



Determination of Lead Ion by a Modified Carbon Paste Electrode Based on Multi-Walled Carbon Nanotubes (MWCNTs) and Poly 4-N-Pyridine Para Styrene Sulfonamide

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Abstract

In the present study, a novel electrode based on multi-walled carbon nanotubes (MWCNTs) modified with poly 4-N-pyridine para styrene sulfonamide for the determination of trace amount of Pb^{+2} was prepared. In order to explore the selectivity, reliability and accuracy of this new type of electrode, a number of electrodes were prepared and tested under various conditions for the determination of trace amount of Pb^{+2} in an aquatic environment. In particular, the modified electrode was used to determine the concentration of Pb^{+2} in a wastewater of Isfahan's Mobarkeh steel and ZobAhan companies. As a result, our modified electrode with an optimized conditions (concentrations of 6 wt% carrier, 12 wt% MWCNTs, 20 wt% paraffin oil and 62 wt% graphite powder) exhibited a high selectivity, a good Nernstian slope (-29.43 ± 0.3 mV/decade), a linear concentration range of (1.0×10^{-1} to 1.0×10^{-8} M), an excellent detection limit of (6.0×10^{-9} M), a fast response time (20s), a long life time (2 months) at a wide range of pH (5.0-8.5).

Key words: Carbon paste electrode, Ligand, MWCNTs, Potentiometric

1 Introduction

Lead is one of the toxic heavy metals which can be a cause for environmental pollutions. Mostly, lead is released in environment from industrial wastewater all over the world. This metal has toxic and serious effects to human health [1-2]. Therefore, it is necessary to develop new methods for accurate estimation of Pb^{+2} concentration in various biological and environmental samples. Different instrumental techniques have been used for determination of Pb^{+2} , such as, electro thermal atomic absorption spectrometry (ETAAS) [3], inductively coupled plasma-optical emission spectrometry (ICP-OES) [4], flame atomic absorption spectrometry (FAAS) [5-6].

One of the methods for measurement of cations is ion selective electrodes (ISEs) [7-11]. Although, working with ISEs is simple and low cost, most of them have serious problems in the presence of interfering ions such as, high detection limit and slow response time. Also, these electrodes cannot be applied for a wide range of cations concentration. Such problems encouraged researchers to develop new methods for the measurement of cations like carbon paste electrodes. The family of carbon components has been widely used for different bed electrodes construction. The surfaces of these electrodes are well reproducible due to Carbon smoothness. Regardless of the good physical and

mechanical properties, electrochemical characteristics are the most favorable characteristics of different forms of Carbon. The most common Carbon electrodes are: Pyrolytic Graphite Electrode (PGE), Glassy Carbon Electrode (GCE), Carbon Fiber Electrode (CFE), Carbon Ceramic Electrode (CCE) and Carbon Paste Electrode (CPE) [12]. Carbon paste electrodes as ion selective electrodes have advantages such as stable response, low ohmic resistance, renewability and they don't need to internal solution [13-16].

Carbon nanotubes (CNTs) have interesting properties such as high mechanical strength, high aspect ratio, high thermal conductivity, high electrical conductivity and high surface area. CNTs as unique materials have been used as modifier of carbon paste electrodes due to increase electrical conductivity and surface area [17-24]. In this work, for the first time a Pb^{+2} carbon paste electrode was made based on poly 4-N-pyridine parastylene sulfonamide and multi-walled carbon nanotubes (MWCNTs) as modifiers. MWCNTs in structure of the proposed electrode provide high surface area and high electrical conductivity.

2 Materials and Methods

2.1. Apparatus

Potentiometric measurements were carried with a CRISON BASIC 20 pH/mV meter. The reference electrode was a Hg/Hg_2Cl_2 (Azar electrode, Iran). pH was measured by a digital pH meter (Jenway pH-meter, UK 3020, Japan). Also, atomic absorption spectrometer

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(Shmadzu, AA-760 of Japan) was used for measurements of Pb^{2+} in different samples.

2.2. Reagents and materials

Carbon graphite powder with a 1–2 μ m particle size, paraffin oil with high purity and chloride salt were purchased from Fluka Company located in Switzerland. All nitrate salts which used in this study were purchased from Merck Company located in Germany. Multi wall carbon nanotubes (purity>95%, with diameter about 20–30 nm, from cheap tubes.com, USA.). All aqueous solutions were prepared with double distilled water. Poly 4-N-pyridine parastyrene sulfonamide (ligand i) as a modifier was synthesized in Organic Chemistry Research Laboratory of Lorestan University in Iran [25].

2.3 Selectivity Modifier

The Carbon paste electrodes usually are categorized into two groups: (i) unmodified carbon paste electrodes [26] and (ii) chemically and biologically modified carbon paste electrodes [27]. There are Four reasons for Carbon paste electrode modification: Pre-concentration of goal analyt components from lean solution on the electrode surface, use of catalytic electrochemical response, immobilization of relating molecules in the electrochemical reactions and Changing the surface electrode physical properties [28]. Different modifiers can be applied to modify the surface of the electrodes as follows: Chemical modifiers like ion-exchange reactants [29], biological modifiers like glucose oxide [30] and the new generation of modifiers like new Carbon shapes such as nanotupes, nanofibers, geraphen, folerone etc. [31–33].

In this work MWCNTs (among mentioned cases) and Poly 4-N-pyridine parastyrene sulfonamide were used as modifiers. Iigand (i) is readily prepared, stable, mild, and efficient oxidizing reagent that can be used for oxidation of different aliphatic and aromatic alcohols in good yields to their corresponding carbonyl compounds in apoptotic solvents at temperature of 38°C and in the CH_2Cl_2 as solvent, so one advantage in using this reagent is the mild condition of the reaction system [25]. The ligand (i) has N and O donor atoms and pyridine ring in its structure, so can create stable complexes with Pb^{2+} . Also, the polymer structure of ligand (i) provides a much-needed hydrophobic environment (Fig. 1.).

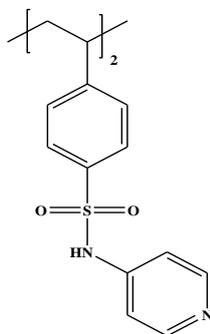


Fig. 1: The structure of ionophore Poly 4-N-pyridine parastyrene sulfonamide (ligand i).

2.4 Carbon paste electrode preparation

For the preparation of the modified electrode, firstly different amounts of the ligand (i) along with adequate amount of graphite powder, MWCNTs and THF were quietly mixed together. Secondly sufficiency amount of

paraffin oil was added to the above mixture and again it was completely blended together. The obtained paste was carefully packed into a polypropylene electrode holder (3mm i.d).For electrical contact a copper wire was used into the polypropylene electrode holder. The prepared electrode surface was carefully polished with soft paper. Finally the modified carbon paste electrode was preconditioned by placing to $1.0 \times 10^{-4}M$ of $Pb(NO_3)_2$ solution at pH of 7(adjusted with appropriate buffer) for 24h.

2.5 Emf measurements

The potential measurements were carried out by using the following assembly. $Hg/Hg_2Cl_2, KCl(satd.) | test\ solution | carbon\ paste\ electrode$. For all emf measurements saturated calomel electrode as reference electrode was used at 25°C. In all experiments the solutions were stirred until the system response remained constant. The activities of different ions were calculated according to the debye-Huckel equation ($\log \gamma = -0.511Z^2[\mu^{1/2}/(1 + 1.5\mu^{1/2}) - 0.2\mu]$) [34].

Where μ is the ionic strength, Z the valiancy and γ is the activity coefficient.

3 Results and Discussion

3.1 Electrode composition and modification

The selection of carbon paste components (Carbone powder and binder), the components ratio in the paste, the paste preparation method (paste tempering, homogenization and compacting of paste in the electrode body etc.), the modifier type and its amount are affective on the carbon paste electrode performance (sensitivity and selectiveness) [35–36]. Therefore, to obtain the optimized composition of Carbon paste for $Pb(II)$ ion potentiometric measurements, several electrodes with different electrode components compositions were prepared.

For this purpose, in this study different ration of MWCNTs and poly 4-N-pyridine para styrene sulfonamide were used to find their optimum ration to measure Pb^{2+} concentration by modified electrode. Therefore, many modified electrodes were made by using different ration of MWCNTs and ligand (i). The electrodes were tested to measure Pb^{2+} concentration which their results have been summarized in Table 1. As can be seen, the results related to electrode (No. 1) didn't indicate any corrective response in absence of MWCNT and present of ligand (i) in carbon paste modified electrode. The prepared electrode exhibited a Nernstian response for concentrations from 0.01M to $3.1 \times 10^{-6}M$ (No. 3). When in composition of electrode was used both carrier and MWCNTs significantly increased selectivity and linear range concentration of ion selective electrode from 0.1M to $5.0 \times 10^{-8}M$ (No. 4) because using MWCNTs increases electrical conductivity as a result the dynamic working range and response time improve. Conforming to results of in Table 1, the best detection limit($6.0 \times 10^{-9}M$) was obtained when that electrode was composed of 6.0 wt% ligand, 62.0 wt% graphite powder 20 wt.% paraffin oil and 12wt% MWCNTs (No. 7) and this electrode exhibited a good Nernstian slope about (-29.43mV/decade). The results shown that slope and dynamic range of calibration carve depend on modifier ration in carbon paste. Also the results showed that the modified electrode for other metal cations didn't have a Nernstian slope and a wide linear range of concentration (Fig. 2.)

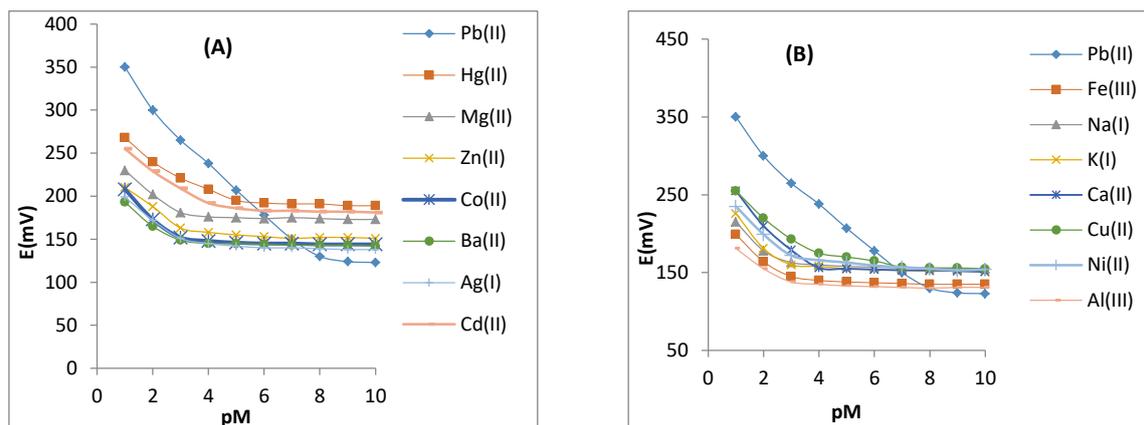


Fig. 2: Potential responses of carbon paste electrode based on ligand and MWCNTS for different metal ions (A and B).

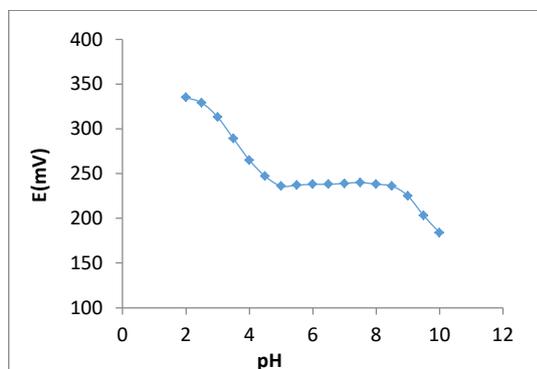
Table 1: The optimization of the carbon paste ingredients.

Composition (%)					Performances		
No.	GP ^a	PO ^b	MWCNTs ^c	carrier ^d	Slope(mV/dec)	DL(pM) ^e	LR(pM) ^f
1	75	25	-	-	-	-	-
2	70	20	10	-	-18.42	2.3	(1.0-2.1)
3	74	20	-	6	-28.61	5.7	(2.0-5.5)
4	64	20	12	4	-29.22	7.5	(1.0-7.3)
5	62	18	12	8	-30.43	7.8	(1.0-7.6)
6	60	20	14	6	-29.61	7.0	(1.0-6.8)
7	62	20	12	6	-29.43	8.2	(1.0-8.0)
8	60	22	12	6	-28.13	6.6	(1.0-6.4)

^a Graphite powder^b Paraffin oil^c Multi wall carbon nano tubes^d Ionophore^e Detection limit^f Linear range

3.2 Effect of pH on the response of the electrode

The effect of pH on the electrode potential response for a fixed concentration of Pb^{2+} solution ($1.0 \times 10^{-4} M$) was investigated by adding adequate amount of HNO_3 or $NaOH$ solution to change pH in the range of 2.0 to 10. The variation of electrode potential response due to changing of pH is shown in Fig. 3. As a result, the electrode potential response remained almost constant at pH range of 5.0 to 8.5. Intensive changes of electrode potential response were observed at pHs higher than 8.5 and lower than 5.0. The decrease of potential below pH 5.0 can be attributed to protonation of the N atoms of the ligand (i) [37].

Fig. 3. pH effect on the potential response of the Pb^{2+} modified CPE for $1.0 \times 10^{-4} M$ Pb^{2+} solution.

On the other hand, the decrease in electrode potential response in the pHs of more than 8.5 can be due to the formation of Pb^{2+} hydroxyl complexes which can reduce

concentration of Pb^{+2} . Therefore, less amount of Pb^{2+} will remind to form complex with the ligand (i). As pH of 7 can show a suitable electrode potential response in, all of remaining experiments were carried out at pH of 7. In order to have a stable pH a buffer solution was used.

3.3 Response time and Reversibility

The response time of an ion-selective electrode is an important factor that is estimated for each work. As we know, response time was specified as the demanded time for the electrodes to reach a cell potential of 90% of the final equilibrium values [38]. The electrode response time depends on electrode composition. The curve of electrode potential response versus time was plotted. The response time was determined from intersection of two extrapolated sections of curve. The electrode response was got constant after 20 seconds so the response time of 20 seconds was used in subsequent potential readings. (Fig. 4) In order to evaluation of response time for the modified electrode, the lead ion concentration was changed in the range of $1.0 \times 10^{-4} M$.

In order to evaluate the reproducibility of the lead sensor, the practical response time was investigated by changing the lead ion concentration in range of 1.0×10^{-1} to $1.0 \times 10^{-8} M$ (Fig. 5). The results show that the sensor responses repeatedly in range of desired. Also the responses of sensor from one concentration to the other and contrariwise were highly reproducible.

The relative standards deviations (RSD %) for low and high $Pb(II)$ ion concentrations were calculated by six times measurements for each concentration. The calculated RSD% for concentration of 1.00×10^{-8} and $1.00 \times 10^{-1} M$ was ± 0.19 and ± 0.13 , respectively.

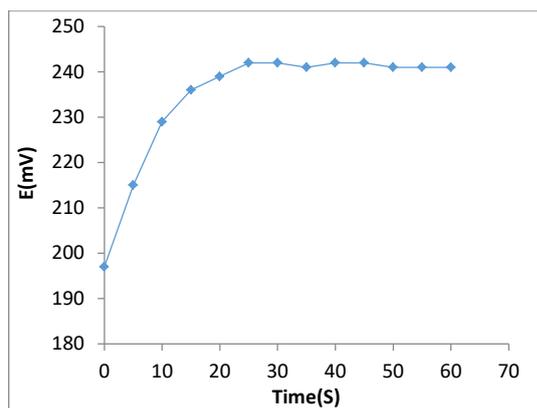


Fig. 4: Plot of time- potential response modified (No. 7) electrode ($1.0 \times 10^{-4} \text{M}$).

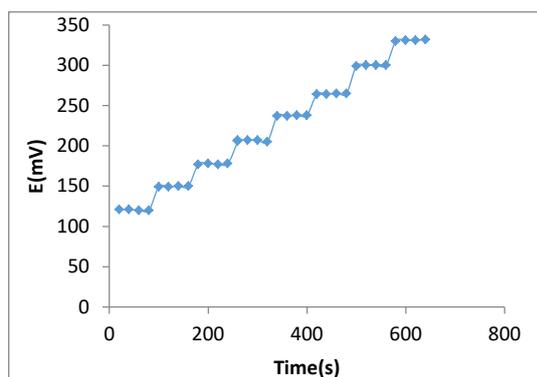


Fig. 5: Dynamic response time of modified carbon paste electrode with MWNTs and ligand (i) in the range of 1.0×10^{-1} to $1.0 \times 10^{-8} \text{M}$

These RSD% values show that the electrode manner in recording potential from low to high concentration was the same as from high to low concentration. These results confirm the electrode responses repeatability in any concentration. Furthermore, for evaluation of the electrode repeatability, several electrodes with optimized composition were made and were tested with Pb(II) ion standard solutions. The responses of the electrode in different tests shown that they are extremely close to each other which it sings of good repeatability of the electrode.

3.4 Electrode lifetime

The electrode lifetime is a period of time in which the electrode performance factors such as slope, linear range and the limit of detection respect to intended species would not change considerably. According to IUPAK suggestion, the lifetime is a period of time in which the electrode sensitivity would reduce to 90 % of its initial value. In the other definition the electrode lifetime is a period of time in which the sensor sensitivity would be more than 70% of Nernstian one [38]. To study the modified Carbone paste electrode lifetime, the electrode was daily used to determine the concentration of Pb(II) ion in standard solution of lead nitrate for 1 hour in day during 8 weeks. After this time there was not considerable change in electrode performance.

3.5 Interference studies

One of the most important ion selective electrode properties is its selectivity which shows the trustworthy of the electrode response. According to definition, all existed species in solution that are effective on the measured potential except the specie that is measured is called inhibitor. The Potentiometric Selectivity coefficient ($K_{A,B}^{\text{Pot}}$) shows the ratio of electrode response of inhibitor ion (B) to electrode response of main ion (A). For this purpose, different methods are used such as separate solution method (SSM) [39], fixed interference method (FIM) [40] and matched potential method (MPM)[41]. In this study fixed interference method was used. In this method, selectivity coefficients of the Pb^{2+} sensor were evaluated graphically with a fixed concentration of the interfering ions (0.1M) and different amounts of the Pb^{2+} ion (1×10^{-1} - $1 \times 10^{-8} \text{M}$), that was calculated by using, Nikolsi-Eizenman equation:

$$k_{A,B}^{\text{pot}} = \frac{a_A}{a_B^{(z_A/z_B)}}$$

where a_A is activity of the primary ion, a_B is constant activity of the interfering ion and z is the charge of ion. In this investigation ,monovalent (Na^+ , K^+ and Ag^+), divalent (Ca^{2+} , Hg^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Mg^{2+} , Ba^{2+} and Co^{2+})and trivalent (Al^{3+} , Fe^{3+}) ions were applied as interfering ions. Results in the presence of interfering ions for the Pb^{2+} have been listed in Table 2. Interfering of various ions followed the underlying model: $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ag}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Al}^{3+} > \text{Fe}^{3+}$

Table 2: The selectivity coefficients of various interfering cations for Pb(II)CPE with fixed interference (FIM) methods.

$\text{M}^{\text{n+}}$	$\log k_{\text{Pb,B}}^{\text{pot}}$	$\text{M}^{\text{n+}}$	$\log k_{\text{Pb,B}}^{\text{pot}}$
Na^+	-5.54	Hg^{2+}	-3.36
K^+	-5.33	Zn^{2+}	-4.18
Cu^{2+}	-4.12	Cd^{2+}	-3.43
Ba^{2+}	-4.96	Co^{2+}	-4.51
Ca^{2+}	-4.78	Al^{3+}	-5.58
Mg^{2+}	-4.83	Ag^+	-4.74
Ni^{2+}	-3.65	Fe^{3+}	-5.65

Also characteristics of modified electrode in this study were contrasted with other works that were listed in Table 3.

3.6 Detection limit, Calibration Curve and Linear range

The sensitivity of ion selective electrode defines as the slope of calibration potential versus the logarithm of main ion activation curve in linear section which is $2.33 \frac{RT}{nF}$ for ideal Nernstian electrodes. The measurement range of ion selective electrode includes the linear section of calibration curve. [50]. A calibration curve was plotted at various concentration of Pb^{2+} (between $1.0 \times 10^{-1} \text{M}$ and $1.0 \times 10^{-10} \text{M}$) to determine of detection limit. Then detection limit was evaluated from the intersection of the two extrapolated sections of the above calibration curve at the lowest portion (Fig. 6) [51]. After application of the above mentioned method, detection limit was obtained around $6.0 \times 10^{-9} \text{M}$.

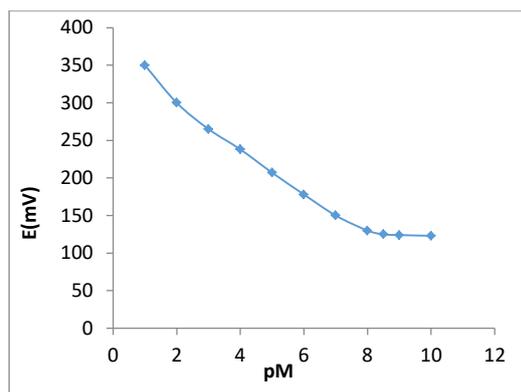


Fig. 6: The calibration curve of the CPE at varying Pb^{2+} concentrations (1.0×10^{-1} to 1.0×10^{-10} M) in the solution.

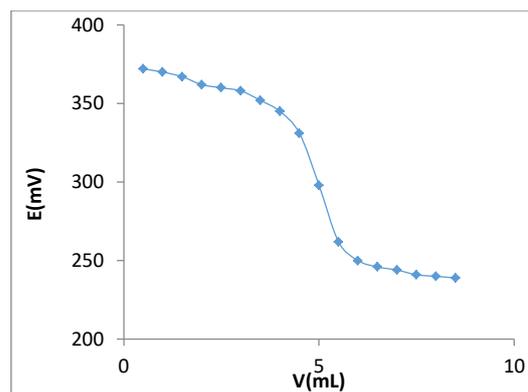


Fig. 7: Potentiometric titration plot of a 50.0mL 0.001 $Pb(NO_3)_2$ M solution with 0.01 M Na_2SO_4 solution.

3.7 Analytical application

3.7.1 Potentiometric titration

To distinguish the applicability of the modified electrode, it was applied as an indicator electrode in potentiometric titration of 50.0 mL 0.001 M $Pb(NO_3)_2$ solution with 0.01 M Na_2SO_4 solution (Fig. 7.). As can be seen in Fig. 5, this electrode can be successfully used for determination of sulfate ions in solutions.

3.7.2 Determination of Pb^{2+} in different wastewaters

The modified electrode was also applied to the determination of Pb^{2+} ion in real samples of wastewater from Isfahan's Mobarkeh steel company and ZobAhan Company (Table 4). Concentration of Pb^{2+} in the above mentioned samples was measured by using two methods including (1) modified electrode and (2) atomic absorption spectrometer. Then results were compared with each other. The results demonstrated that there are good agreements between obtained data of them.

Table 3: Comparison of the response characteristics of different Pb^{2+} ion-selective electrodes

No.	Modifier	slope	LOD	Linear range	ref
1	MWCNTs and nanosilica	29.8 ± 0.2	7.3×10^{-8}	$1.0 \times 10^{-2} - 1.0 \times 10^{-7}$	42
2	-2-aminothiophenol functionalized MWCNTs	29.5 ± 0.3	3.2×10^{-10}	$1.0 \times 10^{-2} - 5.9 \times 10^{-10}$	43
3	4-tert-butylcalix[6]arene	30.0 ± 0.1	6.0×10^{-7}	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$	44
4	N,N'-Bis-thiophen-2-ylmethylene-pyridine-2,6-diamine	29.5	1.8×10^{-6}	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$	45
5	1, 5-diphenylthiocarbazone	29 ± 0.2	3.4×10^{-6}	$1.0 \times 10^{-2} - 5.0 \times 10^{-6}$	46
6	polyaminoanthraquinone particles	28.9	7.7×10^{-7}	$1.0 \times 10^{-1} - 2.5 \times 10^{-6}$	47
7	Poly(n-butyl acrylate)	26.2	-----	$1.0 \times 10^{-2} - 1.0 \times 10^{-9}$	48
8	1,4,8,11-Tetrathiacyclotetradecane	29.9	2.2×10^{-6}	$1.0 \times 10^{-2} - 1.0 \times 10^{-5}$	49
This work	(MWCNTs) and poly 4-N-pyridine para styrene sulfonamide	-29.4 ± 0.3	6.0×10^{-9}	$1.0 \times 10^{-1} - 1.0 \times 10^{-8}$	---

Table 4: Determination of Pb^{2+} in waste waters

No.	sample	Pb^{2+} added (ppm)	Pb^{2+} concentration (ppm)	
			CPE ^a	AAS ^a
1	waste water ^b	-	$0.035 (\pm 0.4)$	$0.029 (\pm 0.3)$
2	waste water ^b	0.2	$0.230 (\pm 0.2)$	$0.228 (\pm 0.2)$
3	waste water ^c	-	$0.039 (\pm 0.3)$	$0.034 (\pm 0.3)$
4	waste water ^c	0.2	$0.242 (\pm 0.2)$	$0.236 (\pm 0.2)$

^aThe average of three measurements.

^bMobarakeh steel co

^cZobAhan co

4 Conclusion

The simultaneous using of Carbon nanotubes and ligand as the modifier of Carbon paste electrode for partial measurement of $Pb(II)$ ion in the aqueous samples shown a good results. The electrode responded to $Pb(II)$ ion in a good Nernstian slope and a low limit of detection 6×10^{-9} M. Also, the prepared electrode exhibited wide linearity in concentration of $Pb(II)$ ion between 1×10^{-1} and 1×10^{-8} M. The results shown that the most of metal ions could not create serious interfere for the selectivity of the carbon paste electrode. Thus the modified electrode with an efficient performance, long lifetime and low cost can be used for accurate determination of $Pb(II)$ ions in the

aquatic samples. This electrode was used in the actual situation to detect the $Pb(II)$ pollution in wastewater like Isfahan's Mobarkeh steel company and ZobAhan Company accurately. Also, the electrode was successfully used for $Pb(II)$ ion potentiometric titration of sulfate anion in samples with trace $Pb(II)$ amounts.

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