Electrochemical determination of trace Cu²⁺ in water samples by using carbon ionic liquid electrode modified with molecularly imprinted polymers

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Abstract

Herein, a carbon ionic liquid electrode (CILE) incorporated with Cu²⁺ ion-imprinted polymeric nanoparticles is explored for the voltammetric determination of Cu²⁺ ions. The procedure is based on the interfacial preconcentration of Cu²⁺ on an imprinted polymer modified CILE through the surface coordination effect. The modified electrode exhibited a significantly increased sensitivity and selectivity for Cu²⁺ compared with the non-modified electrode. The effects of various parameters, such as the amount of ionic liquid, graphite and, IIP nanoparticles, the effect of Cu²⁺ extraction conditions on the electrode response, the accumulation potential and the accumulation time were investigated. The modified electrode showed a linear voltammetric responses to Cu²⁺ in the ranges of 25-1250 nM with a limit of detection (LOD) of 9.4 nM (S/N =3). The interference experiments showed that Cu²⁺ signal was not interfered in the presence of some potential interfering ions and organic species.

Moreover, this electrode presented the high sensitivity and excellent selectivity compared with previously reported methods in the area of electrochemical detection of Cu²⁺. These results demonstrate the feasibility of using the prepared Cu²⁺-imprinted polymer/CILE for efficient determination of Cu²⁺ in water samples.

Introduction

The copper ion (Cu²⁺) Cu²⁺ is an essential trace element in biological systems. This metal ion exists in nature extensively, and due to the tremendous applications, their exposure to environment and thereby in food cycle is also obvious. However, this metal ion could be toxic at high concentrations, and the World Health Organization (WHO) has recommended a concentration no more than 2 mg L⁻¹ to be allowed in drinking water. Hence, several methods to determine copper in food and biological samples have been reported based on inductively coupled plasma (ICP), flame atomic absorption spectrometry, and stripping voltammetry methods.[1-3]

Molecular imprinting is a very powerful technique for the preparation of synthetic polymers, having pre-designed molecular recognition properties. In this technique, the functional monomers are allowed to self-assemble around a template and subsequently cross-linked to each other. After polymerization, the removal of template reveals recognition cavities complementary to template in size, shape, and chemical functionality that can rebind the template efficiently and selectively.[4] Ion imprinted polymers (IIPs) are similar to molecularly imprinted polymers (MIPs), but they recognize given ions after imprinting.[5] In recent years, IIP-based sensors for monitoring metal ions have become a very active area of research.[5-13] For example, imprinted sensors for Cu²⁺,[6,7] Ag⁺,[8] uranium,[9] rare earth ions,[10] dysprosium,[11] Hg²⁺,[12] and some other heavy metal ions[13] have been reported. We have reported several papers describing the application of MIPs as a recognition element for different kinds of molecular analytes.[14-18] To the best of our knowledge there is no report on the application of IIPs in carbon ionic liquid electrode (CILE) for the determination of Cu²⁺.

In a recent paper, our group have reported the synthesis of novel ion-imprinted polymeric nanoparticles using 1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ) as a vinylated chelating agent for selective separation and enrichment of Cu²⁺ ions in aqueous solutions. The IIP was synthesized via precipitation
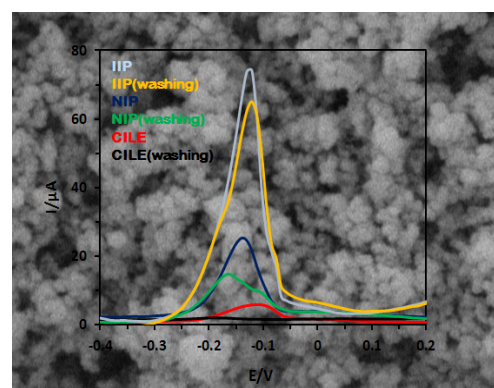
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copolymerization of Cu^{2+}–AQ complex with ethylene glycol in the presence of 2,2'-azobis(isobutyronitrile) as a radical initiator for the preparation of effective binding sites in polymeric network.[18] In this study, copper imprinted polymer nanoparticles (Cu-AQ IIP NPs), as an ion recognition material, was used as a modifying agent and mixed with carbon powder in the presence of (1-ethyl 3-methyl imidazolium hexafluoro phosphate) ($EMIMPF_6$) in order to prepare a Cu^{2+} selective voltammetric sensor.

Experimental

Instruments
All electrochemical experiments were performed with a computer controlled μ-Autolab type III modular electrochemical system (Eco Chemie Ultecht, The Netherlands), driven with GPES software (Eco Chemie). A conventional three-electrode cell with a carbon ionic liquid electrode (CILE) modified with IIP or non-imprinted polymer (NIP) was used as the working electrode. A platinum wire and an SCE electrode were used as the counter and reference electrodes, respectively.

Chemicals
1-ethyl 3-methyl imidazolium hexafluoro phosphate ($EMIMPF_6$) was obtained by Sigma–Aldrich, graphite powder (mesh size < 50 μm) was supplied by Fluka, ethylene glycol dimethacrylate (EGDMA) was supplied by Merck (Darmstadt, Germany), 2,2'-azobis(isobutyronitrile) (AIBN) was obtained from Aldrich (St. Louis, MO, USA), and 1-hydroxy-4-(prop-2'-enyloxy)-9,10-anthraquinone (AQ) was synthesized and purified as described elsewhere.[19] Analytical grade $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, NaOH, HNO_3, and $NaH_2PO_4 \cdot 2H_2O$, were purchased from Merck. Solutions of metal ions were prepared in doubly distilled water. All solvents used were of reagent grade and obtained from Merck. Solutions of pH 2.0–8.0 were prepared by adding NaOH or HNO_3 to $NaH_2PO_4 \cdot 2H_2O$ solutions.

Preparation of Cu^{2+} imprinted polymeric nanoparticles
The Cu^{2+} ion-imprinted nanoparticles were prepared by thermal precipitation polymerization technique.[19] Briefly, In the first step, the complexation was attained by allowing AQ (1 mmol), as vinylated ligand, and $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol), as imprint metal ion (template), respectively. The formation of a red complex was confirmed through spectroscopy. In the second step, EGDMA (20 mmol) and AIBN (0.4 mmol) were added as cross-linker and a free radical initiator, respectively, to the first step solution and stirred at room temperature. Argon gas was bubbled trough the prepolymerization mixture for 5 min and then the reaction vial was sealed and heated in an oil bath at 60 °C for 24 h under magnetic stirring at 400 rpm to complete the thermal polymerization.

The prepared polymer was washed several times with 1:4 (v/v) methanol/water to remove the unreacted materials and then with 0.1 mol L^{-1} HNO_3 for leaching of the imprint metal ions until the wash solution was free from Cu^{2+} ions. Finally, it was washed with double distilled water until a neutral pH is reached. The resulting

fine yellow powder was dried overnight before sorption and desorption studies. The synthesis of non-imprinted polymer (NIP, poly(EGDMA–AQ)) was carried out similar to that of the Cu^{2+}-IIP, but in the absence of any $Cu(NO_3)_2 \cdot 3H_2O$ salt as template, and dried at 80 °C for 2 h.

The resulting imprinted nanoparticles obtained from copolymerization of the Cu^{2+}–AQ complex were characterized by IR spectroscopy, colorimetry, scanning electron microscopy, elemental analysis and N_2 adsorption–desorption isotherms.[18]

Preparation of the sensors
The bare CILE was prepared by thoroughly mixing graphite and $EMIMPF_6$. The IIP modified CILE was prepared by mixing different percentages of graphite powder, $EMIMPF_6$, and IIP (or NIP). This mixture was mixed in a mortar for at least 10 min to become homogeneous. The paste was packed into an end of a teflon holder in which electrical contact was made with a copper rod that runs through the center of the electrode body. The electrode surface was polished using a butter paper to produce reproducible working surface. Electrochemical behavior of Cu^{2+} at these different electrodes was investigated using cyclic voltammetric technique. Best results were obtained at 55:25:10 (w/w%) ratio of graphite powder, $EMIMPF_6$, and IIP (or NIP). This optimized electrode composition was then used for the voltammetric determination of Cu^{2+}.

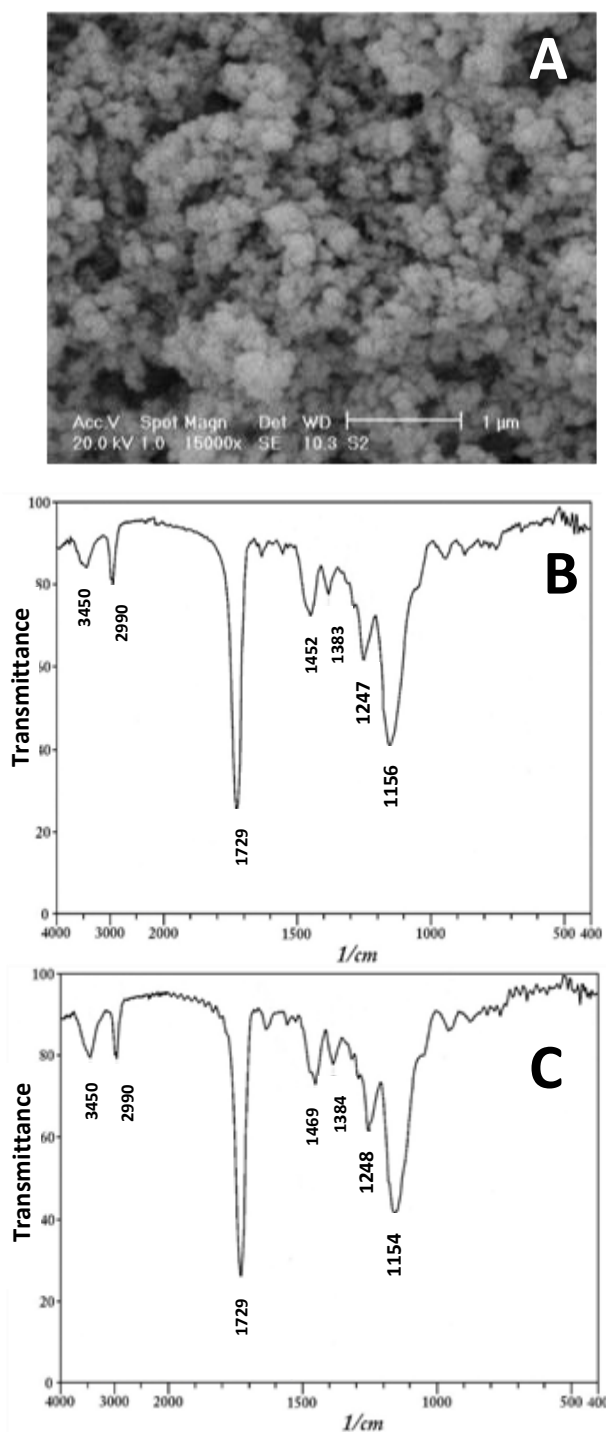## Results and discussion

Characterization of IIP
The resulting ion imprinted nanoparticles obtained from copolymerization of the Cu^{2+}–AQ complex with EGDMA were characterized by FT-IR spectroscopy and scanning electron microscopy, Figure 1. In the FT-IR spectra, the absorptions due to carbonyl group (1729 cm^{-1}), C–O stretch (1156, 1247 cm^{-1}), C–H stretch (2990 cm^{-1}), and CH_3 and CH_2 bends (1383 and 1452 cm^{-1}, respectively) were observed. It is interesting to note that no band is present in the region of 1630–1645 cm^{-1} indicating the absence of C-C groups in polymer materials. This confirms the complete copolymerization of the vinylated AQ ligand and EGDMA.

General analytical procedure
The prepared electrodes were inserted into the phosphate buffer solution with pH 7.0 containing Cu^{2+} stirring at 500 rpm for 8 min. Then, the electrodes were inserted into the washing solution (water, neutral), remaining for 60 s. Differential pulse voltammetric measurements were carried out in a three-electrode cell, in 0.1 M HCl solution. Before the measurements, electrolytic solutions were purged with nitrogen for 5 min. At first, a negative pre-potential of -0.5 V was applied to the electrode for 30 s to reduce the recognized target ions and then current measurements were performed using differential pulse voltammetry (DPV) in the potential range between -0.35 and 0.25 V. To record differential pulse voltammograms, the following instrumental parameters were used: step potential 0.01 V, modulation amplitude 0.05 V, and scan rate 50 mV/s.

Table 1. *Tolerance ratio of interfering species in the determination of 500 nM Cu^{2+}.*

Species	Interferent / analyte mole ratio
Alkaline metals	No interference
Ba^{2+}, Ca^{2+}, SO_4^{2-}, CO_3^{2-}, Mg^{2+}, NO_3^-, HCO_3, Zn^{2+}	1000
Hg^{2+}, Cd^{2+}, Mn^{4+}, Al^{3+}	400
Ni^{2+}, Ag^+	50
Glucose, Fructose, L-histidine, L-cysteine, glycine	200

Electrochemical behavior of the IIP–CILE

The CILE modified with IIP was incubated in the Cu^{2+} solution and meanwhile the solution was continuously stirred. Then, the electrode was inserted in the electrochemical cell and a negative potential was applied to the electrode. Subsequently, the differential pulse voltammetry technique was applied for the determination of Cu^{2+}. The same experiment was carried out in the case of the electrode modified with NIP and CILE. In another experiment, the IIP–CILE, NIP–CILE, and CILE were inserted in the washing solution for 10 s, after removing from the Cu^{2+} solution.
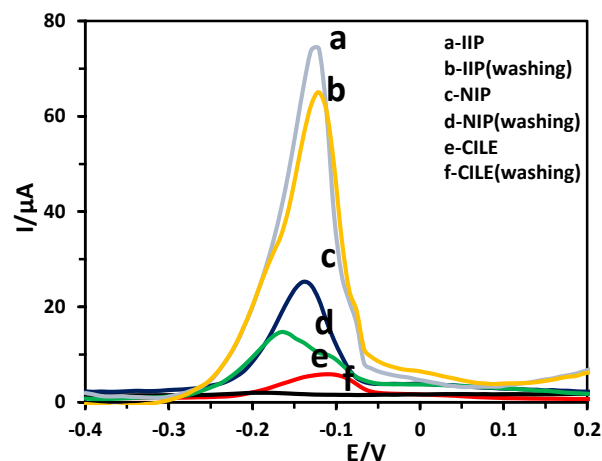
Figure 2. *Comparison of differential pulse voltammetry responses of IIP-CILE and NIP-CILE with and without washing steps; $[Cu^{2+}]$ =2×10^{-7}, extraction time = 8 min, stirring rate = 500 rpm; stripping voltammetry conditions: E-conditioning = −0.5 V, conditioning time = 30 s, E-step = 0.01 V, E-pulse = 0.05 V, and scan rate = 50 mVs^{-1}.*

The obtained voltammetric signals of the mentioned electrodes are shown in Figure 2. It can be seen that the signal obtained for IIP– CILE is noticeably higher than those for NIP– CILE and CILE. This indicates that the existence and properly functioning of the selective cavities in the IIP, created in the polymerization step can uptake Cu^{2+} intensively from the phosphate buffer (pH 7.0) in comparison to NIP–CILE and CILE electrode. According to the voltammogram of Figure 2, washing of the electrodes, after removing them from the analyte solution, decreases three electrode signals, indicating removal of weakly adsorbed ions from the IIP or NIP and CILE. However, the decrease rate in the NIP–CILE and CILE signal is considerably higher than that in the IIP– CILE. This can be related to the fact that most of the adsorbed Cu^{2+} ions are located in the selective sites of IIP that are attracted strongly and selectively to the IIP, while the sites responsible for Cu^{2+} adsorption in the NIP–CILE and CILE are surface adsorption sites with a weak and nonselective attractive nature.

The effect of IIP–CILE composition on its response

To find the best composition for IIP–CILEs, different amounts of ingredients including IIP, graphite, and ionic liquid were changed in the fixed conditions of extraction and voltammetric determination, and the obtained responses were used for conclusion (Figure 3). For initial optimization purposes, the IIP-CILEs were prepared with fixed amounts of graphite and IL and different amounts of IIP. The resulted electrodes at each case were used for Cu^{2+} extraction and determination. The results showing in the Figure 3A indicates that increasing the amount of IIP increased the electrode response, and the maximum signal for the proposed sensor appeared in the IIP amount of 0.013.

Figure 1. (A) *Scanning electron micrograph images of Cu^{2+}-IIP nanoparticles. The FT-IR spectra of **(B)** leached and **(C)** un-leached Cu^{2+}-IIP nanoparticles*

All electroanalytical measurements were made at room temperature. After the measurements, the electrode was regenerated by immersing in a stirring solution containing in 0.05 M EDTA solution for 3 minutes for the next rebinding. The renewed electrode then was checked in the supporting electrolyte before the next measurement to ensure that it does not show any peak within the potential range.

Modifier	Electrode	Concentration range	Detection limit	Interference	Ref.
2-Aminothiazole	Carbone paste	7.5×10^{-8} to 2.5×10^{-6}	3.1×10^{-8}	Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+}	[22]
Alirazin red S (KRS)-$K_2S_2O_8$	Carbone paste	8.0×10^{-10} to 3.0×10^{-8}	1.6×10^{-10}	Ni^{2+},Fe^{3+},Cd^{2+},Pb^{2+},Fe^{2+},Cr^{3+},Co^{2+}	[20]
phenylcinnamohydroxamic acid	Carbone paste	1.0×10^{-8} to 1.0×10^{-6}	15.0×10^{-10}	Hg^{2+}, Cr^{3+}, Fe^{3+}, Ag^+,Au^{3+}, Al^{3+}	[21]
Calix[4]arene	Carbone paste	5×10^{-8} to 16×10^{-7}	1.1×10^{-8}	Ag^+, Zn^{2+},Cd^{2+}, Pb^{2+}	[23]
nanoporous silica gel with dipyridyl group	Carbone paste	1.0×10^{-7} to 1.0×10^{-2}	8.0×10^{-8}	Ag^+,Cd^{2+}, Pb^{2+}	[24]
IIP	CILE	$2.5.0\times10^{-8}$ to 1.25×10^{-6}	9.4×10^{-9}	Ag^+, Ni^{2+}	This work

The effect of IIP–CILE composition on its response

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For the IIP amount, the higher amounts of IIP increase the sensor response due to providing more recognition sites on the electrode surface, however, increasing of the IIP more than a threshold amount (0.025) leads to a decrease in the prepared sensor response, probably due to reducing the electrode surface tenacity.

Washing effect

As described previously, the washing of the electrode results in the removal of weakly adsorbed species from the electrode surface. This can be used for improving the sensor selectivity and omitting the interference effects, if proper washing conditions are applied.

It was found that pure water is a proper washing solvent for this aim. In this washing media the NIP–CILE signal was considerably decreased, while the signal decrease of IIP–CILE due to the washing was not considerable. Different organic solvents such as ethanol, acetone, methanol and acetonitrile were added to the water (5% in water) and tested as the washing solution. No improvement for aimed signal from the mentioned mixtures was observed.

The optimum time of immersing the electrode in the washing solution was also investigated. It was found that the difference between the response of IIP–CILE and NIP–CILE increased till 60 s and afterwards the signal reached to partly steady state. Thus, 60 s was chosen as the optimal washing time.

Evaluation of the effect of Cu^{2+} extraction conditions on the electrode response
The effect of pH

The effect of pH of Cu^{2+} solution on the Cu^{2+} extraction in the electrode was studied. For this purpose the prepared electrode was incubated into the solutions with various pH values, for 20 min at a constant stirring rate. After the mentioned time, the electrode was removed from the solution and immersed in to the washing solution. Then, it was immersed in the solution of the electrochemical cell, followed by differential pulse voltammetry. The results are shown in Figure 4A. As seen, the binding of Cu^{2+} ions increased with increasing pH and reached to maximum at pH 7.0. As expected, due to the involvement of hydroxylate group of AQ in complexation with Cu^{2+} ion, the sorption of Cu^{2+} ion at lower pH values are highly dependent on the pH of solution, because of the
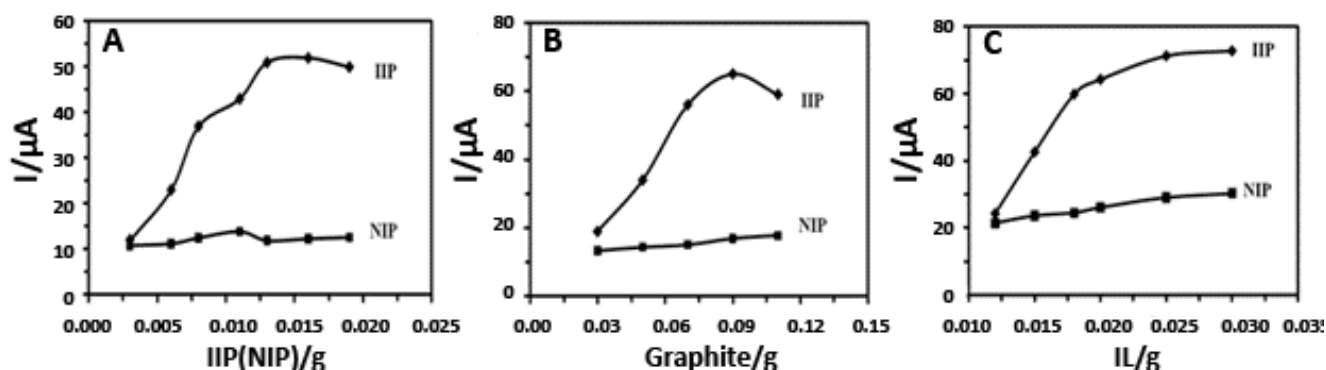
Figure 3. The effect of electrode composition (IIP, graphite, and IL) on its response, extraction time = 8 min, stirring rate = 500 rpm; stripping voltammetry conditions: E-conditioning = −0.5 V, conditioning time = 30 s, E-step = 0.01 V, E-pulse = 0.05 V, and scan rate = 50 mVs^{-1}.
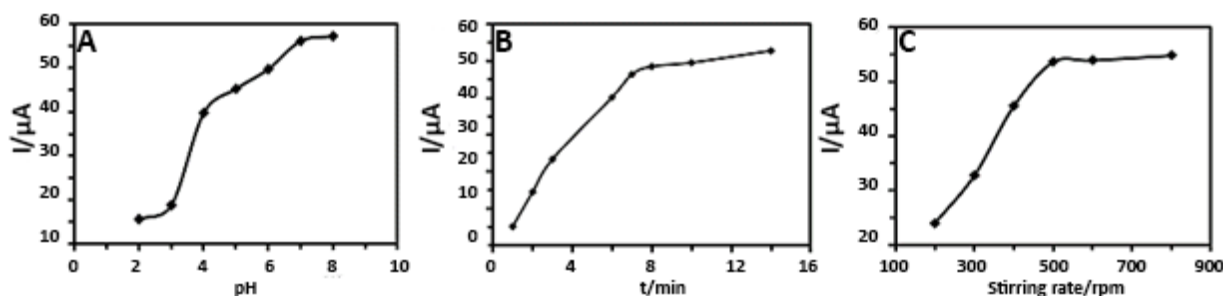
Figure 4. *Evaluation of the extraction condition effects on the electrode response.*

competition of proton with Cu^{2+} ion for hydroxylate site of AQ, so that smaller amounts of Cu^{2+} ions are adsorbed by the polymer. As the pH increased, the protonation of ligand is suppressed and condition becomes more favorable for complex formation and sorption of Cu^{2+} ions to the imprinted sorbent.

The effect of extraction time and stirring rate
The effect of extraction time on the electrode signal is shown in Figure 4B. According to this figure, the increasing of extraction time leads to an increase in the Cu^{2+} extraction. However, after 8 min the response increasing with time enhancement is not considerable. Thus, the time of 8 min was selected for the extraction. It was found that the stirring rate of Cu^{2+} solution in the extraction step had considerable effect on the electrode final response. The optimum value of 500 rpm was found to be optimum for the stirring rate (Figure 4C).

The effect of pH and electrolyte type of electrochemical determination
After accumulation of Cu^{2+} ions on the electrode surface at open circuit condition and its washing with the washing solution, the electrode was inserted into an electrochemical cell, containing the electrolyte solution with various pH values. This was carried out in order to investigate the effect of the electrolyte pH on the electrode response. It was found that the acidity of pH is crucial for obtaining strong and stable signals. Therefore, the acid concentration was selected to be 0.1 M and all measurements have been performed at this concentration level. Next, the effects of different electrolytes, providing the acidic media for the voltammetric analysis were tested. The obtained results are illustrated in Figure 5. It is clear that the type of the electrolyte considerably influences the response behavior of the electrode, with respect to the signal amplitude, background current and potential shift. It can be seen that HCl (0.1 M) leads to better results, in term of higher signal amplitude and lower background current.

Effect of reduction potential and time Cu^{2+} grafted in electrode
The effect of reduction potential on the peak currents of Cu^{2+} extracted by IIP-CILE examined over the range from -300 to −800 mV. As it can be seen in Figure 6A in the potential range from −400 to −600 mV the peak currents of three species were independent of reduction potential and had their maximum values. A potential of −500 mV was used for the optimized analytical procedure.

The influence of reduction time on the peak current of Cu^{2+} extracted by IIP-CILE was also investigated (Figure 6B). Variation of the reduction time showed that the peak current of Cu^{2+} grafted CILE-IIP increased with increasing time, gradually leveling off at periods longer than 30 s, presumably due to completely reduction Cu^{2+} extracted by modified electrode. Thus deposition time of 30 s was used throughout, as it combines good sensitivity and relatively short analysis time.
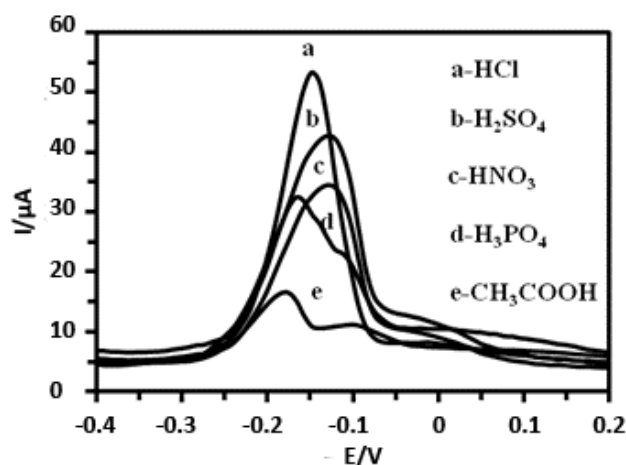

Figure 5. *Effect of different electrolyte on the sensor response to Cu^{2+}, the acid concentration was 0.1 M.*

Analytical characterization
Under the optimized experimental conditions, the IIP-CILE was applied for the successive determination of Cu^{2+} by DPV. Figure 7 shows the DPV signals of the IIP-CILE toward Cu^{2+} at the wide range of concentrations 25–1250 nM. As seen, a very good linearity of peak current versus Cu^{2+} concentration was obtained with correlation coefficient of 0.998, and the sensitivity of the electrode was 0.0603 µA nM^{-1} (inset). The limit of detection was found to be 9.4 nM at a signal to noise of 3. Obviously, the IIP-CILE exhibited a very wide linear range and very low detection limit in determination of Cu^{2+}. This detection limit is significantly lower than that of modified GCE previously reported.

Table 3. *Determination of Cu^{2+} in different samples by the IIP-CILE and ICP technique.*

Sample	Amount found by IIP-CILE (nM)(n=5)	RSD(%)	Amount found by ICP(nM)(n=5)	RSD(%)
River water	9.4	±3.8	10.1	±4.3
Mineral water	26.7	±4.1	25.8	±2.9
Tap water	14.6	±4.9	15.3	±3.3

Reproducibility of proposed electrode was investigated by using DPV. In order to evaluate the reproducibility of the IIP-CILE, 50 nM of Cu²⁺ solution was determined by five separately produced electrodes by using DPV. The obtained results show a RSD% equal to 4.6 for the described determination. Moreover, repeatability was examined by performing seven replicate measurements for 500 nM Cu²⁺ by the same electrode that resulted in a RSD% = 3.14.
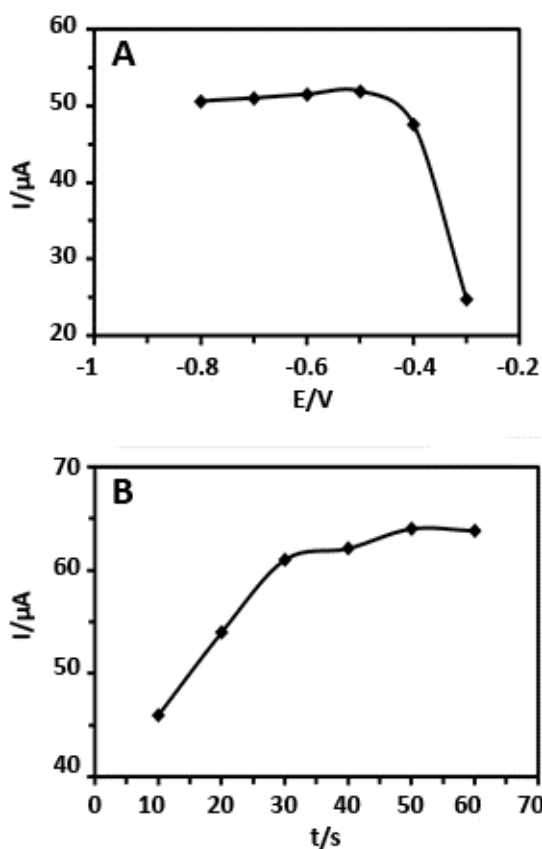

Figure 6. *Evaluation of the effect of reduction potential and time Cu²⁺ grafted in electrode.*

Selectivity of IIP on the electrode

Although, the oxidation potential of most potential interferer metals are far from that of Cu²⁺, competitive sorption among these metal ions influences uptake of Cu²⁺ by the modified electrodes. This results in reduction of the amount of uptake Cu²⁺, compared to the single-metal ion system. In order to avoid this problem the used modifying agent in the electrode must have either high selectivity to the analyte of interest or considerable adsorption capacity.

Imprinted polymers can provide the mentioned characteristics, enabling us to prepare a sensor with high selectivity toward the analyte of interest. When copper imprinted polymer is used as the modifying agent in the electrode, it can selectively uptake the analyte, while other existed cations are not adsorbed noticeably on it. On the other hand, this material usually has high adsorption capacity, thereby, no lack of selective adsorption sites for analyte is observed even in the presence of high concentrations of competitive ions. In this study, we investigated on the selectivity of proposed sensor by applying it to the determination of Cu²⁺ and some potential interferer ions and organic species. The obtained results are shown in Table 1. As can be seen, the presence of some potential interfering inorganic and organic species present in samples studies, at the concentration evaluated, do not affect the Cu²⁺ determination using the IIP-CILE.

Comparison of IIP-CILE with some of the previously

A number of analytical characteristics of the IIP-CILE sensor were compared with those of some previously reported voltammetric Cu²⁺ sensors in Table 2. As can be seen, the IIP-CILE sensor shows very good analytical characteristics, compared to majority of the depicted sensors. It can be seen that Co²⁺,[20] Hg²⁺,[21] Pb²⁺,[20,22-24] Cd²⁺,[20,22-24] Ni²⁺,[22] and Cr³⁺ [20,21] presented significant interference in Cu²⁺ electrodes. Previously reported Cu²⁺ electrodes have a very small value of selectivity coefficient in most cases, and the linear range and detection limit of the proposed electrode is somewhat similar to those recently published papers. The main advantage of this electrode is its highly resistance capability against the interference effect of some potential interfering ions such as Pb²⁺, Zn²⁺, and Cd²⁺ and some organic species.

Determination of Cu²⁺ in real samples

The proposed method was directly applied to the determination of Cu²⁺ in in real water samples. The results given in Table 3, show the high sensitivity of the proposed method. According to this table, the obtained results are comparable with those obtained by ICP method. Thus the sensor provides a good alternative for the determination of Cu²⁺ in real water samples.
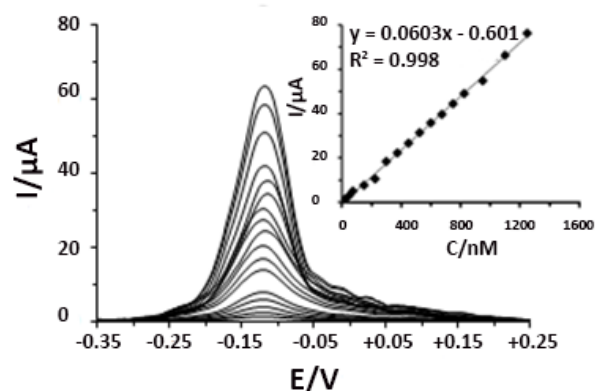

Figure 7. *Differential pulse voltammograms of different concentrations of Cu²⁺ at an IIP–CILE. Calibration curves of Cu²⁺ at an IIP–CILE (inset). Other conditions are as Figure 1.*

Conclusion

In this paper, a simple and efficient procedure was proposed for the synthesis of nano-sized Cu²⁺-imprinted polymer nanoparticles based on the precipitation polymerization methodology. The IIP material, used as the recognition element of a carbon ionic liquid electrode, showed very excellent affinity for Cu²⁺, according to differential pulse voltammetry response of the IIP CILE in comparison with the NIP-CILE. Importantly, the resulting IIP modified electrode shows high reproducibility and can also be readily renewed. These features provide possibilities for the material to be incorporated into existing technologies, where problems of interference and electrode fouling have already been reduced for determination of Cu²⁺ in natural water samples.

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