



Preparation of nano-sized Pb^{2+} imprinted polymer and its application as the chemical interface of an electrochemical sensor for toxic lead determination in different real samples

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ABSTRACT

In this work, a new nano-structured ion imprinted polymer (IIP) was synthesized by copolymerization of methacrylic acid– Pb^{2+} complex and ethylene glycol dimethacrylate according to the precipitation polymerization. Methacrylic acid acted as both functional monomer and complexing agent to create selective coordination sites in a cross-linked polymer. A carbon paste electrode modified with IIP-nanoparticles was used for fabrication of a Pb^{2+} sensitive electrode. Differential pulse stripping voltammetry method was applied as the determination technique, after open circuit sorption of Pb^{2+} on the electrode and its reduction to metallic form. The IIP modified electrode showed a considerably higher response, compared to the electrode embedded with non-imprinted polymer (NIP). This indicated that the suitable recognition sites were created in the IIP structure in the polymerization stage. Various factors, effective on the response behavior of the electrode, were investigated and optimized. The introduced sensor showed a linear range of 1.0×10^{-9} to 8.1×10^{-7} M and detection limit of 6.0×10^{-10} M ($S/N=3$). The sensor was successfully applied for the trace lead determination in different samples.

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1. Introduction

Lead is an important environmental pollutant, found in soil, water and air with no biological function, but many toxicological effects to human life [1–3]. The determination of lead is difficult due to its low concentrations in environmental samples [2]. Lead, is distributed widely in nature and enters our body system through air, water, and food. The toxicity of lead has been studied extensively. Pb^{2+} binds with the –SH group in enzymes or proteins and acts as an enzyme inhibitor. It interferes with calcium metabolism and gets deposited in bone. Lead poisoning in humans causes severe damage in kidneys, liver, brain, reproductive system, central nervous system and sometimes causes death. All these findings cause great concern regarding public health, demanding accurate determination of this metal ion at trace and sub-trace levels [4–6].

Great efforts have been made to analyze lead in trace levels by means of a wide range of spectrometric methods such as electrothermal atomization atomic absorption spectrometry (ET-AAS), sequential multi-element flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry (GFAAS), elec-

trothermal atomic absorption spectrometry, inductively coupled plasma-mass spectrometry (ICP-MS), hydride generation atomic absorption spectrometry and flame atomic absorption spectrometry (FAAS) [7–15].

On the other hand, different kinds of sensors including optical [16], potentiometric [17,18] and voltammetric [19,20] sensors have been widely used for lead determination. However, voltammetric methods are highly favorable techniques for the determination of metal ions because of its low cost, high sensitivity, easy operation and the ability for portability. Stripping analysis of lead have been reported by using different electrodes such as silver electrode [19], bismuth/poly (ρ -amino benzene sulfonic acid) film electrode [20], boron-doped diamond electrode [21], mercury film supported on wax impregnated carbon paste electrode [22], Gold electrode [23] and titanium dioxide [24].

In order to enhance the sensitivity and selectivity of the electrochemical determination of lead(II), chemically modified electrodes have received increasing attentions in the past decades. The modifiers used include bismuth [25–42], organic chelating groups [43–50], clay nano particles [51], $\text{SiO}_2\text{--Al}_2\text{O}_3$ mixed-oxide [52], zeolite [53], PAN-incorporated nafion [54] and silica [55].

However, most of these procedures have difficulties achieving the sensitivity required for the determination of low levels of lead(II) ion in some real samples. Moreover, these materials do not provide a suitable selectivity toward Pb^{2+} in the presence of some potential interfering species like Cu^{2+} , Ag^+ , etc. Therefore, there is

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still an urgent demand to introduce a high selective modifier for using in this field.

Molecular imprinting is a promising technique for the preparation of polymers with predetermined selectivity and high affinity [56,57]. Molecularly imprinted polymers (MIP) demonstrate very good thermal and chemical stability and can be used in aggressive media [58]. These materials possess several advantages over their biological counterparts including low cost, ease of preparation, storage stability, repeated operations without loss of activity, high mechanical strength, durability to heat and pressure, and applicability in harsh chemical media. MIP has become increasingly attractive in many fields of chemistry and biology, particularly as an affinity material for sensors [59–63], binding assays [64], artificial antibodies [65,66], adsorbents for solid phase extraction [67–71], and chromatographic stationary phases [72–75].

On the other hand, ion-imprinted polymers (IIPs) are similar to MIPs but, they recognize metal ions after imprinting, while retaining all the virtues of MIPs. The production of polymers exhibiting selective binding of a specific cation, involves the formation of cavities equipped with complexing agents so arranged as to match the charge, coordination number, coordination geometry and size of the target cation [76].

Different kinds of imprinted polymers have been reported for recognition of lead ions [77–79].

We have recently reported several papers describing the application of MIP particles as a recognition element of the electrochemical sensors such as voltammetric and potentiometric sensors for different kinds of molecular analytes [80–83]. In this study, a lead imprinted polymer, as an ion recognition material, was synthesized by a new formulation. According to the IIP synthesis method, Pb^{2+} was first extracted into acetonitrile as $Pb(MAA)_2$ and then the polymerization was started in the presence of ethylene glycol dimethacrylate as cross-linking agent. By this means, the Pb^{2+} selective cavities with carboxylic acid coordination sites were created in the cross-linked polymer. The prepared Pb^{2+} -IIP was subsequently applied for preparation of IIP based sensor.

2. Experimental

2.1. Instrument and reagents

Electrochemical data was obtained with a three-electrode system using a potentiostat/galvanostat model PGSTAT302, Metrohm. The carbon paste electrodes modified with IIP or non-imprinted polymer (NIP) was used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

Methacrylic acid (Merck, Germany) and ethylene glycol dimethacrylate (EDMA) (Sigma–Aldrich, USA) were purified by distillation under reduced pressure. 2,2'-(2-methyl propionitrile) was obtained from (Acros Organic, Geel, Belgium) and used as an initiator. $Pb(NO_3)_2$ were from (Merck, Germany). Other chemicals were of analytical grade and were purchased from (Merck, Germany).

2.2. $Pb(II)$ imprinted polymer preparation

In order to prepare $Pb(II)$ imprinted polymer, 4 mmol of $Pb(CO_3)_2$ (prepared by reaction of $Pb(NO_3)_2$ and Na_2CO_3) and 12 mmol of methacrylic acid were contacted with 20 mL acetonitrile and then the mixture was stirred for 24 h. The mixture was then centrifuged and the supernatant was separated for polymer preparation. Then, 22 mmol EGDMA and 0.02 g initiator were dissolved in 5 mL acetonitrile and then added to the previous solution. The resulting mixture was purged with N_2 gas for 10 min. The polymerization was carried out in water bath at 70 °C for 24 h. The polymeric

particles, obtained after polymerization, were firstly washed with ethanol and then with HCl solution (2 M). Thiourea solution (0.1 M) was also used for removal of target ions from the polymer particles. Finally, the particles were washed several times with distilled water and dried at 60 °C. The non-imprinted polymer (NIP) was prepared using the same protocol except that $Pb(II)$ did not exist in the polymerization mixture.

2.3. Preparation of the sensors

In order to prepare the sensor (IIP-CP), 0.03 g graphite was homogenized in a mortar with 0.007 g of powdered IIP for 10 min. Subsequently, n-eicosane (0.015 g) was melted in a dish, heated at 45–50 °C. The graphite/IIP blend was then added to the melted n-eicosane and mixed with a stainless steel spatula. The final paste was used to fill a hole (2.00 mm in diameter, 3 mm in depth) at the end of an electrode body, previously heated at 45 °C. After cooling at room temperature, the excess of solidified material was removed with the aid of a paper sheet. The electrode can be reused after each experiment by moving of the electrode surface on a paper sheet in order to extrude a thin layer of the electrode surface.

2.4. Determination procedure

The prepared electrode was inserted into the solutions containing the Pb^{2+} (pH 5.8), being at stirring state (500 rpm). Then, the electrode was inserted into the washing solution (water, neutral), remaining in this solution for 15 s. The electrode was finally placed in the electrochemical cell containing 10 mL of HCl (0.12 M). At first, a negative pre-potential of -1.4 V was applied to the electrode for 15 s to reduce the recognized target ions and then the differential pulse stripping voltammetry was performed in the potential range of -0.8 to -0.3 V.

3. Results and discussion

3.1. $Pb(II)$ ion imprinted polymer

In order to prepare IIP, 4 mmol of $Pb(CO_3)_2$ was contacted with methacrylic acid, dissolved in acetonitrile. Lead carbonate was not soluble in acetonitrile. However, interaction of Pb^{2+} with methacrylic acid resulted in lead-methacrylate complex that could be transferred into acetonitrile. Precise determination (titration with EDTA) showed that 1.6 mmol of primarily used Pb^{2+} (4 mmol) could be transferred to acetonitrile in the form of $Pb(\text{methacrylate})_2$ during the described experiment. After addition of EGDMA and initiator, the polymerization reaction was started. Scanning electron microscopy image of the obtained polymer particles is shown in Fig. 1. As can be seen, the sizes of synthesized polymer particles are at nano-scale range. Different polymeric particle sizes ranged from about 50 nm to approximately 500 nm can be distinguished in the depicted image.

There was no considerable difference among the FT-IR spectra of the examined polymers in all recorded regions except the region of ~ 1500 – 1700 cm^{-1} . FT-IR spectra of the unleached IIP, leached IIP and also NIP are shown in Fig. 2(a), (b) and (c), respectively. Presence of strong stretching vibration band at ~ 1721 cm^{-1} is related to the $\nu_{C=O}$ of carboxylic acid group of methacrylic acid, situated mainly at the surface of polymeric particles. This band can be seen in all examined polymers. Though, there is no band in the region of 1500 – 1700 cm^{-1} for NIP, an evident band for the unleached IIP can be observed at the mentioned region (~ 1610 cm^{-1}), ascribed to the $-C=O$, linked to Pb^{2+} via coordination bonding. This band is less strong than that is located at ~ 1721 cm^{-1} because, these types of $-C=O$ groups are mainly situated in the interior sections of IIP

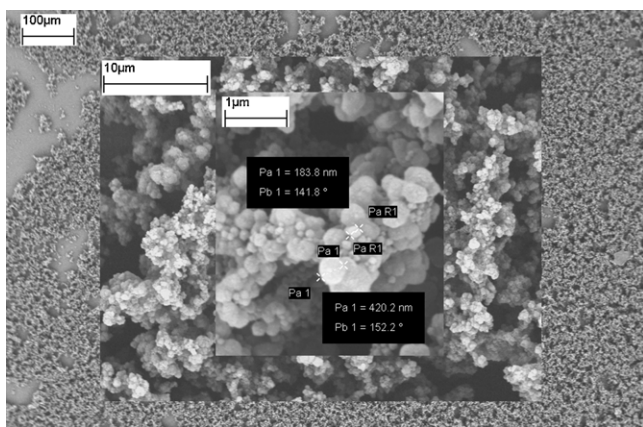


Fig. 1. Scanning electron microscopy images of prepared of IIP.

particles. It can be seen that the washing of the IIP and removal of Pb^{2+} leads to a considerable decrease at the height of vibration band of the $-C=O$ coordinated to Pb^{2+} . These observations can be a right evidence for the presence and properly interaction of the selective recognition sites in the IIP particles which are created during imprinting process.

3.2. Comparison of the IIP-CP electrode with NIP-CP electrode and evaluation of the washing effect on the responses of the electrodes

The carbon paste electrode modified with IIP or NIP was incubated in the Pb^{2+} solution meanwhile the solution was stirred continuously. Then, the electrode was inserted into the electrochemical cell and a negative potential was applied to the electrode. Subsequently, differential pulse voltammetry technique was applied for the determination of lead. In order to evaluate the washing effect on the electrode responses, the IIP-CP and NIP-CP electrodes were inserted in different washing solution for 10 s, after being removed from the Pb^{2+} solution. The obtained voltammetric signals of the two mentioned electrodes were shown in Fig. 3. It can be seen that the obtained signal for IIP-CP (voltamogram, a) electrode is higher noticeably than that of NIP-CP electrode (voltamogram, d), indicating the existence and properly functioning of the selective cavities in the IIP, created in the polymerization step. Washing of the electrodes, after removing them from the analyte solution, decreases both electrode signals, indicating removal of weakly adsorbed ions from the IIP and NIP surface sites. It is also clear that the thiourea washing solution decreases both IIP-CP and NIP-CP signals more than pure water. Also, in this case, the response difference between IIP-CP and NIP-CP electrodes is decreased considerably. This implies that the thiourea solution interfere with selective sites of IIP for conserving adsorbed Pb^{2+} ions. Therefore,

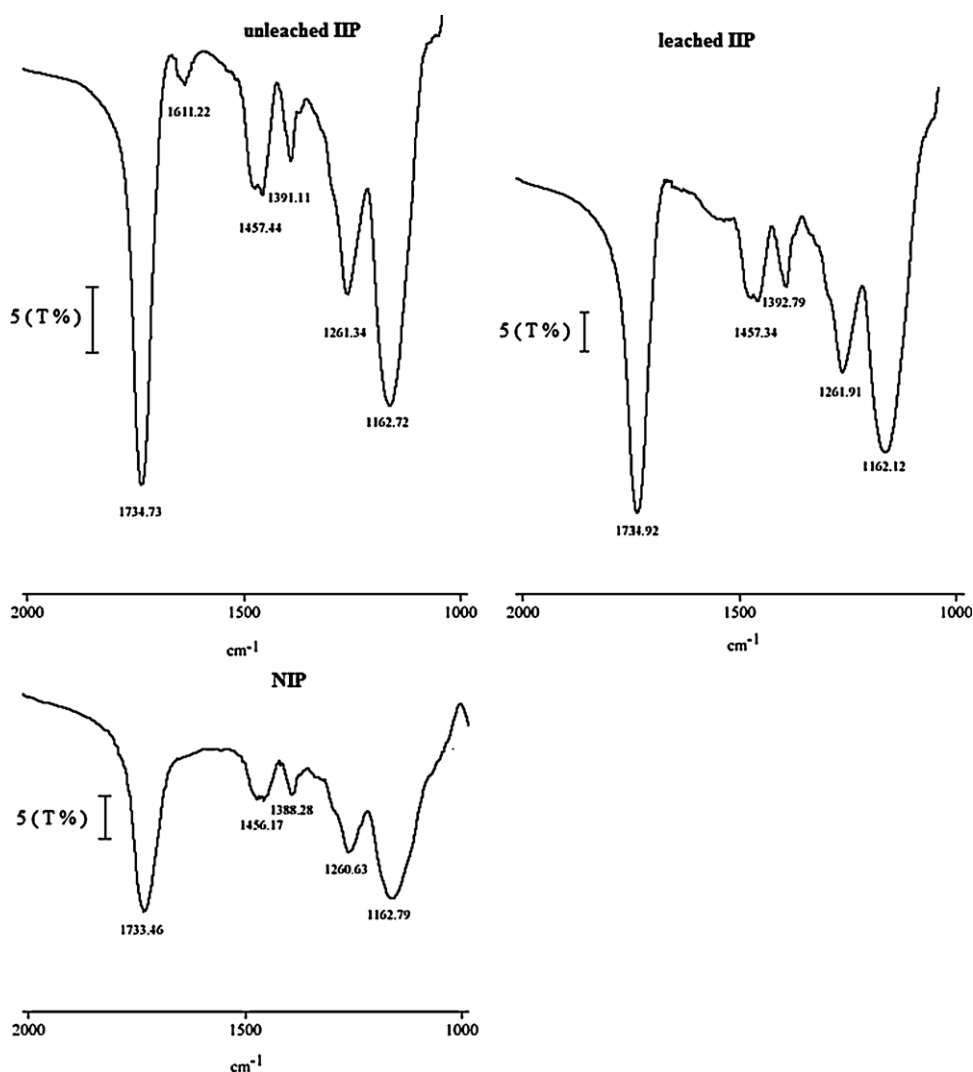


Fig. 2. FT-IR spectra recorded for unleached IIP, leached IIP and NIP.

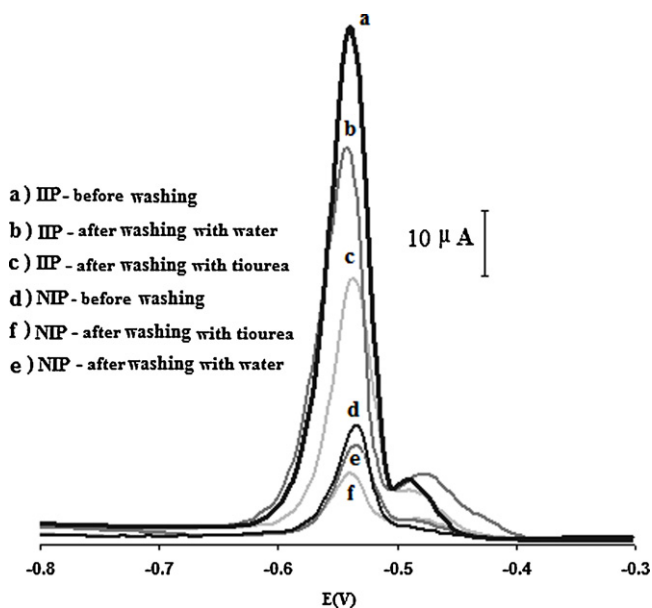


Fig. 3. Comparison of differential pulse voltammetry responses of IIP-CP electrode and NIP-CP electrodes with and without washing steps; $[Pb^{2+}] = 5 \times 10^{-7}$, extraction time = 15 min, stirring rate = 700 rpm; stripping voltammetry conditions: E-conditioning = -1.0 V, conditioning time = 20 s, E-step = 0.01 V, E-pulse = 0.1 V, pulse time = 0.01 s, Scan rate = 0.1 V s^{-1} .

we decided to use pure water in place of thiourea for electrode washing.

3.3. Evaluation of the selectivity of IIP-CP electrode

The selectivity of Pb^{2+} imprinted polymer in the IIP-CP composition was investigated by incubation of the electrode in different solutions containing a mixture of Pb^{2+} (5×10^{-7} M) and some other cations at various concentrations and subsequently electrochemical analyzing. The obtained results are shown in Fig. 4(a), (b), (c) and (d). It can be seen that the presence of Cu^{2+} , Cd^{2+} and Fe^{2+} in the Pb^{2+} solution, at the identical concentrations, does not significantly influence the voltammetric response of Pb^{2+} . It is clear that Cd^{2+} cannot interfere with the Pb^{2+} signal even at 25-fold molar excess although, at this concentration ratio a detectable signal for Cd^{2+} is observed. This indicates that the essential selective sites in the IIP are affected by the Cd^{2+} and thus these foreign ions are extracted at the sites with lower selectivity. However, at 50-fold molar excess, Cd^{2+} affects significantly the signal of Pb^{2+} , indicating the presence of competition between these ions for capturing the high selective cavities in the IIP. The same behaviors can be seen in the case of Fe^{3+} and Cu^{2+} . However, the interference threshold is different from that of Cd^{2+} . In these cases the interference indication appears at about 15-fold molar excess. It can be seen that the addition of CN^- can nullify the interference effect of Cu^{2+} in the determination of Pb^{2+} by the developed sensor. Here, although the Cu^{2+} interfere with the Pb^{2+} at 15-fold molar excess, however the presence of CN^- in the solutions decrease intensively the effect of even 100-fold molar excess of Cu^{2+} in the Pb^{2+} solution. In the case of Hg^{2+} (Fig. 2(d)),

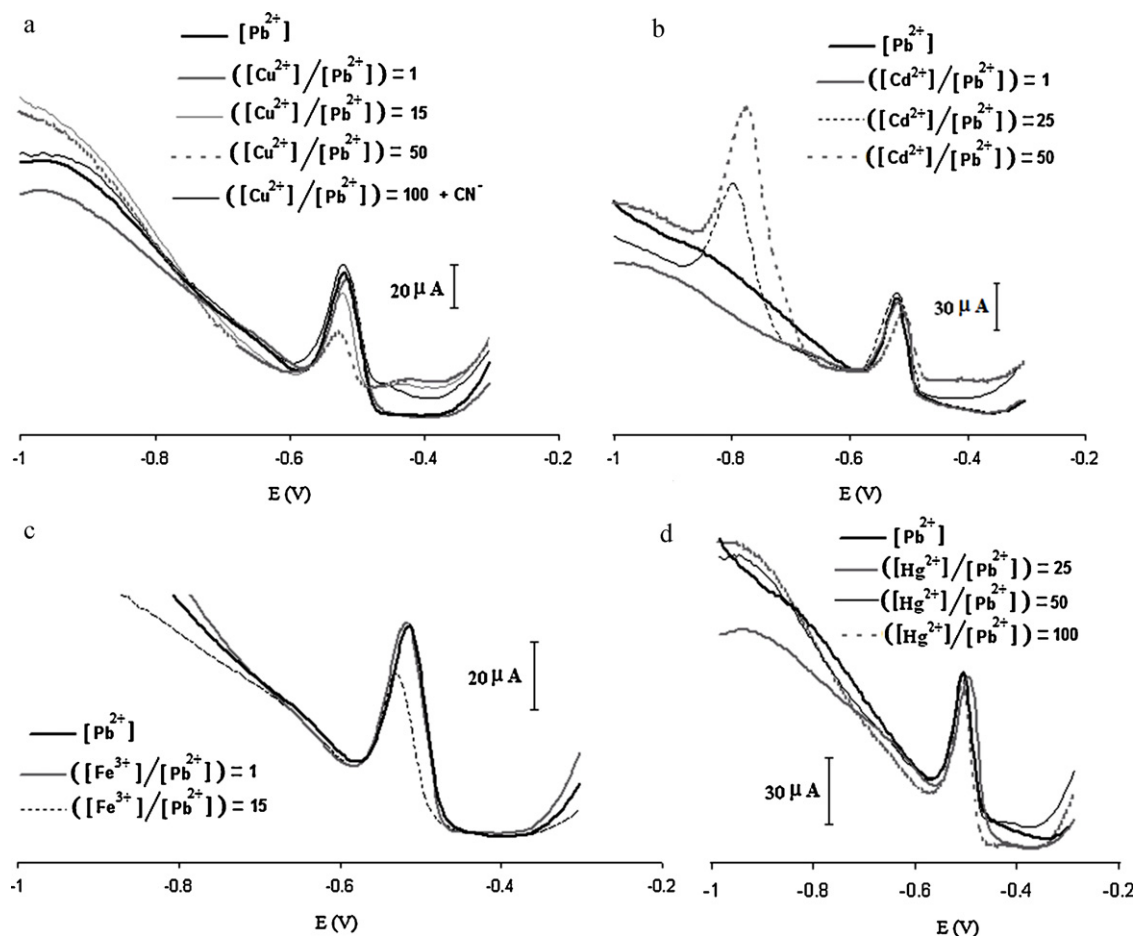


Fig. 4. Comparison of the electrode selectivity for Pb^{2+} ion in the presence of different interfere ions at various concentrations; $[Pb^{2+}] = 5 \times 10^{-7}$, extraction time = 15 min, stirring rate = 700 rpm; stripping voltammetry conditions: E-conditioning = -1.0 V, conditioning time = 20 s, E-step = 0.01 V, E-pulse = 0.1 V, pulse time = 0.01 s, Scan rate = 0.1 V s^{-1} .

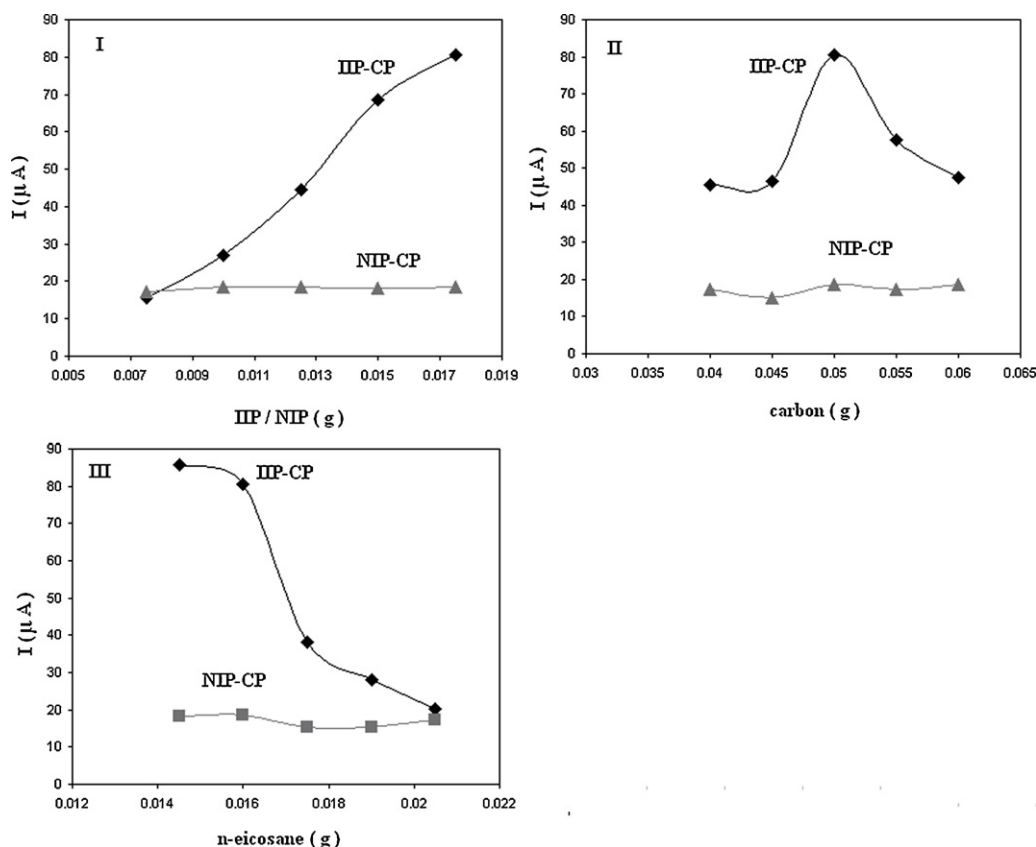


Fig. 5. the effect of electrode composition on its response, extraction time = 15 min, stirring rate = 700 rpm; stripping voltammetry conditions: E-conditioning = -1.0 V, conditioning time = 30 s, E-step = 0.01 V, E-pulse = 0.1 V, pulse time = 0.01 s, Scan rate = 0.1 V s $^{-1}$.

it can be seen that the presence of 100-fold excess of this ion cannot affect significantly the Pb^{2+} signal. These observations indicate that a sophisticated arrangement of carboxylic acid groups in the pre-designed cavity of an IIP leads to an interesting selectivity for the target ion.

3.4. The effect of IIP-CP composition on its response

In order to find the best composition for IIP-CP electrode, the amount of different components of the electrode including IIP, carbon and n-eicosane was changed in the fixed conditions of extraction and voltammetric determination and then the obtained responses were used for conclusion. In order to obtain suitable results for final conclusion, the response of NIP-CP electrode, prepared at the conditions similar to IIP-CP electrode, was compared with that of IIP-CP electrode.

As shown in Fig. 5(I), the IIP-CP signal is enhanced as the IIP content of the electrode is increased. On the other hand, increasing of NIP amount in the NIP-CP electrode does not influence the electrode signal and the electrode retains its initial signal. Therefore, the increasing of IIP amount in the electrode increases the selective recognition cavities in the electrode, increasing the capacity of the electrode surface for target ion up-taking. In spite of the depicted results in Fig. 5(I), it was found that the physical property of the surface of the final electrode was not practically suitable by using of IIP higher than a determined amount. Thus, 0.017 g was selected as optimal for IIP amount in the IIP-CP electrode. The effect of carbon and n-eicosane amounts on the prepared electrode response was investigated by varying of these parameters amounts in the IIP-CP and NIP-CP electrodes, followed by recording the obtained signals. The results are shown in the Fig. 5(II) and (III). It can be seen that, there is an optimum amount for carbon in both IIP-CP

and NIP-CP electrodes although, the variation in the NIP-CP signal with changing of carbon content of the electrode is not so considerable. Higher amounts of carbon can decrease the number of selective sites of IIP in the electrode surface, resulting in interference in target ions extraction in the electrode surface. On the other hand, lower amount of carbon leads to a decrease in conductivity of the electrode and thus decreasing the rate of electron transferring.

It can be seen that the presence of higher amounts of binder (n-eicosane) in the IIP-CP electrode leads to a decrease in the electrode response. When the binder amount reaches to 0.0205 g, it can be seen that the IIP-CP signal is as much as that of NIP-CP signal. This is due to the decreasing of the electrode surface conductivity by increasing the binder amount that acts as an insulating material in the electrode surface.

3.5. Evaluation of the effect of Pb^{2+} extraction conditions on the electrode response

In order to optimize the stirring rate in the extraction period, Pb^{2+} was extracted in the prepared IIP-CP electrodes at various stirring rates, whereas the other extraction parameters were the same and constant. The obtained results showed that the greater the stirring rate, the higher the electrode response for Pb^{2+} , indicating considerable effect of the stirring rate on the Pb^{2+} extraction in the IIP-CP electrode. The growth in target ion voltammetric response with the stirring rate increasing continued up to 500 rpm. However, further enhancement in stirring rate did not affect considerably the extraction amount. Therefore, the stirring rate of 500 rpm was chosen as optima for this variation.

The increasing of the sample volume led to higher electrode response. However, after an optimum amount, increasing of sample volume decreased the electrode response because of lowering

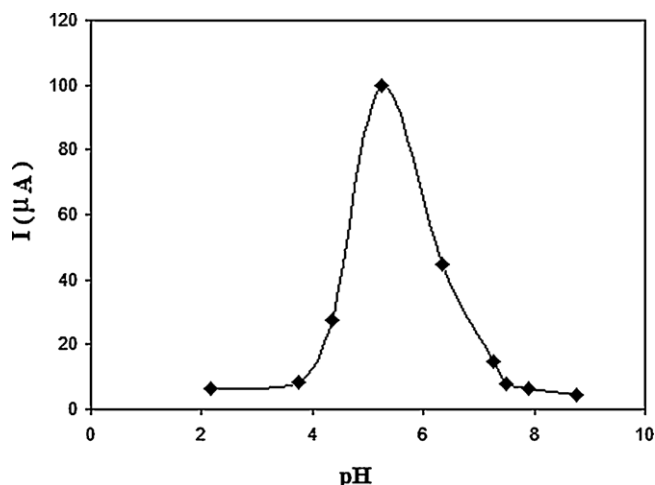


Fig. 6. the effect of Pb^{2+} solution pH on the IIP-CP electrode response.

the target ion extraction in the electrode. Thus, 30 mL was selected as an optimal for sample volume.

The effect of pH of extraction solution on the Pb^{2+} extraction in the electrode was also studied. For this purpose, the prepared electrode was inserted into the solutions with various pH values where they were incubated for 10 min at the constant stirring rate. After the mentioned time, the electrode was removed from the solution and immersed into the solution of the electrochemical cell. The result of this experiment is shown in Fig. 6. As can be seen, the pH condition fixing seems to be an urgent task in this work. As can be seen the best pH for Pb^{2+} extraction in the electrode is equal to 5.8. At higher and also lower pH, the electrode response decreases sharply. The response lowering at acidic pH can be attributed to the protonation of carboxylic groups of complexing agent present in the selective cavities of IIP, decreasing the complexing capability of $Pb(II)$ with the IIP sites. Diffusion of the counter ions into the pores of IIP, at alkaline pH, can probably swell the IIP and reduce the interaction of $Pb(II)$ with selective cavities, reducing the electrode signal in alkaline pH media. Therefore, precisely adjustment of pH is of most important. The phosphate buffer was applied for adjusting the pH of extraction.

The increasing of extraction time led to an intensive increase in the Pb^{2+} extraction amount in the electrode till about 30 min. After, the response increasing rate with time enhancement was not so considerable. In order to decrease the Cd^{2+} analyzing time, as much as possible, the time of 30 min was selected for the extraction time.

3.6. Optimization of the pre-potential magnitude and its applied time

In this work, a definite pre-potential was applied to the electrode for a determined time and then the potential was scanned for recording the oxidation peak. It is clear that the pre-potential magnitude and its applying time can influence the sensor performance. Thus, the effect of these parameters on the response magnitude of the developed sensor was investigated. Increasing of the time of the applied pre-potential (–1.0 V) in the time range of 20–60 s resulted in slightly increase in the electrode response. However, higher than 60 s the electrode response started to considerably decrease, probably due to the diffusion of species far from the electrode surface. Therefore, a pre-potential time of 50 s was chosen for the sensor.

On the other hand, the variation of the electrode response with pre-potential magnitude changing showed an optimum at –1.4 V. Increasing the negative potential magnitude, applied to the electrode, increases the rate of reduction in the electrode surface.

Table 1

Interference levels for some tested ions in the determination of $Pb(II)$ by developed sensor.

Species	Interference level
Alkali and earth-alkali	No interference
Co^{2+} , Zn^{2+} , Ni^{2+} , Cr^{3+} , Hg^{2+} , Ag^+	No interference
Cd^{2+}	>50
V^{3+} , Mn^{2+}	>100
Cu^{2+} , Fe^{2+}	>10

No interference: no interference effect even at 200-fold molar excess of the aimed foreign ion.

However, at more negative potentials the reduction of solvent can interfere with the target ions reduction and this can lead to reduced signal of the electrode.

3.7. Analytical characterization

After the optimization and establishment of the determination method for the prepared IIP-CP sensor, various species were examined with respect to their interference with the determination of Pb^{2+} . In this sensor, the preconcentration of Pb^{2+} involves the adsorption of Pb^{2+} at open circuit potential, followed by the stripping/detection step which is performed in a clean medium. This is advantageous in eliminating the interferences during the stripping step because, many interference species can be left in the sample solutions. However, during the preconcentration step, interference may be caused by competitive adsorption of the metal ions to the binding sites of IIP.

The tolerance limit was established as the maximum concentration of foreign species that caused a relative error of 5% in the analytical signal. For 50 nM of lead(II), the detected interference levels for different agents are shown in Table 1. As can be seen, the presence of alkaline and earth alkaline cations as well as some potential interfering cations such as Co^{2+} , Zn^{2+} , Ni^{2+} , Cr^{3+} , Hg^{2+} do not significantly influence the electrode signal. 50-fold excess of Cd^{2+} and 10-fold excess of Fe^{3+} and Cu^{2+} influence significantly the prepared sensor response. It was found that adding of CN^- (0.005 M) in the Pb^{2+} solution can decrease the interference effect of Cu^{2+} and Fe^{3+} without influencing the Pb^{2+} signal. By this means, the interference levels were reached to 100-fold and 25-fold excess for Cu^{2+} and Fe^{3+} , respectively. In order to evaluate the reproducibility of the IIP-CP electrode, 50 nM of Pb^{2+} solution was determined by five separately produced electrodes. This way, a RSD% equal to 2.6 was calculated for the described determination. Moreover, five separate determinations of Pb^{2+} by the same electrode resulted in a RSD% = 3.4 ($n = 5$). This can be an indicative of the repeatability of the method. In this case, the next determination by the electrode was carried out after renewing the electrode surface by polishing the electrode surface on a paper sheet. The calibration graph (shown in Fig. 7) of the prepared sensor showed a linear relationship over Pb^{2+} concentration in the range of 1.0×10^{-9} to 8.1×10^{-7} M with a detection limit of 6.0×10^{-10} M ($S/N = 3$). Each point of the calibration graph is the average of three replications. The detection limits of 5.0×10^{-8} M and 1.0×10^{-7} M were also calculated for the NIP-CP and CP electrodes, respectively.

3.8. Determination of Pb^{2+} in real samples by proposed sensor

Determination of lead(II) was carried out in real water samples. The samples were tested before addition of lead(II) with the optimized sensor and it was found that the tap and river water samples were lead(II) free. Thus, 50 mL of those samples was spiked with different concentrations of lead(II). Then, the determination method was executed step by step, according to the proposed procedure. The edible refined salt samples were prepared by dissolving

Table 2
Determination of Pb(II) in different samples by the IIP-CP electrode and ICP technique.

Sample	IIP-CP sensor (n=4)		ICP (n=3)	
	Spiked (nM)	Found (nM)	Recovery (%)	Found (nM)
Tap water	100.0	114.0(±3.1)	114.0	108.0(±5.80)
	54.1	59.1(±2.1)	110.0	–
	16.7	15.5(±0.7)	93.0	–
River water	100.0	107.0(±3.7)	107.0	–
	54.7	51.7(±1.9)	95.0	55.1(±3.58)
	16.7	15.7(±0.8)	94.0	–
Salt	–	0.65 ^a (±0.03)	–	–
	1 ^a	1.57 ^a (±0.05)	95.0	–
Wastewater	–	2.54 ^b (±0.08)	–	2.71 ^b (±0.18)
	1 ^b	3.66 ^b (±0.13)	–	3.37 ^b (±0.22)

^a $\mu\text{g g}^{-1}$.^b μM .**Table 3**
Comparison of the IIP-CP electrode with some previously reported Pb²⁺ voltammetric sensors.

Electrode	Linear range	Detection limit	Interference level				[Ref]
			Hg ²⁺	Cu ²⁺	Cd ²⁺	Fe ³⁺	
Carbon paste modified with 1,4-bis(prop-2'-enyloxy)-9,10-Anthraquinone	2–10,000	1	>100	<1	>30	>100	[47]
Screen-printed electrodes modified with functionalized mesoporous silica	0–480	4.3	–	<1	–	–	[84]
Carbon electrode modified with montmorillonite-bismuth	4.8–115	0.96	<1	<1	–	–	[85]
Boron-doped diamond electrode	2–100	2	–	<1	–	–	[21]
Bismuth/poly (p-aminobenzene sulfonic acid) film electrode	4.8–627	3.8	>50	>30	–	>30	[20]
Gold-based screen-printed sensor	0–240	2.4	<1	<1	<1	–	[23]
Bismuth nanoparticle modified boron doped diamond electrode	96–960	9.2	–	–	–	–	[39]
Carbon paste modified with organofunctionalised SBA-15 nanostructured silica	300–7000	40	–	–	>2.5	–	[55]
Cyclodextrin-modified gold electrodes	17–930	7.1	–	–	<1	–	[48]
Screen-printed carbon electrode modified with 1-(2-pyridylazo)-2-naphthol modified	0–3378	72	–	<1	–	–	[43]
Carbon paste modified with zeolite	25–100	17.3	<1	<1	<1	<1	[53]
IIP-CP electrode	1–810	0.6	No	>10	>50	>10	This work

a determined amount of the salt in water. It was found that this sample contained trace level of Pb²⁺. Thus, the salt pb²⁺ content was first determined according to the obtained signal and then it was spiked with a determined amount of Pb²⁺, followed by calculation the percent recovery. Moreover, a wastewater sample suspected to contain a considerable amount of Pb²⁺ was analyzed by the

developed method and then spiked with a known amount of Pb²⁺ solution, followed by re-determination of Pb²⁺. In order to verify the validity and applicability of the method the Pb²⁺ content of some of the previously analyzed solutions, were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) technique and the results were compared with those of our developed technique. The results of aforementioned studies are summarized in Table 2 and clearly certify the applicability of this method for determination of Pb²⁺ in various real samples.

3.9. Comparison of IIP-CP electrode with some of the previously reported Pb²⁺ voltammetric sensors

A number of analytical characteristics of the IIP-CP sensor were compared with those of some previously reported voltammetric Pb²⁺ sensors. The results are summarized in Table 3. As can be seen, the IIP-CP electrode shows very good analytical characteristics, compared to majority of the depicted sensors. Although, the IIP-CP electrode offers the lowest detection limit among the considered electrodes; perhaps, the main advantage of this electrode is its highly resistance capability against the interference effect of some potential interfering ions such as Cu²⁺ which in most cases interfere whit Pb²⁺ determination even at concentration lower than that of Pb²⁺.

4. Conclusion

In this paper a new electrochemical sensor for determination of lead ions at trace levels was introduced. Application of IIP as a novel

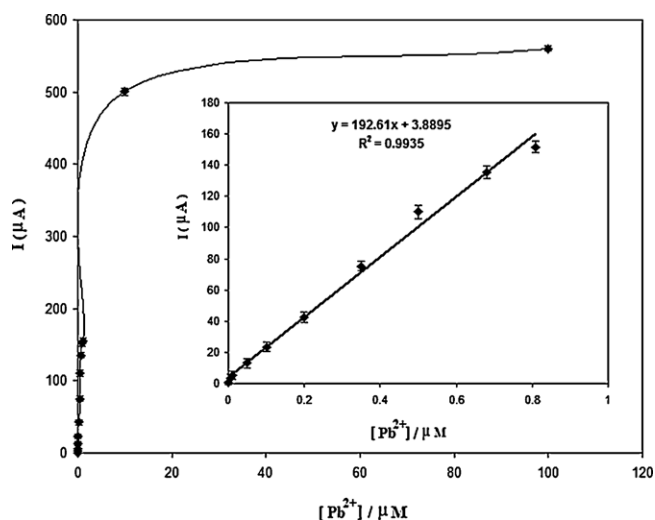


Fig. 7. calibration curve of the developed mercury ion sensor in the optimized conditions; inset: the linear range of the calibration curve.

modifying agent in the carbon paste electrode made it very selective for lead determination in the presence of common potential interfering agents. The IIP, used in the carbon paste composition, acted as the selective chemical interface of the sensor as well as a pre-concentration agent.

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