ORIGINAL RESEARCH PAPER

Preparation a multi-walled carbon nanotubes-carbon paste electrode based on a sulfanyl phenyl Schiff's base for selective determination of mercury(II) in environmental water samples

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ABSTRACT

The electrochemical property of a recently synthesized ligand, 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol has been investigated with the construction of a modified carbon paste electrode to find out of mercury ions in real samples. To modify the electrode, paraffin oil and multi-walled carbon nanotubes (MWCNT) were used as binder and modifier respectively. Under the optimized conditions, the electrode exhibits a Nernstian slope of 30.0±0.2 mV per decade for mercury(II) ions over a broad concentration range 1×10^{-7} to 1×10^{-1}M with a R^2 value of 0.996 at pH 4.5 in a 5 sec response time. The detection limit of the method for Hg^{2+} was 2.3×10^{-8} mol l^{-1}. The influence of several potentially interfering ions such as K^+, Ag^+, Cd^{2+}, Ni^{2+}, Ca^{2+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}, La^{3+} and Fe^{3+} on the determination of Hg^{2+} was studied and no significant interference was observed. The proposed modified carbon paste electrode was successfully applied to the determination of mercury ions in real water samples.

Keywords: *Hg-Selective Electrode, Modified Carbon Paste, MWCNT, Potentiometry, Sulfanyl Phenyl Derivative*

INTRODUCTION

Recently, different physical, chemical and biological methods can be used to contamination removal from wastewater. Some of them involve coagulation, foam flotation, ion exchange, adsorption, electrolysis, chemical precipitation, and membrane process. The Adsorption technique is interesting methods because has been found to be more effective and low-cost treatment process to remove pollutants of water [1-10]. Diseases such as hearing loss, mental deterioration, dialogue difficulty, impaired vision, vestibular dysfunction, and autism have been reported by Mercury which is one of the most toxic elements in the world [11].

Atomic spectroscopic methods are powerful analytical techniques for the determination of elements in a great number of samples. However, these techniques are quite expensive and time-consuming and may not be obtainable in all the laboratories. Thus, the development of uncomplicated methods for selective determination of mercury in trace amounts in different matrices is serious [12]. Electrochemical methods offer several advantages over these methods, such as ease of use, low cost, direct detection, miniaturization, and fast response times. Modified carbon paste electrodes are simple and selective tools for the determination of heavy metal ions that have been extensively developed in recent years. The operation mechanism of such modified carbon paste electrodes depends on the properties of the modifier materials used to import selectivity towards the target species [13].

The aim of this work is to introduce a potentiometric carbon paste electrode (PCPE) for Hg^{2+} determination based on its complexation reaction with 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol, L as an excellent ion carrier with N, O and S as donor atoms. For this point, the spectrophotometric of the complex is carefully studied. The new synthetic

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ligand, **L,** then mixed with graphite powder, MWCNTs and paraffin oil for constructing of a selective CPE sensor to the potentiometric determination of Hg^{2+} in environmental water samples.

L
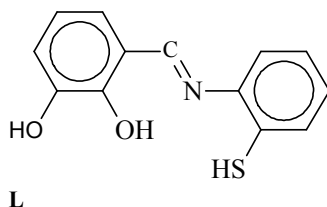
EXPERIMENTAL
Material and instruments

High viscosity paraffin (density=0.88 g cm^{-3}) from Fluka was used as the pasting liquid for CPE. Graphite powder (particle diameter=0.10 mm) from Merck and MWCNT with purity >95%, from Nanostar Tech. Co., Tehran, Iran were used as the working electrode substrates. All other reagents were of analytical reagent grade and were used as received. Double-distilled water was used throughout and test solutions were buffered in a 0.02 mol L^{-1} solution of acetic acid/sodium acetate and pH adjusted by the addition of 1 mol L^{-1} sodium hydroxide or hydrochloric acid solutions.

A Jenway (USA) model 3020 pH meter with a combined glass electrode was used after calibration against standard Merck buffers for pH determinations. A Shimadzu (Japan) model 1650PC double-beam spectrophotometer was used for running the electronic absorption spectra (controlled to ±0.1 °C). A totally glass Fisons (UK) double distiller was used for the preparation of doubly distilled water. 1H, 13C NMR spectra were recorded at 298K on a Bruker AM 500 instruments (1H: 500.130 MHz; 13C: 125.758 MHz). Infrared spectroscopy measurement was recorded in the range 400–4000 cm^{-1} on a Shimadzu FT-IR spectrometer model 8400S (Japan). The mass spectra measurement was performed using Shimadzu GC-MS spectrometer model 17A-QP5050.

Preparation and Characterization of Schiff's base 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol (L)

The new Schiff's base L, with the chemical name of 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol, was synthesized and purified from the reaction between 2-aminobenzenethiol and 2,3-dihydroxybenzaldehyde in ethanol [14,15]. The yellow solid product was filtered and the product was recrystallized from ethanol. The L was characterized

by FT-IR, 1H NMR, 13C NMR and Mass spectroscopy and the analytical data are as follows: $C_{13}H_{11}NO_2S$, Yield: 75%; mp: 96 °C. IR (KBr): υ_{O-H}=3450, υ_{S-H}=2525 and $\upsilon_{C=N}$=1600cm^{-1}. 1H NMR (500 MHz, DMSO): δ = 3.00 (S*H*), 4.11-4.73 (2H, OH phenolic), 6.80-7.56 (7H, Ar–*H*), 8.05 (1H, *H*C=N). 13C NMR (125 MHz, DMSO): δ = 118.16, 118.95, 119.87, 122.46, 122.51, 125.63, 127.00 (C-ring), 146.76 (1C, C-N), 151.85 (1C, C=N). MS: m/z (%) = 245.0 (M$^+$).

Procedures

The modified carbon paste was prepared by hand mixing different amounts of the graphite powder, MWCNTs, paraffin oil and new synthetic ligand with a mortar and crusher. The mixture was packed into polyethylene syringes (2.5 mm diameter). Electrical contact to the carbon paste was established via inserting a thin copper wire thorough flank. For all measurements the modified carbon paste electrode as an indicator electrode and the Ag/AgCl as a reference electrode were placed in the different concentrations of Hg(II) solutions. The potential was recorded after each Hg(II) addition, and then plotted as a logarithmic function of Hg(II) activity.

RESULTS AND DISCUSSION
Preliminary Studies

3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol shows an absorbance maximum at about 310 nm. By increasing the addition of Hg^{2+}, a decrease in absorbance is observed at this wavelength as shown in Fig. 1. For most of the other studied metal ions, i.e., Ag^+, Cd^{2+}, Ni^{2+},
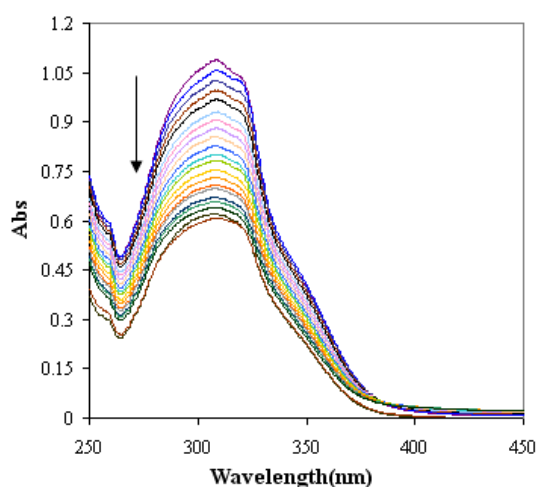

Fig. 1. Absorbance spectra of a 1×10^{-5} mol l^{-1} solution of L in methanol, at different Hg^{2+} concentrations. The arrow shows the direction of absorbance changes by increasing the metal ion concentration.

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Zn^{2+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, Co^{3+}, Mn^{2+}, Al^{3+} and Fe^{3+} negligible or small variations in the absorbance maximum are observed by increasing the same mole ratio of corresponding ions. According to the shape reported in Fig. 2, it should be noted that the largest variation is observed for Hg^{2+}, while for the other studied ions variation is unimportant. Based on the relatively high selectivity of **L** for Hg^{2+}, as was concluded from its absorbance variation, the mentioned compound, L was expected to act as a proper ionophore in preparation of novel ion-selective carbon paste electrode for Hg^{2+} ion [16].

Thus, in preliminary experiments, **L** was used as a neutral carrier to prepare carbon paste electrodes (with the same composition) for a variety of metal ions. The potential responses of various ion selective electrodes based on L are shown in Fig. 3.

As it can be seen, except for the Hg^{2+} ion, the excepted Nernstian slopes (59, 29.5 and 20 mV per decade for the mono-, di- and trivalent cations, respectively) were not observed for other metal ions. This is maybe due to the high selectivity of the ionophore for mercury ions over other metal ions, as well as the rapid exchange kinetics of the resulting ligand Hg^{2+}-L complex [17].

The Influence of Carbon Paste Electrode Composition

Because for a given ionophore, the selectivity and sensitivity of the carbon paste electrodes-based on the sulfanyl phenyl derivative depend significantly on the carbon paste composition, the nature and amount of liquid and chemical additions used. The influences of these parameters on the potential response of the Hg(II) electrodes were investigated.
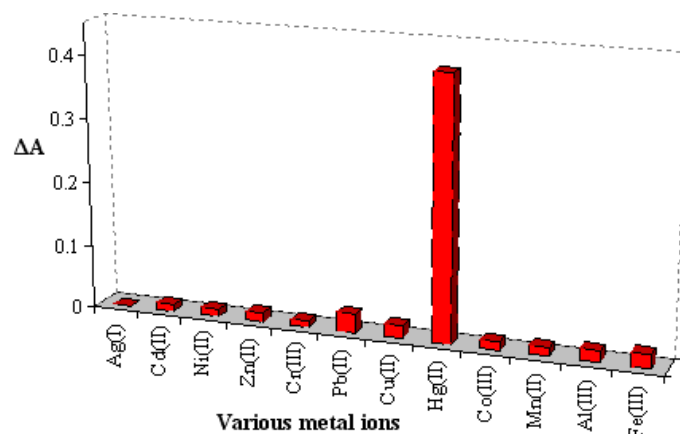

Fig. 2. The absorbance variations of the methanolic solutoion of 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol at maximum wavelength for all the ions studies.
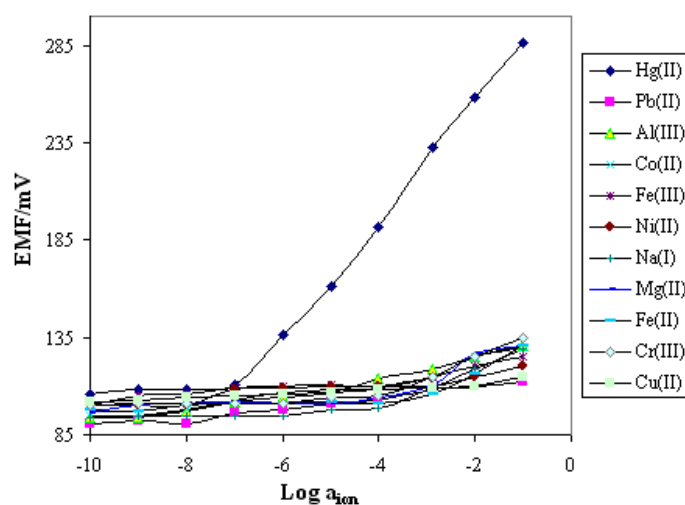

Fig. 3. The potential responses of various ion-selective electrode based on the 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol.

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Therefore, different carbon paste compositions were tested and the results were summarized in Table 1. The ion carrier is the most important component of any ion-selective electrodes. To test the selectivity of the sulfanyl phenyl derivative as well as the role of the composite concentration on its behavior, the ionophore was used to fabricate a series of nano-composite CPEs having a variety of compositions.

A liquid for use as pasting in a carbon paste electrode should complete certain conditions. They should be sufficiently chemically inert, insulating, nonvolatile, water-immiscible, and forming paste mixtures of fine uniformity. By means of paraffin oil in the carbon paste electrodes yields more efficient extraction of ions with high charge density into the carbon paste surface. In addition, with MWCNTs in the composition of the carbon paste not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of

the sensor improves to Nernstian values. Also, using MWCNTs leads to the expanding of the surface of paste by fabrication of three-dimensional nanostructures, as well as diminishing the ohmic resistance of the paste [13,18].

Obtained results from Table 1, indicate that the MWCNTs-modified carbon paste electrode with the graphite powder/paraffin oil/sulfanyl phenyl derivative/MWCNTs percentage ratio of 65/22.5/2.5/10 was selected as the optimized composition for the preparation of the Hg-selective electrode (no. 6). It exhibited a Nernstian slope of $30.0\pm(0.2)$ mV decade^{-1} in a wide mercury ion concentration range between 1.0×10^{-7} and 1.0×10^{-1}M (Fig. 4). The LOD for the electrode was equal to 2.3×10^{-8}M. This LOD was calculated when the linear regions of the calibration graphs were extrapolated to the baseline potentials [19].

Effect of pH of the Test Solution

The responses of Hg^{2+}-CPE based on 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol towards pH changes in aqueous solution are very important parameters, which allow to

Table 1. The optimization of the MWCNTs- modified carbon paste mercury(II)-selective electrode.

| Entry	Composition (wt%)				Electrode characteristics			
	Ligand (mg)	Graphite powder(mg)	Paraffin Oil(mg)	MWCNT	Slope (mV decade^{-1})	R^2	LR(M)	LOD
1	_	66	23	11	7.0501±0.3	0.958	$10^{-3}\times10^{-6}$-1×1	2.2×10^{-6}
2	1	66	23	10	15.481±0.2	0.990	1×10^{-7}-1×10^{-4}	3.1×10^{-7}
3	0.5	66.5	23	10	19.34±0.4	0.990	1×10^{-6}-1×10^{-4}	2.5×10^{-7}
4	1.5	66.5	22.5	9.5	27.239±0.4	0.981	1×10^{-6}-1×10^{-4}	1.8×10^{-7}
5	2	65.5	22.5	10	29.954±0.2	0.930	1×10^{-7}-1×10^{-3}	1.5×10^{-6}
6	2.5	65	22.5	10	30.0±0.2	.0996	1×10^{-7}-1×10^{-1}	2.3×10^{-8}
7	5	63	23	9	15.178±0.3	0.956	1×10^{-6}-1×10^{-4}	2.4×10^{-6}
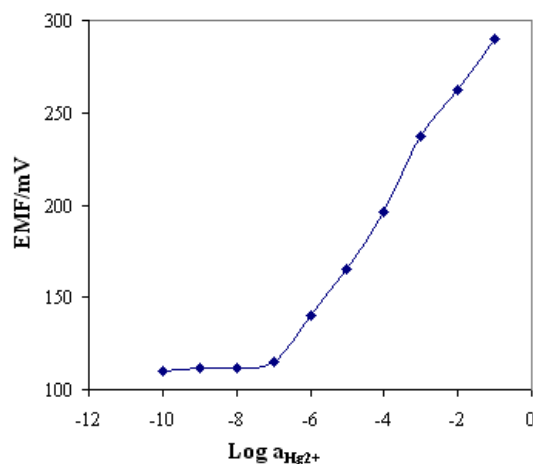
Fig. 4. The calibration curve of the Hg^{2+} electrode (composition no. 6) based on the 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol.
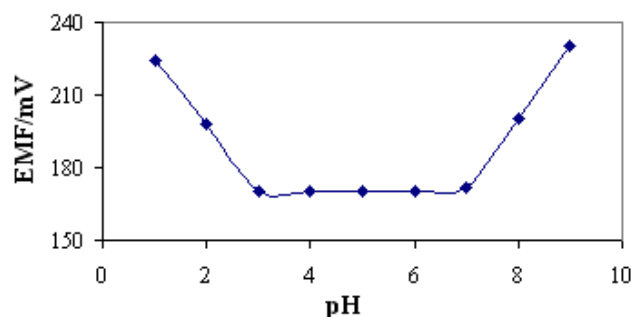
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Fig. 5. The plot of potential vs pH of MWCNT-modified carbon paste mercury electrode at 8.0×10^{-5} mol L^{-1} Hg^{2+}.
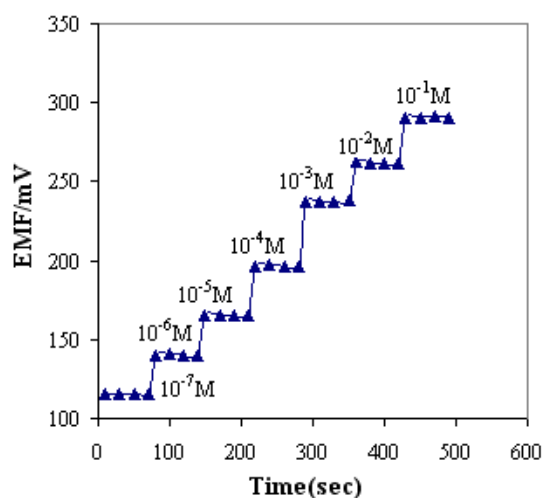

Fig. 6. The dynamic response time of the carbon paste mercury electrode for step changed in the Hg^{2+} concentration.
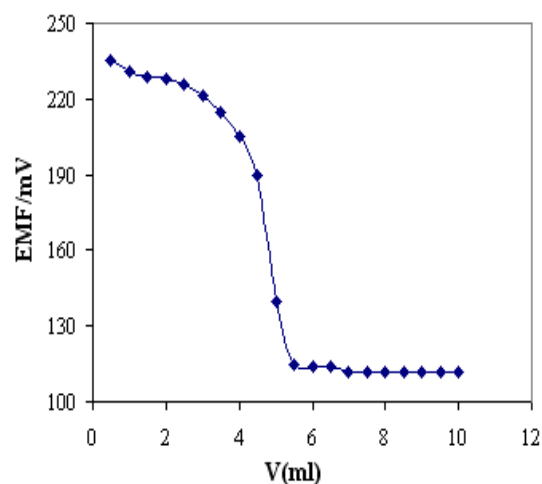

Fig. 7. Potentiometric titration curve of 50.0 mL of 1.0×10^{-3} M solution of Hg^{2+} with 1.0×10^{-2} M EDTA at pH 4.5, using Hg^{2+}-CPE based on 3-((3-mercaptophenyl) aminomethyl) benzene-1,2-diol as an indicator electrode.

optimize the measuring conditions of selected analytes and to find out the mechanism of the potentiometric responses. As seen in Fig. 5, the pH changes from 3.0 to 6.7 caused the same potential response. Beyond this range, considerable potential increased were seen. At pH<3.0, the potential increased, indicating that the electrode responded to hydrogen ion concentration while, above pH 6.7, the increased potential could be due to the response of the sensing material of the proposed electrode for alkali cations [13,20].

Dynamic Response Time of the Hg(II)-Carbon Paste Selective Electrode

Commonly, dynamic response time is an important parameter for any ion-selective electrode. Fig. 6 illustrates a representative plot of the potential changes vs time for modified carbon paste electrode based on the new synthetic ligand 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol as a neutral carrier after additions of the

Hg^{2+} ion concentrations in a series of solution from 1.0×10^{-7} to 1.0×10^{-1} mol L^{-1}. As it is obvious in Fig. 6, the electrode reaches its equilibrium response, very fast (ca. 5 sec) in the whole concentration range. This is probably due to the very fast exchange kinetics of complexation-decomplexation of Hg^{2+} with the mentioned neutral carrier on the composite interface-test solution [17,20].

Life-Time Study

The stability and lifetime of the proposed Hg(II)-carbon paste electrode were tested by four same electrodes. They were used at length of two months (1 hour per day). After their 8 week utilization, the mean slopes of the electrodes were found to be 30.0 (± 0.2) and 28.9 (± 0.1), before and after this period, respectively. Consequently, the mentioned sensors are stable within this period with a minimum lifetime of 2 months.

Table 2. Selectivity coefficients of various interfering ions for the Hg(II) sensor, calculated by two solutions method.

Interfering ion (j)	$K_{I,J}$	Interfering ion (j)	$K_{I,J}$
K+	2.0×10^{-4}	Pb^{2+}	2.1×10^{-4}
Ag+	5.1×10^{-5}	Cd^{2+}	2.5×10^{-4}
Mg^{2+}	1.2×10^{-3}	Ca^{2+}	2.0×10^{-3}
Co^{2+}	2.9×10^{-3}	La^{3+}	3.0×10^{-3}
Fe^{2+}	1.4×10^{-3}	Al^{3+}	1.4×10^{-3}
Ni^{2+}	6.0×10^{-3}	Cr^{3+}	5.5×10^{-3}
Cu^{2+}	6.0×10^{-3}	Fe^{3+}	5.5×10^{-3}

Potential Responses of the Hg(II)-Carbon Paste Selective Electrode

The influence of interfering ions on the potential response behavior of the ion-selective electrodes is usually described in terms of the potentiometric selectivity coefficients, $K_{I,J}$. In this work, the potentiometric selectivity coefficients were determined by the two solutions method (TSM) that is based on the Nikolsky–Eisenman equation [21]. This method involves measuring potentials of a pure solution of the primary ion (1.0×10^{-3} mol l^{-1}), E_I, and a mixed solution containing the primary and interfering ions, E_{I+J}. The potentiometric selectivity coefficient is calculated by inserting the value of the potential difference, $\Delta E = E_{I+J} - E_I$, into the following equation:

$$K_{I,J} = \{ a_{I (e}{}^{\Delta E \times Z_I \times F / (RT)} {}_{-I)} \} / \{ a_J {}^{(Z_I / Z_J)} \} \qquad (1)$$

where a_I and a_J are the activities of analyte and interferent ions. When the selectivity coefficient is

1.0 the membrane responds equally to the analyte and the interferent. As seen in Table 2, the selectivity coefficients are in the order of 10^{-2} or lower, which seems to indicate that these cations have negligible contact on the functionality of the proposed Hg(II) membrane sensors.

Analytical Application of the Hg(II)-Carbon Paste Selective Electrode

The optimized Hg(II) selective electrode was found to work well under laboratory conditions. The Hg(II)-carbon paste selective electrode based on **L** was successfully applied as an indicator electrode in the successful titration of a Hg^{2+} (1.0×10^{-3}) with EDTA (1.0×10^{-2}) at pH 4.5. The resulting titration curve is shown in Fig. 7. As can be seen from Fig. 7, the endpoint of the titration is sharp and the number of mercury ions can be accurately determined from the resulting titration curve with the proposed electrode. The applicability of the Hg(II) selective electrode was tested to the recovery of Hg^{2+} ion in several natural water samples collected from the west of Iran. Data in Table 3 clearly revealed that the amount of mercury in the real water samples can be accurately determined by the proposed selective electrode without any primary sample treatment.

Comparison

Table 4 compares the main analytical characteristics (i.e., sensing material, type of sensor, linear range, detection limit, slope, response time, interferences, the working pH range and

Table 3. Determination of Hg^{2+} content in different real samples. The experimental conditions are as in Fig. 7.

Samples	Hg(II) ion (mol L^{-1})		
	added	found	% recovery
Tap water 1	1.0×10^{-3}	$9.98(\pm0.06) \times 10^{-4a}$	99.8
Tap water 2	1.0×10^{-4}	$1.01(\pm0.11) \times 10^{-4}$	100.1
Tap water 3	1.0×10^{-5}	$9.88(\pm0.18) \times 10^{-6}$	98.8
Spring well sample	1.0×10^{-5}	$1.03(\pm0.10) \times 10^{-5}$	103

^{a}mean of three determinations.

Table 4. Comparison of the characteristics of the proposed sensor with those of the previously reported Hg^{2+} sensor.

Compared parameter	Ref. 3	Ref. 10	This work
Sensing material (Ionophore)	1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triazene	Ethyl-2-(benzoylamino)-3-(2- hydroxy-4- methoxy phenyl)-2-propenoate	3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol
Type of sensor	CPE^a	CPE	CPE
Linear range (M)	$5.0 \times 10^{-9} - 1.0 \times 10^{-4}$	$3.0 \times 10^{-7} - 3.1 \times 10^{-2}$	$1 \times 10^{-7} - 1 \times 10^{-1}$
Detection limit (M)	2.5×10^{-9}	1.0×10^{-7}	2.3×10^{-8}
Slope (mV/decade)	29.3±(0.2)	48.5±(1.0)	30.0±(0.2)
Response time (sec)	ca. 5	ca. 5	ca. 5
Interferences	No interference	No interference	No interference
Working pH range	2.0–4.3.	1.0–4.0	3.0–6.7
Method of selectivity determination	FIM & MPM	FIM	TSM

^{a}carbon paste electrode.

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method of selectivity coefficients determination) of the represented electrode based on 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol with those of some of the previously reported sensors for the determination of Hg^{2+} [13,20]. Due to the advantages of the proposed method with respect to previously reported ones, it may be used as an alternative method for Hg^{2+} determination.

CONCLUSIONS

In the current study, the modified carbon paste selective electrode based on 3-((3-mercaptophenyl) aminomethyl)benzene-1,2-diol and MWCNTs are introduced for the Hg^{2+} determination. This electrode presented the best response characteristics with a Nernstian slope behavior of 30.0 ± 0.2 mV per decade for the Hg^{2+} ions at pH 4.5, over a concentration range of 1×10^{-7} to 1×10^{-1} M with a detection limit of 2.3×10^{-8} M and a fast response time of 5 sec. The proposed electrode system found to work well under laboratory conditions. It was successfully used as indicator electrode for the titration of Hg^{2+} ions with known EDTA solutions and also applied to the quantitative recovery of low levels of mercury ions from tap water samples.

ACKNOWLEDGMENTS

CONFLICTS OF INTEREST

There are no conflicts to declare.

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