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## A New Platform Based on the Fe<sub>3</sub>O<sub>4</sub> Nanoparticles, Ligand and Ionic Liquid: Application to the Sensitive Electrochemical Determination of the Lead Ion in Water and Fish Samples

Vida Izadkhah\*, Mosayeb Rezaei and Jafar Mahmoodi

*Department of Chemistry, Hamadan Branch, Islamic Azad University, Hamadan, Iran*

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In the present paper, the use of a modified electrochemical sensor for the determination of Pb<sup>2+</sup> is described. The sensor is based on a carbon paste electrode modified with nitro benzoil diphenyl methylene phosphorane, N-octylpyridiumhexafluorophosphate (OPPF6) and Fe<sub>3</sub>O<sub>4</sub> nanoparticles. In this work, the oxidation of lead at the modified electrodes was investigated by square wave voltammetry (SWV). The structure of the nanoparticle was investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectrum. The effective parameters on the response of the electrode such as the effect of the electrode composition, pH of the solution, deposition potential and accumulation time, and also instrumental SWV method were studied. In optimum conditions, the anodic stripping voltammetry (ASV) was used for the determination of Pb<sup>2+</sup>. It is found that the calibration graphs of Pb<sup>2+</sup> are linear in the concentration ranges from 1.20-120 nM. The detection limit of the method was 0.9 nM. The sensor was applied to validate its capability for the analysis of Pb<sup>2+</sup> in the water and fish samples.

**Keywords:** Voltammetric determination, Lead ion, Modified electrode, Anodic stripping voltammetry, Fe<sub>3</sub>O<sub>4</sub> nanoparticle, Ionic liquid

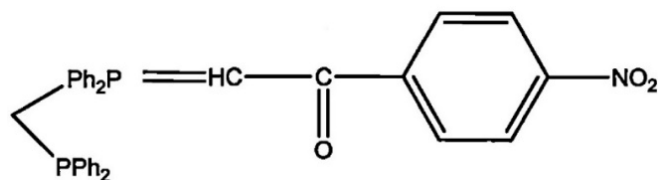
### INTRODUCTION

The pollution of heavy metals such as lead is one of the most serious environmental problems. That is highly toxic to many organs of both humans and animals, including nervous, immune, reproductive, and gastrointestinal systems [1]. So, it is necessary to establish a rapid, sensitive and selective method that can quantitatively determine this metal ion. Up to now, many methods have been proposed to determine metal ions, such as atomic absorption spectrometry (AAS) [2-6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7-12], spectrophotometry [13], high performance liquid chromatography [14], reversed-phase liquid chromatography [15], and ion chromatography [16]. However, they rely on expensive and sophisticated

instruments and are time-consuming severely restricted their practical applications.

Anodic stripping voltammetry (ASV) is one of the most favourable techniques for the determination of heavy metal ions, such as lead, because of its low cost, high sensitivity, easy operation and the ability to analyze element speciation [17]. Hanging mercuric drop electrode (HMDE) and a mercury film electrode (MFE) are widely used in electrochemical stripping analysis due to readily renewable, reproducible surface, high overpotential for hydrogen evolution and its ability to dissolve many metals [18]. Use of metallic mercury to detect toxic heavy metal ions is a debatable issue [19] because of its high toxicity, stability, and volatility. Therefore, various mercury-free electrodes including gold-coated electrodes [20,21], silver electrodes [22,23], glassy carbon electrodes [24], carbon paste electrodes [25], carbon nanotube electrodes [26] are applied for sensitive metal determinations.

\*Corresponding author. E-mail: izadkhahv@gmail.com



Scheme 1. Structure of the synthesized N-BDMP

Another important class of novel materials for various electrochemical applications are ionic liquids (IL) and nanoparticle materials, due to their unique chemical and physical properties. IL is a liquid electrolyte consisting of a small anion and a large organic cation such as imidazolium and pyridinium [27]. Different advantages could be achieved by using this composite electrode, such as (i) a remarkable increase in the rate of electron transfer of different organic and inorganic electroactive compounds, (ii) a marked decrease in the overvoltage for biomolecules, and (iii) a higher current density for a wide range of compounds tested. All these properties allow a sensitive, low-potential, simple, low-cost, and stable composite electrode for the detection of biomolecules and other electroactive compounds [28].

In recent decade, nanoparticles have been employed for modification of electrochemical sensors for determination of ions, drug and biomolecules [29-31]. Sensors based on nanostructured materials take advantages of the increased electrode surface area, increased mass-transport rate, and fast electron transfer compared to electrodes based on bulk materials [32,33]. In addition to novel properties, nanomaterials open up new approaches to fabricate the electrodes cost-effectively by minimizing the needed materials and waste generation [34]. Various ligands have been reported for selective determination of ions by modified carbon paste electrode [35,36]. In this paper, a simple and effective carbon ionic liquid electrode modified with nitro benzoyl diphenyl methylene phosphorane (N-BDMP) (Scheme 1) was developed, and the sensor was applied to the determination of  $Pb^{2+}$  by using square-wave anodic stripping voltammetry (SWASV). The modifier, N-BDMP, can pre-concentrate  $Pb^{2+}$  from aqueous solution to the surface of the modified electrode by formation a complex between N-BDMP and a metal ion, and

significantly increases the sensitivity and selectivity of determination [36]. Also, because of the high stability and electrical conductivity of ionic liquid and magnetite nanoparticle, the proposed electrode has a wide linear range of concentrations, high sensitivity, good selectivity, and reproducibility for the determination of  $Pb^{2+}$  in water and food samples.

## EXPERIMENTAL

### Materials and Apparatus

All the reagents used were of analytical grade. Double distilled water (DDW) was used throughout. Laboratory glassware was kept overnight in a 10% (v/v)  $HNO_3$  solution and then rinsed with DDW. Graphite powder with a 10  $\mu m$  particle size and highly pure paraffin oil were purchased from Merck. The ionic liquid N-octylpyridiniumhexafluorophosphate (OPPF6) was purchased from Shanghai Chengjie Chemical Co., Ltd. and was used for the preparation of conventional carbon paste electrode. The magnetite nanoparticle and N-BDMP (Scheme 1) were synthesized according to references [37,38] respectively and applied. Stock solutions of  $Pb^{2+}$  were prepared by dissolving their corresponding nitrate salts (from Merck) into the redistilled water and diluted to various concentrations.

Voltammetric measurements were performed using a Behpajoh model BHP-2065 potentiostat/galvanostat. The electrochemical cell was assembled with a conventional three-electrode system: an Ag/AgCl reference electrode (Metrohm) and a platinum wire as the counter electrode. A modified or unmodified carbon paste electrode was used as the working electrode. A Metrohm model 713 pH-meter was used for pH adjustments.

The surface morphology of the electrodes was characterized by a scanning electron microscope (MIRA

FEG-SEM, TESCAN). A 40 kHz universal ultrasonic cleaner water bath (RoHS, Korea) was used. The crystal structure of the synthesized materials was determined by an X-ray diffractometer (XRD, 38066 Riva, d/G. Via M. Misone, 11/D (TN) Italy) at ambient temperature.

### Electrode Preparation and Modification

CPE was fabricated by hand-mixing graphite powder and paraffin oil (75/25 w/w%) thoroughly in a mortar to form a homogeneous carbon paste. N-BDMP/CPE was prepared by mixing 15% (w/w) N-BDMP, 60% (w/w) graphite powder with paraffin oil (25% w/w) in a mortar and pestle. N-BDMP/IL/CPE was prepared by mixing 15% (w/w) N-BDMP, 60% (w/w) graphite powder with IL (25% w/w) in a mortar and pestle. The N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE was prepared by mixing 15% (w/w) N-BDMP, 10% (w/w) Fe<sub>3</sub>O<sub>4</sub> nanoparticles and 50% (w/w) graphite powder with 25% (w/w) IL in a mortar and pestle. The mixture amount of 0.2 g was homogenized in a mortar for 30 min. Each paste was transferred and firmly packed into one end of a glass tube (internal diameter of 4.0 mm) with a copper wire inserted through the opposite end to establish electrical contact. Before use, the surfaces of unmodified/modified electrodes were smoothed on a piece of weighing paper.

### Samples Preparation

Water samples including mineral and tap water were utilized to evaluate the applicability of the proposed electrode for monitoring the target ion in real samples. The water samples were filtered through a standard 0.45 μm filter. Before the test, the pH of the samples was adjusted to 3.5 by using Britton-Robinson buffer solution and 0.1 M HCl solution.

The proposed method was applied to determine lead in fish samples. Dried fish was purchased from the local fish market. 1.0 g of dried fish sample was placed in a round-bottom flask, and 10 ml of HNO<sub>3</sub> (65%), 10 ml of H<sub>2</sub>SO<sub>4</sub> (98%), 10 ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5%) and 8 ml of KMnO<sub>4</sub> (5%) were added and refluxed at 250 °C for about 2 h. The digested fish sample was cooled to room temperature [38]. Appropriate amounts of 2 M of NaOH solution was added to neutralize the excess of HNO<sub>3</sub> and diluted to 100 ml in a volumetric flask. An aliquot of the solution was treated

under the recommended procedure.

### Analytical Procedure

The analysis of Pb<sup>2+</sup> using square wave anodic stripping voltammetry (SWASV) was carried out in a 10.0 ml aliquot using the following steps: (a) pre-conditioning step: potential 0.0 V for 60 s was applied before each measurement to ensure dissolution of remaining deposits; (b) the pre-concentration step proceeded at -1.1 V vs. Ag/AgCl for 240 s; (c) the square-wave anodic stripping voltammograms were recorded when swept from -1.2 V to -0.1 V vs. Ag/AgCl after a 10 s quiescence. Experimental parameters: deposition potential, -1.1 V; accumulation time, 240 s; pulse amplitude, 100 mV; SW frequency, 40 Hz. In the pre-conditioning and pre-concentration processes, the detection solutions were stirred with a magnetic stirrer.

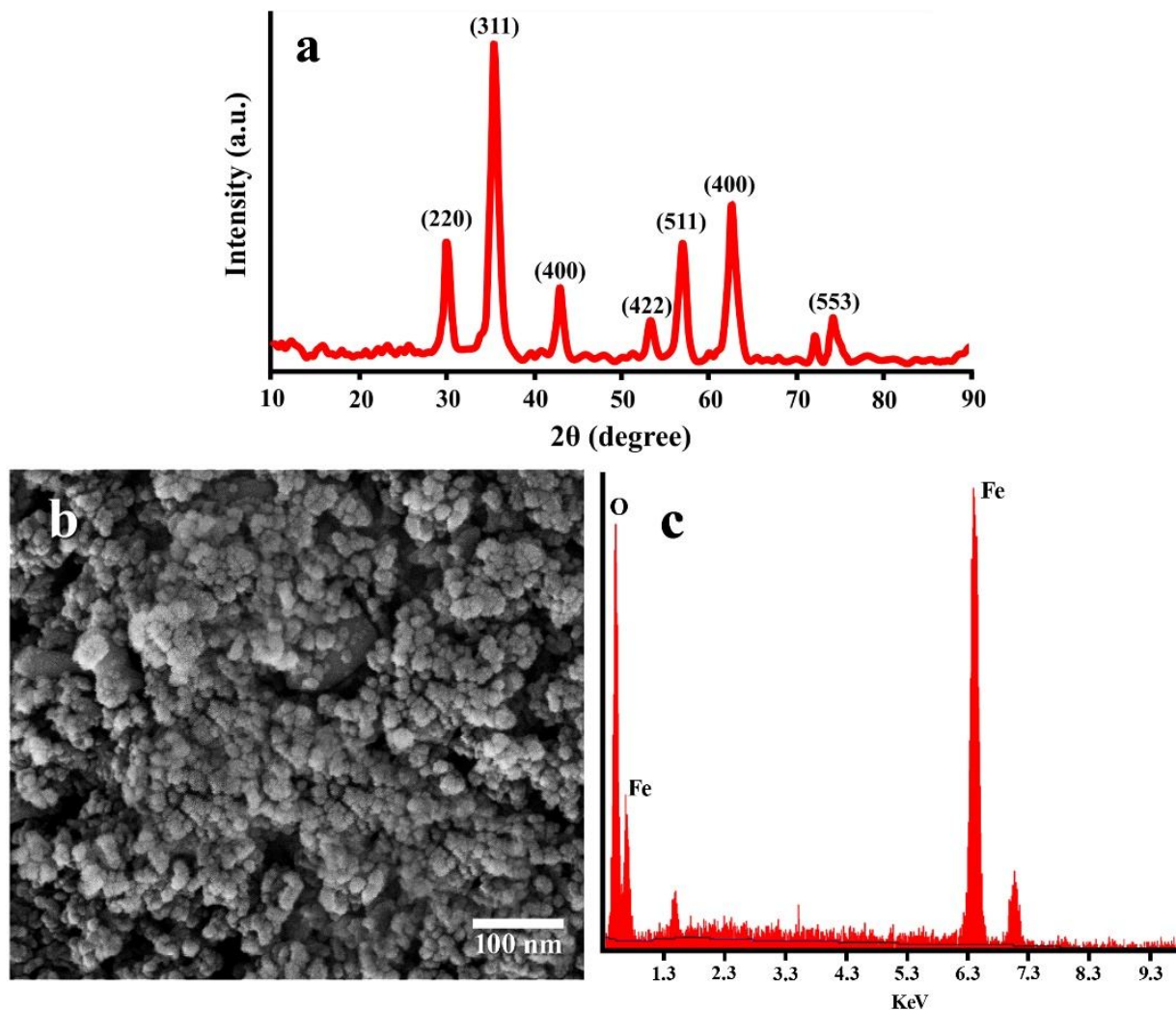
## RESULTS AND DISCUSSION

### Characterization of the Modified Electrode

**Characterization of the synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles.** Figure 1a shows the XRD pattern of the synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles [37]. This pattern shows diffraction peaks that are indexed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 5 3) reflection characteristics of the cubic spinel phase of Fe<sub>3</sub>O<sub>4</sub> (JCPDS powder diffraction data file no. 79-0418), revealing that the resultant nanospheres are mostly Fe<sub>3</sub>O<sub>4</sub>. The average crystallite size of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles was estimated to be 9.0 nm from the XRD data according to Scherer equation [39]. The SEM of Fig. 1b shows spherical Fe<sub>3</sub>O<sub>4</sub> nanoparticles. These images show the irregular stone like morphology for Fe<sub>3</sub>O<sub>4</sub>. Figure 1c shows the energy-dispersive X-ray spectrum for the Fe<sub>3</sub>O<sub>4</sub> nanoparticles indicating the presence of elements Fe and O.

### Surface morphologies of the modified electrodes.

Scanning electron microscopy (SEM) was used to characterize and compare the morphology of different kinds of modified electrode. The unmodified CPE (Fig. 2a) is characterized by irregularly shaped micrometre-sized flakes of graphite; there are no conducting media available between carbon layers. Figure 2b shows a SEM image of N-BDMP/IL/CPE with more uniform surface topography



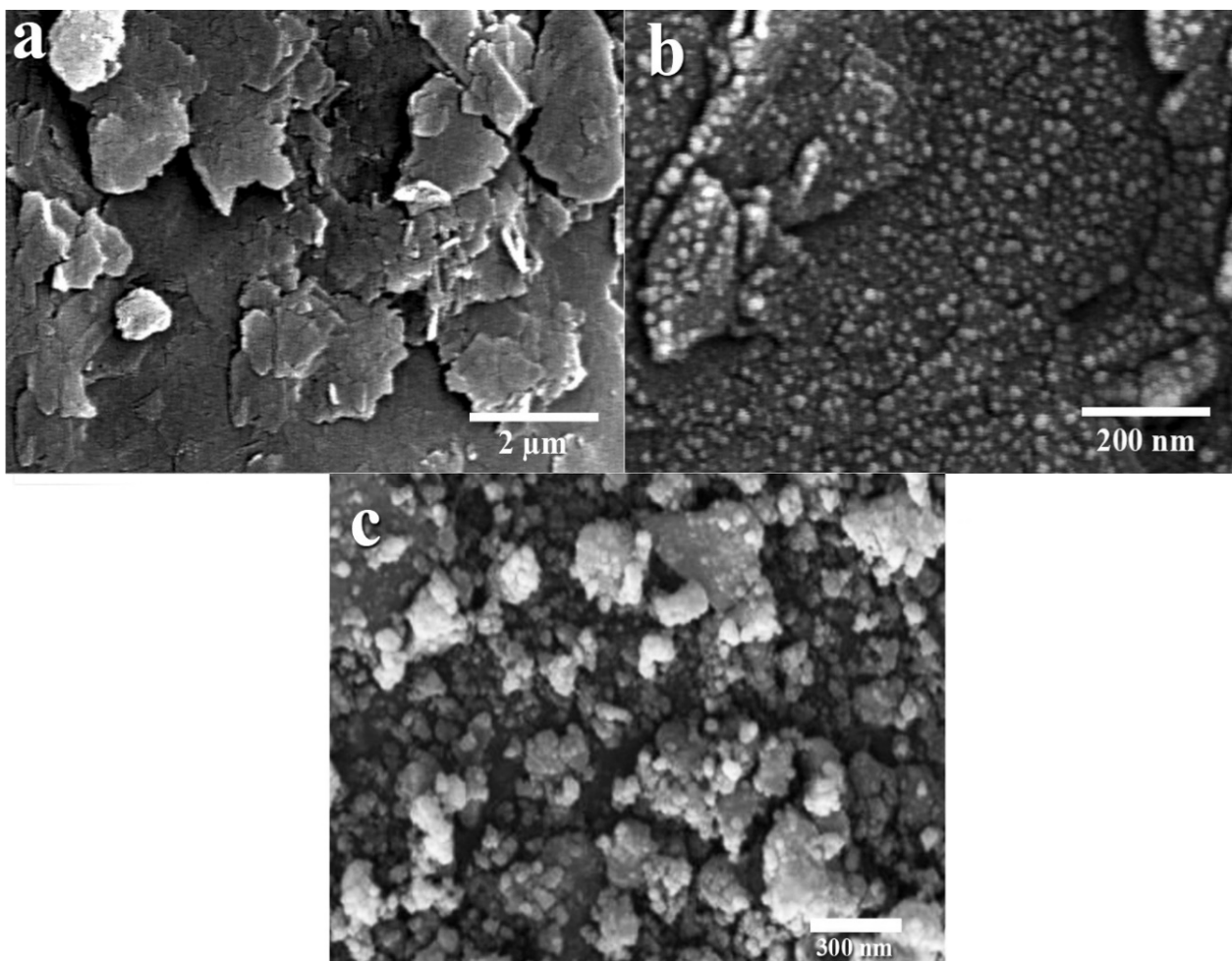
**Fig. 1.** The XRD pattern of Fe<sub>3</sub>O<sub>4</sub> nanoparticles (a), SEM images of Fe<sub>3</sub>O<sub>4</sub> (b), Energy dispersive X-ray spectrum for Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

these nanoparticles are well distributed in the graphite sheets matrix. Figure 2c displays a typical morphology of N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE.

### Voltammetric Behaviours of Pb<sup>2+</sup>

Figure 3a shows the square-wave anodic stripping voltammograms of 5.0 nM Pb<sup>2+</sup> in 0.1 M KNO<sub>3</sub> with pH 3.5 and the deposition time 240 s, at the CPE, N-BDMP/CPE, N-BDMP/IL/CPE and N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE. CPE did not show any peaks in the potential range of -0.550 to

-0.250 V vs. Ag/AgCl (Fig. 3I). In the absence of metal ions, N-BDMP/CPE did not show any stripping peaks in the potential region -0.550 to -0.250 V vs. Ag/AgCl. Therefore, this electrode can be used for the quantification of metal ions which are active in this potential region. In the presence of Pb<sup>2+</sup>, the N-BDMP/CPE showed one peak for Pb<sup>2+</sup> at -0.404 V vs. Ag/AgCl (Fig. 3II). The signals at the N-BDMP/IL/CPE (Fig. 3III) were remarkably enhanced than those at the N-BDMP/CPE, which can be interpreted that the ionic liquid can effectually increase the rate of



**Fig. 2.** The SEM images of CPE (a), N-BDMP/IL/CPE, N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/ CPE.

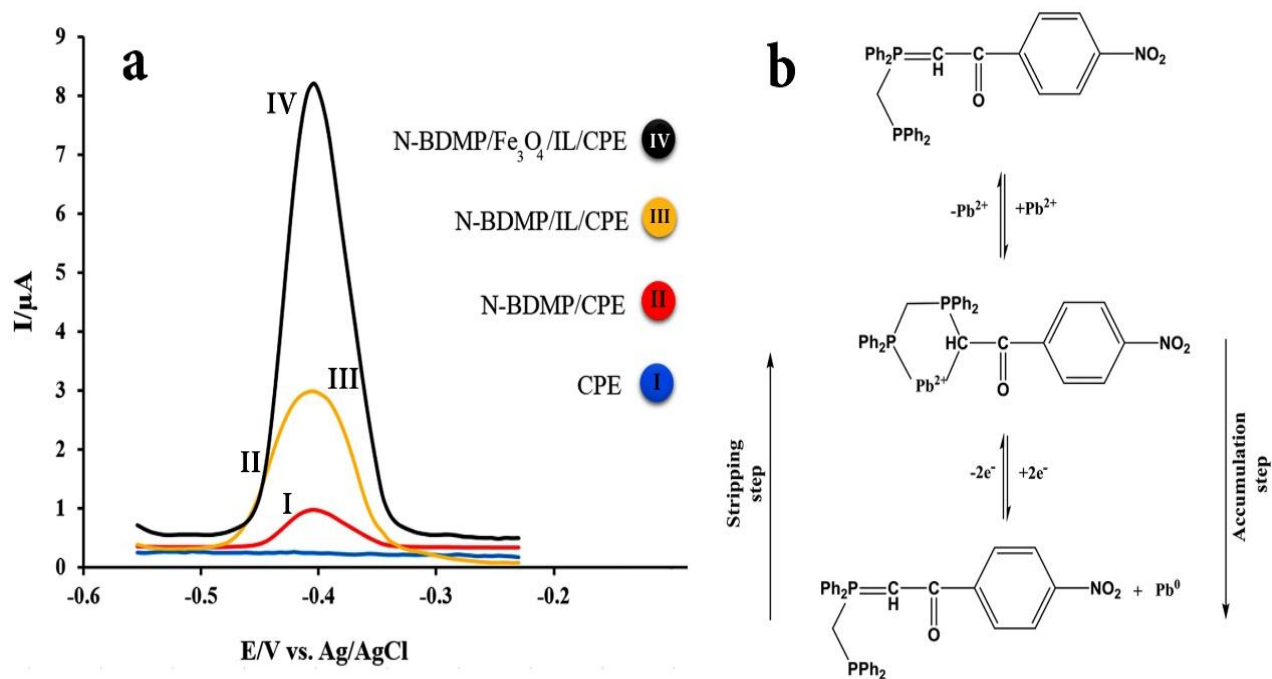
metal preconcentration from aqueous solution to the surface of the electrode. As can be seen from Fig. 3IV, the peak currents of Pb<sup>2+</sup> at the N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE is more intense than that at N-BDMP/IL/CPE. This result indicated that more Pb<sup>2+</sup> was deposited on the electrode surface when the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were modified in the carbon ionic liquid electrode. Fe<sub>3</sub>O<sub>4</sub> nanoparticles decreased the interfacial resistance, increased the electrode contact area and enhanced the electrochemical properties of the modified electrode.

According to the previous report [37,38], the following mechanism for the oxidation of Pb<sup>2+</sup> at the modified electrode can be proposed (Fig. 3b (Scheme)).

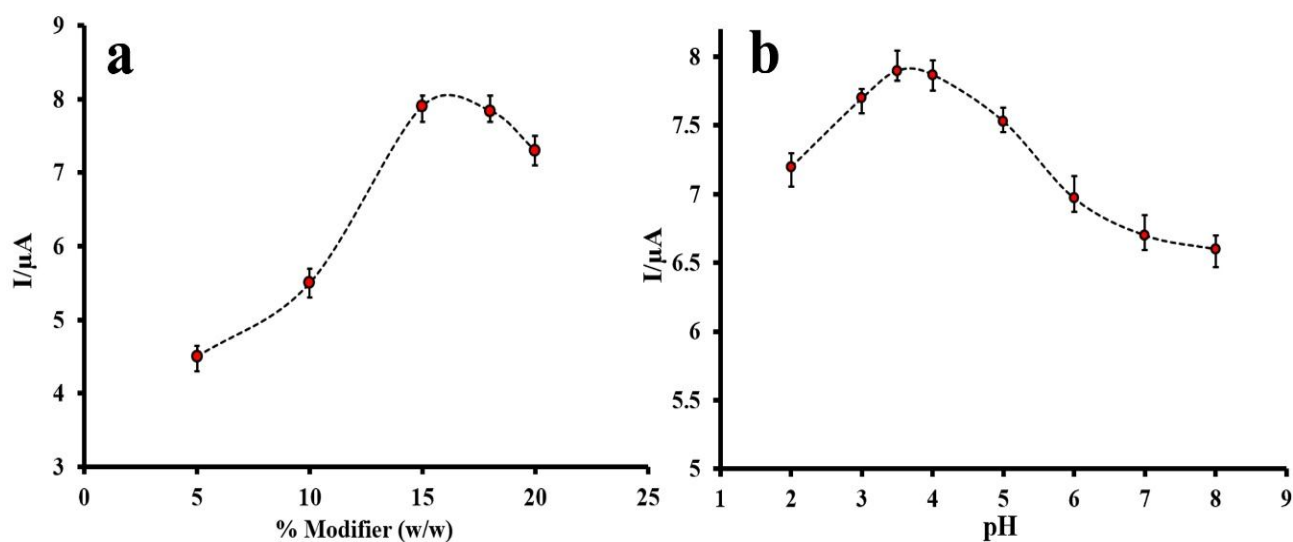
### Optimization of Analytical Conditions

To optimize the performance of N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE, for the electrochemical determination of Pb<sup>2+</sup> in aqueous solution, the parameters influencing the response of the metal including supporting electrolyte, pH of the solution, accumulation time, deposition potential and amount of N-BDMP were investigated.

**Effect of the electrode composition.** The composition of the electrode can play an important role and influences the electroanalytical response of the electrode. Therefore, the comparison of the electroanalytical performance of the five-carbon paste electrodes with different contents of N-BDMP (5-20%) was investigated in the first place. All



**Fig. 3.** a: Square-wave anodic stripping voltammograms of 5.00 nM  $Pb^{2+}$  in .1 M  $KNO_3$  with pH 3.5, the deposition time 240 s and deposition potential -1.1 V at the CPE (I), N-BDMP/CPE (II), N-BDMP/IL/CPE (III) and N-BDMP/ $Fe_3O_4$ /IL/CPE (IV). b: Scheme of Redox mechanism of  $Pb^{2+}$  at the modified electrode.



**Fig. 4.** Effect of modifier on the response of electrode ( $C = 5$  nM, pH = 3.5, deposition time 240 s and deposition potential -1.1 V), b: Effect of pH on the response of electrode ( $C = 5$  nM, 15% modifier, deposition time 240 s and deposition potential -1.1 V).

five modified electrodes exhibited well defined and undistorted voltammetric stripping signals for the tested metal in Britton-Robinson buffer solution with peak potentials observed around -0.404 V vs. Ag/AgCl (Fig. 4a). The peak current intensity was increased by increasing the amount of N-BDMP because its concentration on the surface of the modified electrode increased correspondingly. At 15% (w/w) of modifier, the largest peak current was obtained. However, the continuous increase in the amount of modifier caused a decrease in the peak current, because an excessive amount of N-BDMP may result in a decrease in the conductivity of the electrode [36]. So, the best ratio of N-BDMP in Fe<sub>3</sub>O<sub>4</sub>/IL/CPE composition was 15% (w/w).

**Effect of buffer solution and pH.** Electrochemical behaviours of metal ions are affected by the different buffer solutions. The effects of some buffer solutions, such as acetate buffer, phosphate buffer, and Britton-Robinson buffer solution on stripping peak currents of Pb<sup>2+</sup> were studied. In this experiment, three separated solutions included each buffer solution (0.1 M, pH = 3.5) and the analyte (5 nM) were prepared, then transferred to electrochemical cell and determination was done and the electrochemical current of peak, the lowest background current, and shape of peak were checked out. The largest stripping peak current, the lowest background current, and the best shape of the oxidation peak related to lead were observed for 0.1 M Britton-Robinson buffer solution [36].

The influence of pH on the determination of Pb<sup>2+</sup> in the range of 2-8 was also investigated (Fig. 4b). The anodic peak current increased by increasing the pH up to 3.5 and decreased at higher pH values for Pb<sup>2+</sup>. Under pH = 3.5 proton can compete with Pb<sup>2+</sup> in complexation with N-BDMP and at higher pH values OH<sup>-</sup> can form Pb(OH)<sub>2</sub> thus electrochemical response decreased. Therefore, pH 3.5 was used as an optimum pH [35,36,38].

**Effect of deposition potential and accumulation time.** Anodic stripping voltammetry is a two-step technique in which the first step consists of the electrolytic deposition of a chemical species onto the surface of a modified electrode surface by reducing at a constant potential. The second step consists of the application of a voltage scan to the electrode causing an electrolytic dissolution, or stripping the various

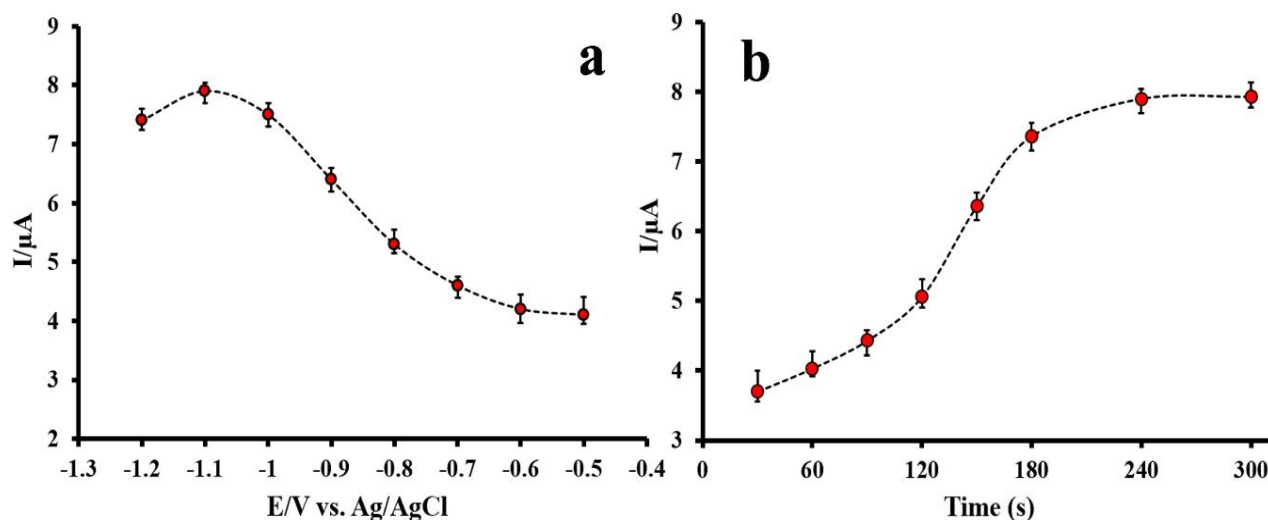
species into the solution at characteristic potentials. So, the preconcentration conditions include deposition potential and accumulation time, therefore, have a significant impact on the stripping signals of analyte [40]. The stripping currents of Pb<sup>2+</sup> noticeably increased with the deposition potential shifting from -0.5 to -1.1 V vs. Ag/AgCl and then decreased rapidly at more negative potentials (Fig. 5a). However, it could cause a relatively higher background current, which is mainly attributed to the hydrogen evolution at such negative potentials. Moreover, a more negative preconcentration potential would increase the possibility of codeposition of interfering species. In addition, when the deposition potential became more negative, the reproducibility of stripping currents for Pb<sup>2+</sup> became poor, because hydrogen evolution was beginning to be significant in the medium at such negative potentials. Also, the hydrogen bubbles might damage the metal alloys deposited on the electrode surface and decrease the stripping current signals at very negative potentials [41].

Furthermore, Fig. 5b illustrates the stripping voltammetric peak current versus accumulation time for Pb<sup>2+</sup> over various adsorption times. Variation of the accumulation time over the range 30-300 s at a preconcentration potential of -1.1 V vs. Ag/AgCl showed a gradual enhancement for the response of the electrode up to 240 s and remained nearly constant with longer preconcentration times. As a consequence, the accumulation time of 240 s was selected as an optimum for further studies.

**Effect of other instrumental parameters.** Optimum conditions for the SWV response were recognized by measuring the current dependence on solution pH and some instrumental parameters, counting resting time (s), pulse amplitude (mV), voltage step (mV), frequency (Hz), and pulse amplitude. These parameters were optimized for obtaining maximum signal-to-noise ratio. Optimum values for the studied parameters are given in Table 1.

### Interference Study and Calibration Graph

The influence of various foreign species on the determination of 5.00 nM Pb<sup>2+</sup> was investigated. The tolerance limit was taken as the maximum concentration of the foreign substances caused an approximately ±5%



**Fig. 5.** Effect of deposition potential and accumulation time on response of electrode (C = 5 nM, pH = 3.5, 15% modifier).

**Table 1.** Optimum Values for the Studied Parameters

Parameter	Range studied	Optimum value
Accumulation potential (V)	-0.5 to -1.3	-1.1
Accumulation time (s)	0-300	240
Resting time (s)	0-30	10
Pulse amplitude (mV)	10-150	100
Voltage step (mV)	1-10	5
Frequency (Hz)	10-100	40

relative error in the determination. The experimental results indicate that 250-fold excess  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^{+}$  and  $\text{K}^{+}$  and 300 times of  $\text{NO}_3^-$ ,  $\text{SCN}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  and 350 times of sulfite and nitrite and also 80 times of Hydrazine have no significant influences on the signal of  $\text{Pb}^{2+}$ . However, 170-fold excess  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  was found to reduce the responses to  $\text{Pb}^{2+}$ , because  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  can

compete with  $\text{Pb}^{2+}$  for the complexation with N-BDMP on the surface of N-BDMP/ $\text{Fe}_3\text{O}_4$ /IL/CPE and affect the accumulation of  $\text{Pb}^{2+}$ . The effect of  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  ions on the response of electrode for determination of  $\text{Pb}^{2+}$  is shown in Fig. 6, indicating that the presence of these ions can change the oxidation current of deposited  $\text{Pb}^{2+}$  more than 5% when the concentration of  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  ions was more



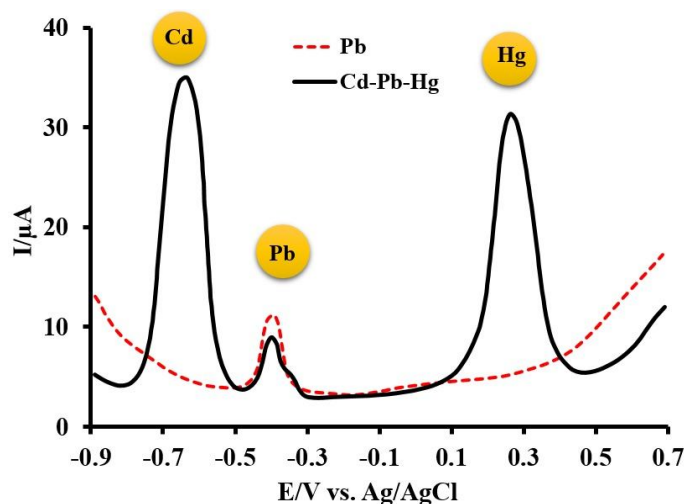


Fig. 6. SWVs of N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE in the presence of 5 nM Pb<sup>2+</sup> and 850 nM Cd<sup>2+</sup> and Hg<sup>2+</sup>.

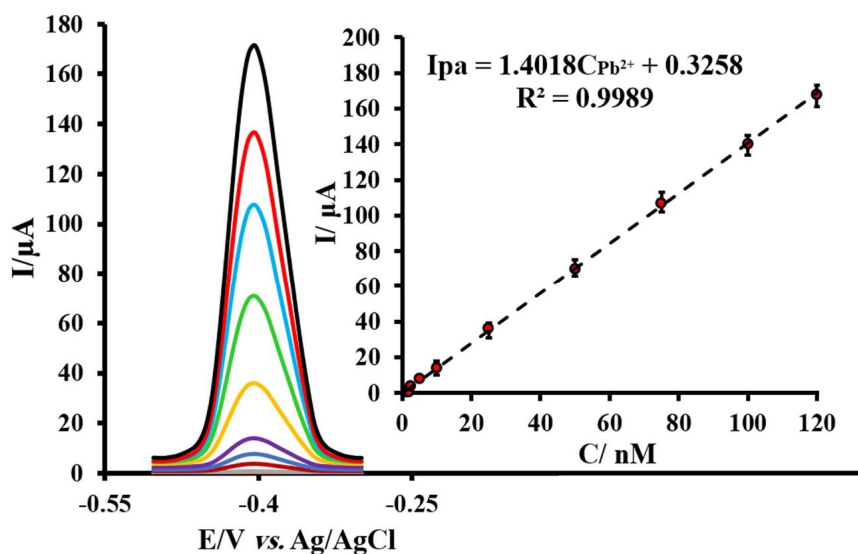


Fig. 7. The SWVs and the calibration curves of Pb<sup>2+</sup> at N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE.

than 850 nM [36].

To verify the linear relationship between peak current and Pb<sup>2+</sup> concentrations in the range from 1.20-120.00 nM, a calibration graph was constructed under optimum conditions (Fig. 7). The following regression equation was obtained by the least-square technique with the peak current  $I_{pa} = 1.4018 C (Pb^{2+}) + 0.3258$  and a regression coefficient

of 0.9989 (for n = 3), where I<sub>pa</sub> is the peak current (in μA), and C is Pb<sup>2+</sup> concentration (in nM). The limit of detection (LOD) of 0.9 nM was calculated at a signal-to-noise (S/N) ratio of 3.

The reproducibility of the N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE for Pb<sup>2+</sup> determination was investigated with intra and inter-assay precision. The intra-assay precision of the sensor was

**Table 2.** Determination Results of Pb<sup>2+</sup> in Water Samples and Fish Sample (n =5)

Sample <sup>a</sup>	Added (nM)	Found (nM) <sup>b</sup>	Recovery (%)	ICP-OES
Tap water	0.00	28.53 ± 0.14	-	29.17 ± 0.11
	20.00	48.39 ± 0.18	99.30	48.63 ± 0.16
Mineral water	0.00	ND <sup>b</sup>	-	ND
	20.00	20.21 ± 0.20	101.05	20.03 ± 0.10
Dried fish	0.00	6.34 ± 0.15	-	6.22 ± 0.17
	20.00	27.01 ± 0.18	103.35	26.39 ± 0.13

<sup>a</sup>Average value of five replicate measurements. <sup>b</sup>Not detected.

evaluated by assaying 5.00 nM Pb<sup>2+</sup> with the same N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE. The relative standard deviation (RSD) for 10 successive determinations was about 2.3%, demonstrating an excellent detecting reproducibility.

Additionally, the inter-assay precision, or the fabrication reproducibility, was estimated by detecting 5.00 nM Pb<sup>2+</sup> induplicate with 10 sensors prepared in the same manner independently. The RSD was 3.5%. Thus, the proposed method had an excellent reproducibility for Pb<sup>2+</sup> determination.

The storage stability of the designed sensor was also investigated. For detection of 5.00 nM Pb<sup>2+</sup>, there was no significant decrease in current response in the first 7 days. Only about 8.55% decrease occurred after 20 days. Therefore, the stability of the proposed electrode was good enough for the continuous operation.

### Determination of Pb<sup>2+</sup> in Real Samples

In order to further demonstrate the excellent performance of the proposed sensing system, its applicability was evaluated by the analysis of Pb<sup>2+</sup> as a model analyte in real samples. The amount of Pb<sup>2+</sup> in real samples was determined with the proposed modified electrode using the standard addition method. The obtained results were given in Table 2. It could be seen that there is a

good agreement observed not only between the obtained values by our proposed method and the reference method (ICP-OES) but also between the spiked and found values of Pb<sup>2+</sup>. These results clearly indicate that the system presented here can be used successfully for analysis of the real samples.

### CONCLUSIONS

The present work reported a new voltammetric sensor, N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE, for sensitive determination of Pb<sup>2+</sup> with high selectivity, low detection limit, and wide linear range. With the modified electrode, Pb<sup>2+</sup> could be detected in a linear calibration range of 1.20-120.0 nM with a detection limit of 0.9 nM. Compared to other electrodes (shown in Table 3), the proposed electrode shows good advantages such as wide linear ranges and low LODs. This study has demonstrated that the N-BDMP/Fe<sub>3</sub>O<sub>4</sub>/IL/CPE can be applied to the detection of Pb<sup>2+</sup> in water samples and fish sample with excellent sensitivity and selectivity by SWV.

### ACKNOWLEDGEMENTS

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**Table 3.** Comparison of some Figures of Merit Related to the Different modified Electrodes for the Determination of Pb<sup>2+</sup>

Electrode	Method	Linear range (nM)	Detection limit (nM)	Ref.
Mn <sub>3</sub> O <sub>4</sub> /GCE	SWASV	20-680	0.0966	[42]
MMT-Ca/CPE	SWASV	4-483	1.45	[43]
Antimony film electrode	SWASV	24.1-482.6	7.24	[44]
[Ru(bpy) <sub>3</sub> ] <sup>2+</sup> -GO/Au electrode	DPV	50-250	1.41	[45]
C60-Chit/GCE	DPASV	5-6000	1	[46]
Bi/AuNP-SPCE	DPASV	4.8-724	0.096	[47]
BDD	DPASV	48.3-483	9.6	[48]
HAp/ITO	DPV	100-1000	0.001	[49]
IAP30/RTI	SWASV	29-500	0.8	[50]
Diamond/Graphite electrode	DPASV	120.7-1207	23.45	[51]
alk-Ti <sub>3</sub> C <sub>2</sub> /GCE	SWASV	100-550	41	[52]
ERNGO/GCE	SWASV	10-1000	0.8	[53]
EDTA_PANI/SWCNTs/Stainless steel electrode	DPV	2000-37000	1650	[54]
N-BDMP/Fe <sub>3</sub> O <sub>4</sub> /IL/CPE	SWASV	1.2-120	0.9	This work

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