fe-NPs or Fe-NWs) were carried out in order to determine their electroactive surface areas. These studies were performed using the well-known inner-sphere redox probe potassium ferro-/ferricyanide (2 mmol/L) in 0.1 mol/L KCl supporting electrolyte.

Prior to the CV measurements in the solutions containing metal ions, the influence of the accumulation time on the peak current was determined. The accumulation time varied from 0.5 to 5 min and the corresponding current value was measured for a 0.5 μmol/L concentration of Cu(II), Pb(II), and Zn(II) solutions.

The potential values used in obtaining the cyclic voltammograms were selected in order to determine the preconcentration potential values for each metal employed in CV: initial potentials of –0.3, –0.8, and –1.8 V and final potentials of 0.2, 0.2, and –0.1 V for Cu, Pb, and Zn were obtained, respectively. The peak height was evaluated with the GPES software.

3. Results and discussion

The morphologies of the initial materials used to the preparation of CPE are presented in Fig. 1. The SEM images indicate clearly that the application of the external magnetic field in the process caused the formation of iron nanowires.

It is also worth noting that the Fe-NWs reveal a specific structure, that is, they are composed of nanoparticles that are aligned in straight and long chains. According to the SEM measurements, the diameters of both iron nanomaterials are about 100 nm, whereas the average length of Fe-NWs is about 5 μm. The commercial graphite powder consists of nonhomogeneous flakes whose specific surface areas are much higher than those observed for iron nanomaterials.

The low temperature (77 K) nitrogen adsorption–desorption isotherms of the iron nanowires, iron nanoparticles, and graphite powder are presented in Fig. 2.

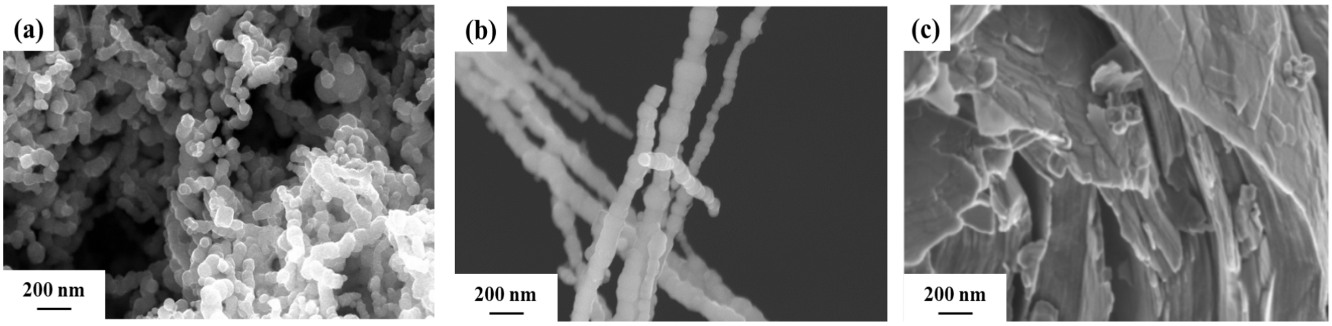

Fig. 1. SEM images of (a) iron nanoparticles (Fe-NPs), (b) iron nanowires (Fe-NWs), and (c) graphite powder; magnification of 50,000 times.

The specific surface areas (BET) of the modifying materials and graphite reveal that Fe-NWs possessed the highest value of 17.4 m^2/g, while a specific surface area of Fe-NPs was about 9.0 m^2/g.

The graphite used for CPE preparation had a specific surface area of 4.3 m^2/g. The addition of any of the modifiers would increase the contact surface area per gram of graphite available for conductivity measurements. Therefore, it was expected that Fe-NWs would have much greater influence because even graphite: Fe-NWs ratio of 9:1, would significantly increase the total surface area of the composite. The micropore volume values were in the same order as follows: 0.007, 0.004, and 0.002 cm^3/g. These values were very low and constitute only 10%–20% of the total pore volume. The obtained results were in good agreement with the SEM images, in which it can be observed that the Fe-NPs tend to form large dense agglomerates due to their magnetic interactions. This resulted in a decrease in the available surface area for the adsorption of nitrogen. In turn, the magnetic anisotropy, in particular shape anisotropy, of Fe-NWs limited the creation of clusters.

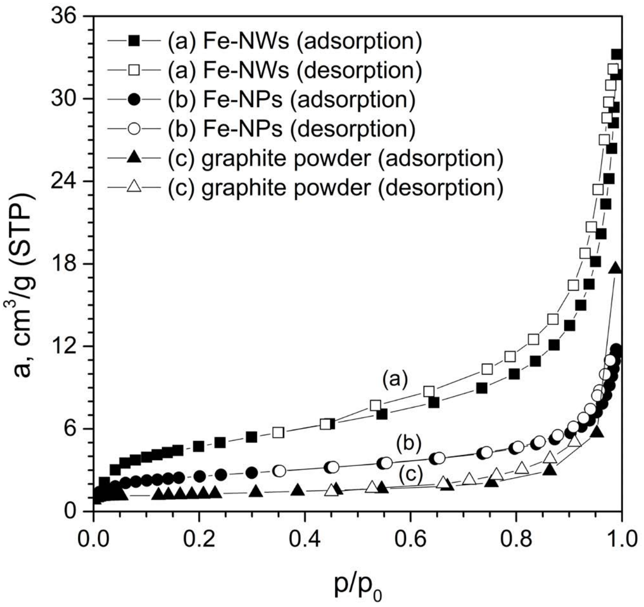

Fig. 2. Nitrogen adsorption–desorption isotherms collected at 77 K for (a) iron nanowires (Fe-NWs), (b) iron nanoparticles (Fe-NPs), and (c) graphite powder; STP – standard temperature and pressure.

The X-ray diffraction (XRD) patterns of the Fe-NPs, Fe-NWs, and graphite powder, are presented in Fig. 3. The peak positions of α-Fe phase and graphite were detected and they are assigned according to the JCPDS cards no. 87–0722 and 75–1621, respectively. The obtained results indicate clearly that the CPEs consist of carbon and iron materials. Nevertheless, the XRD signal associated with the Fe nanomaterials is much smaller than for graphite.

It is also worth noting that no diffraction peaks of the iron oxides were observed in the XRD patterns. This indicates that the iron nanomaterials were quite stable in air and also that they were not modified during the CPE preparation.

The XRD patterns for graphite powder revealed that it is not "perfectly crystalline". The reflex from the oblique plane (101) is wider than other reflections, that is, the ordering of graphite planes is slightly inferior to the ideal graphite crystal 2H. The interplanar distance d_{002} = 0.3365 nm is also in good agreement with those provided by the International Centre for Diffraction Data ICDD graphite standards pattern 00–56–160 (d_{002} in range 0.334–0.338 nm).

The results of the electrochemical characterization of the modified CPE (10% of modifier – Fe-NPs or Fe-NWs) are shown in Fig. 4. The peak current I_p for a reversible process is described by the Randles–Sevcik equation:

$$I_p = 2.69\times 105 AD^{1/2}n^{3/2}\nu^{1/2}C \tag{3}$$

where A is the area of the electrode (cm^2), n is the number of electrons participating in the reaction, D is the diffusion coefficient of the molecule in solution (m^2/s; for the solution in the performed experiment, $D = 7.6\times 10^{-6}$ cm^2/s [35]), C is the concentration of the probe molecule in the solution (potassium ferro-/ferricyanide redox couple solution with 0.1 M KCl), and ν is the scan rate (V/s). Based on the results presented in Fig. 4, the values of the active electrode areas were found to be 0.198 cm^2 for the CPE modified with Fe-NPs and 0.255 cm^2 for the CPE modified with Fe-NWs. The active electrode area of the unmodified CPE was equal to 0.089 cm^2. Taking into consideration the larger electrode area which is proportional to the electrical current, the Fe-nanowires were chosen as modifiers for the CPEs in further investigations.

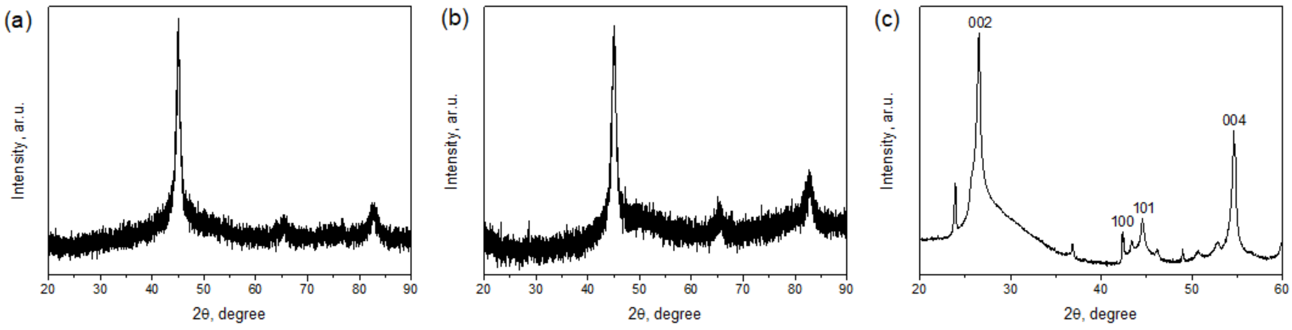

Fig. 3. XRD patterns of (a) iron nanoparticles, (b) iron nanowires, and (c) graphite powder.

The results of the studies on the influence of the accumulation time on the peak current observed on the cyclic voltammograms registered in Cu(II), Pb(II), and Zn(II) ion solutions are presented in Fig. 5. The peak current increased with an increase in the accumulation time for all metal ions up to about 2.5–3.5 min and then became stable. On the basis of registered dependencies, the necessary 3.5 min accumulation time was taken into account for further research. In general, this duration is similar to those found in the literature [36,37]. This may be associated with good access to the surface of the Fe-nanomaterials for solution components due to the small proportion of micropores in their porous structure.

After establishing the preliminary conditions, cyclic voltammetry experiments were performed. The CV voltammograms for 1 and 5 μmol/L Cu(II), Pb(II), and Zn(II) solutions on the CPEs modified with 10% Fe-NWs are shown in Fig. 6. In each case, the cyclic voltammetry measurements were carried out with a scan rate of 0.05 V/s. The peak current heights and potentials were evaluated by the GPES software.

The peak parameters are summarized in Table 1. For the unmodified CPE in 1 μmol/L Cu(II) solution the oxidation peak current was equal to 0.14 μA and reduction peak 0.09 μA. For the 5 μmol/L solution these were 0.21 and 0.13 μA, respectively. The modification of CPE with Fe-NWs (10%) caused a significant increase in the peak current: in 5 μmol/L Cu(II) solution for oxidation peak 27-times, and for reduction peak 23-times, in 1 μmol/L Cu(II) solution for oxidation peak 9.3-times, and for reduction peak 12.2-times. These results are markedly better in comparison with those obtained for activated carbon SX2 (Norit) as CPE modifier (10%), despite the fact that it has a much larger specific surface area (885 m^2/g [38]) than Fe-NWs (17.4 m^2/g). In the case of activated carbon as a modifier, the peak current increased only 7.5 and 2.8-times for 5 and 1 μmol/L Cu(II) solution, respectively. At this point, it should be noted that the electrochemically active surface of the CPE modified with activated carbon determined using the Randles–Sevcik equation was 0.121 cm^2. The porous structure of Norit SX2 activated carbon is a large extent microporous. However, the surface of iron nanowires, though smaller, is more accessible for the components of the solution [38]. Even more pronounced enhancements of the peak current were observed for the solutions containing Pb(II) and Zn(II).

The calibration curves (described with the linear regression equation $y = ax + b$) were plotted as functions of the

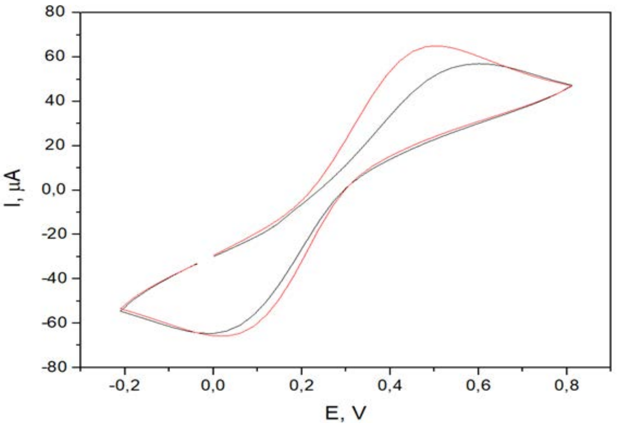

Fig. 4. Cyclic voltammograms of the modified carbon paste electrodes (with 10% Fe-NWs – red line, 10% Fe-NPs – black line) in 2 mmol/L potassium ferro-/ferricyanide redox couple solution with 0.1 M KCl (scan rate 100 mV/s).

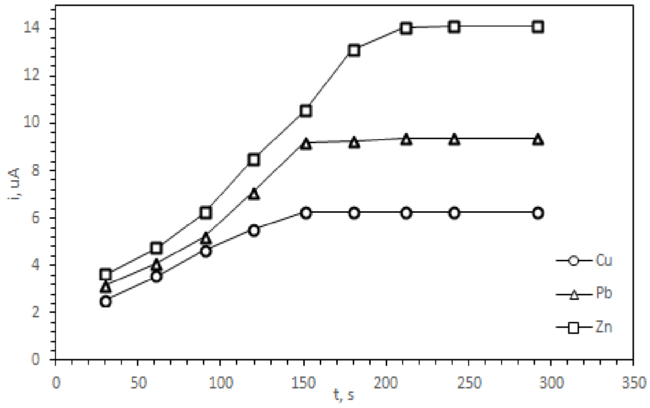

Fig. 5. Effect of accumulation time on peak current of modified carbon paste electrode (10% Fe-nanowires) in 5 μmol/L Cu, Pb, and Zn solutions.

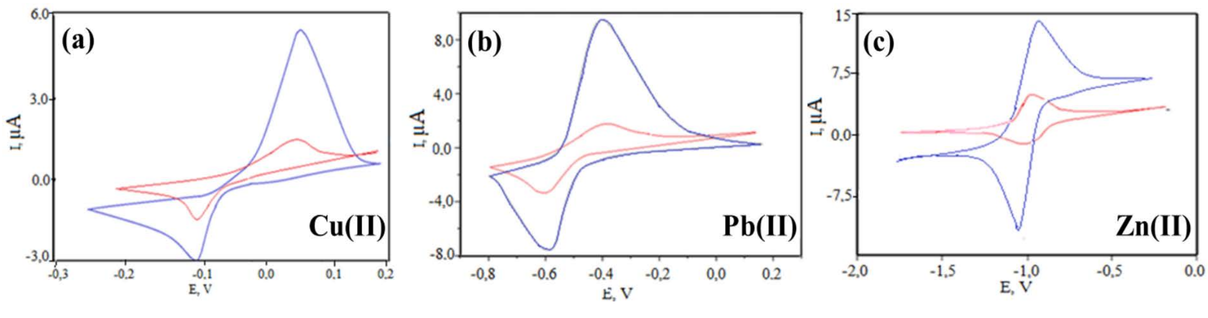

Fig. 6. Cyclic voltammetry curves of 5 μM (blue line) and 1 μM (red line) obtained for (a) copper solution marked as Cu(II), (b) lead solution marked as Pb(II), and (c) zinc solution marked as Zn(II). Working electrode: CPE modified with 10% Fe-NWs. Scan rate 0.05 V/s.

Table 1
Peak currents and potentials for cyclic voltammograms in Cu(II), Pb(II), and Zn(II) ion solutions registered on modified CPEs (10% Fe-NWs)

Metal ions solution	Concentration (μmol/L)	Peak current (μA)				Potential (V)			
		CPE		CPE + 10% Fe NWs		CPE		CPE + 10% Fe NWs	
		Ox	Red	Ox	Red	Ox	Red	Ox	Red
Cu(II)	5	0.21	0.13	5.7	3.0	0.06	–0.12	0.06	–0.13
	1	0.14	0.09	1.3	1.1	0.06	–0.11	0.06	–0.12
Pb(II)	5	0.24	0.17	8.6	7.7	–0.43	–0.58	–0.43	–0.58
	1	0.15	0.10	2.7	1.4	–0.41	–0.57	–0.41	–0.57
Zn(II)	5	0.27	0.19	13.6	12.4	–0.97	–1.06	–0.97	–1.05
	1	0.17	0.12	4.3	2.4	–0.99	–1.01	–0.99	–1.00

Table 2
Analytical curves and corresponding LOD and LOQ values for bare and modified (10% Fe-NWs) CPEs in Cu(II), Pb(II), and Zn(II) ions solutions

Metal ions solution	Range of concentration (μmol/L)	CPE	R^2	LOD (μmol/L)	LOQ (μmol/L)	CPE + 10% Fe NWs	R^2	LOD (μmol/L)	LOQ (μmol/L)
Cu(II)	1–5	$I_p = 0.0175 \cdot C + 0.123$	0.991	2.13	7.09	$I_p = 1.101 \cdot \mathrm{C} + 0.205$	0.990	0.076	0.25
Pb(II)	1–5	$I_p = 0.0225 \cdot C + 0.128$	0.990	1.79	5.97	$I_p = 1.475 \cdot C + 1.250$	0.992	0.25	0.85
Zn(II)	1–5	$I_p = 0.025 \cdot C + 0.145$	0.993	1.76	5.88	$I_p = 2.325 \cdot C + 1.981$	0.989	0.26	0.85

oxidation peak current (I_p, μA) against the concentration of metal ions (C, μmol/L) in the range from 1.0 to 5.0 μmol/L. Moreover, in order to evaluate the sensitivity of voltammetric analysis, the limit of detection (LOD) and quantitation (LOQ) values were determined for each investigated solution and were calculated from the calibration curves as 3 and 10 σ/a, respectively, where a is the slope of the calibration curve, and σ is the standard deviation of the peak currents for the blank signal. The fitted linear equations and corresponding correlation coefficient (R^2) as well as LOD and LOQ values obtained for the calibration curves of Cu(II), Pb(II), and Zn(II) solutions are collected in Table 2. Comparing the obtained results, one can see that the modified CPEs exhibit much lower LOD and LOQ than the unmodified electrodes. It is also worth noting that the LOD and LOQ values determined for the Cu(II) solutions with the CPEs modified with Fe-NWs are at the same level as for the CPEs modified with Norit SX2 activated carbon (LOD = 0.088 μmol/L; LOQ = 0.293 μmol/L).

Comparing the performance of the investigated electrode for the detection of heavy metals in aqueous solutions to other reported modified CPE, it can be noticed that their increases in peak current in the relation to unmodified CPE were always lower than that for Fe-nanowires. For instance, the use of SBA-15 mesoporous silica as modifier of CPE caused the approximately 7-fold increase in peak current, although its specific surface area was about 1,500 m^2/g [36]. The increase in anodic currents at the modified electrode demonstrated that the SBA-15 mesoporous silica played an important role in the accumulation process of Pb(II), Cu(II), and Hg(II) on the electrode surface with some advantages in sensitivity. The modification of CPE with graphene showed a three-fold increase of peak current in a comparison with the unmodified electrode [24], whereas very similar modification with Cr_2O_3 led to about 1.5-fold increase in peak current [7]. On the other hand, the performance of the organic modifier like carbon waste materials originating from coconut shells in detecting heavy metal ions could achieve only approximately 5-fold higher electrochemical response than the standard CPE [39]. Therefore, the CPEs modified with the iron nanowires investigated in this work exhibit better performance in terms of sensitivity, stability, and reproducibility than other reported modified CPE. These features fulfill all necessary requirements to find the potential applications of our electrodes in the detection of traces of heavy metals in aqueous solutions.

4. Conclusion

The use of iron nanoparticles and iron nanowires as the CPE modifiers and their application in the detection of heavy metal ions in water has been presented. The preliminary electrochemical tests indicated that significantly higher values of the active electrode areas were observed for the CPE modified with both iron nanomaterials than the unmodified CPE. Nevertheless, the CPE with iron nanowires revealed the highest active area among all electrodes investigated in this work, therefore this was the only one chosen for detailed electrochemical measurements.

In general, the small addition of iron nanowires, that is, 10% enhanced notably the current signal related to the presence of Cu(II), Pb(II), and Zn(II) ions in aqueous solutions. The modification of CPE with Fe-NWs resulted in a significant increase in the peak current from 9.3 to 50.4-times depending on the metal ion and its concentration in the solution. Moreover, although the specific surface area of Fe-NWs estimated from the low temperature N_2 adsorption isotherm was about 17.4 m^2/g and was much lower than that for a commercial activated carbon SX2 (Norit) (885 m^2/g) and SBA-15 mesoporous silica (1,500 m^2/g), the CPEs modified with this nanomaterial achieved much better electrical responses. Also, the important validation parameters such as LOD and LOQ were superior for the modified electrodes. These features indicate that the Fe-NWs are excellent materials for the CPE modifiers and they can improve the detection of metal ion traces in water.

The obtained results indicate the need for further and more detailed research on the CPEs modified with use iron nanowires.

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