

Full Paper

Carbon Nanotube Composite Coated Stainless Steel Disk Electrode with Polypyrrole Film as Ion-to-electron Transducer for the Determination of Hg(II)

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Abstract- An ion-selective electrode for mercury (II) ion is fabricated based on primarily electrodeposition of polypyrrole on the surface of stainless steel electrode, followed by coating with multiwall carbon nanotubes (MWCNTs), poly (vinyl chloride) (PVC) composite membrane which is modified with a new enamine ionophore. Polypyrrole film because of its good stability and conductivity was prepared as an intermediate layer of solid contact electrode. The combination of conducting polymers with those of MWCNTs leads to an improved performance of the resulting sensing devices. The electrode showed a Nernstian slope of 29.34 ± 0.25 mV decade⁻¹ over a wide concentration range of 5.0×10^{-7} to 1.0×10^{-2} M with the detection limit of 1.4×10^{-7} M of Hg(NO₃)₂. The proposed electrode exhibited a very good selectivity toward Hg (II) ion over a variety of metal ions. The response of this nanocomposite membrane electrode remains stable for at least two months without observing any considerable deviation. The practical applicability of this sensor as an indicator electrode in potentiometric titration of Hg (II) ions with EDTA and in titration of mixed halides are demonstrated. This electrode was also successfully applied for the determination of mercury ions in river water samples.

Keywords- Carbon nanotube, Polypyrrole, Sensor, Mercury (II) coated ion selective electrode, Solid-contact electrode

1. INTRODUCTION

Mercury is one of the most important environmental contaminants and is an element of the health concerns. The effects of short-term, high-level exposure to the various forms of mercury are well-established. The chronic exposure of humans to elemental or inorganic mercury, which might be experienced in some occupational situations, has been shown to result in persistent damage to the central nervous system and a wide range of effects including progressive anemia, gastric disturbance, excessive salivation and a metallic taste in the mouth and tenderness of the gums [1]. Accurate determination of mercury in environmental samples is recognized to be essential for assessing environmental quality such as the toxicity and its ability to bioaccumulation in living organisms [2].

The most frequently used techniques for quantification of Hg^{2+} are atomic absorption/emission spectrometry (AAS/AES) [3], inductively coupled plasma mass spectrometry (ICPMS) [4], atomic fluorescence spectrometry (AFS) [5], high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [6] and flame photometry [7]. Although these methods are powerful techniques for the determination of Hg^{2+} but they require sophisticated and expensive instrumentation, skilled personnel, complicated sample preparation and long period of time measurement.

Ion-selective electrodes (ISEs) based on a polymeric membrane with ion-carriers have now become a routine analytical tools in the fields of environmental, medicinal and agricultural analysis. ISEs offer several advantages such as speed, low cost, ease of preparation, simple instrumentation, relatively fast responses, good detection limit, wide dynamic ranges and reasonable selectivity [8,9].

Most of previous mercury selective electrodes have classical arrangement, such as internal solution ion-selective electrodes (IS-ISEs). A promising direction in ion-selective electrode development is the all-solid-state construction, where the internal solution, typical for a classical construction, is eliminated. Research and development of solid-contact ISEs (SC-ISEs) had already started in the beginning of the 1970 s with the invention of the coated-wire electrode (CWE) [10]. Absence of a liquid phase eliminates risk of leakage or need of refilling; it also enables miniaturization and shapes tailoring. Furthermore CWEs are extremely simple, inexpensive and easy to prepare. The main drawback of the CWEs is obviously the poor potential stability resulting from the blocked interface that forms between the purely electronic conductor (metal) and the purely ionic conductor (ion-selective membrane) as well as formation of a water layer between polymeric membrane and the solid contact [11,12]. Both sources of the instability can be eliminated by the use of lipophilic and redox-active self-assembled monolayers [13,14]. Conducting polymers are a more versatile possibility and have been extensively investigated during recent years. The preparation of these conducting polymers can conveniently be performed by electropolymerization directly in aqueous electrolyte solution containing the related monomer. Ideally, the charge transfer

process (ion recognition and signal transduction) in this kind of electrode can be described by the following steps (i) ion transfer at the membrane-solution interface, (ii) ion transport in the membrane, (iii) coupling of ion and electron transfer in the membrane, (iv) electron transport in the membrane, (v) electron transfer at the substrate-membrane interface, and (vi) electron transport in the substrate [15]. Another route to deal with potential instability is the utilization of nanocarbon materials as an ion-to-electron transfer in SC-ISEs [16-18]. This has an essential role in enhance the hydrophobicity of the membrane, therefore the eliminating undesirable water layer at the interface [19] and producing a more stable potential signal.

In this work, polypyrrole (ppy) was electrodeposited on stainless steel disk as a working electrode followed by coating ion-selective membrane on it. Stainless steel has unique features such as corrosion resistance, inexpensiveness, accessibility and good conductivity. MWCNTs were added directly into the membrane cocktail which led to more stable and sensitive membrane [20-22]. Introduction of CNTs into a polymer matrix improves the electric conductivity as well as the mechanical properties of the polymer matrix [23,24]. Furthermore MWCNT has high charge transfer properties and high surface/volume ratio of CNTs. This contribute to enlarging the contact area between the polymeric membrane and the nanotubes, thus minimizing the resistance at this interface as well [16]. Because of their complementary electrical, electrochemical and mechanical properties, the combination of the well-known characteristics of conducting polymers with those of MWCNTs lead to an improved performance of the resulting sensing devices. Moreover new synthesized Enamine has been used as an ionophore to guarantee the selectivity of proposed electrode toward the mercury ion.

Our method has many advantages, including low cost, easy preparation, requirement of a simple and inexpensive potentiometric instrument. The obtained results demonstrate that this electrode in most cases is superior to previously reported mercury-selective electrodes.

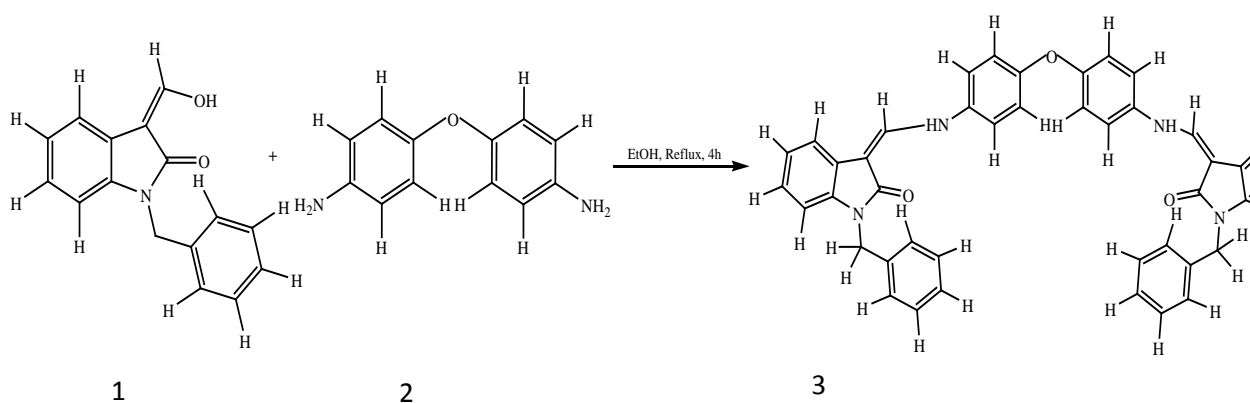
2. EXPERIMENTAL

2.1. Reagents and chemicals

PVC of high relative molecular weight was purchased from Fluka. Analytical reagent grade pyrrole, nitric acid, sulfuric acid, tetrahydrofurane (THF), acetonitrile, sodium hydroxide, nitrate salts of all the cations, K₂EDTA, sodium salt of halides, multi-walled carbon nanotubes, (all were from either Fluka or Merck chemical companies) were used as received without further purification. O-nitrophenyloctyl ether (o-NPOE), dimethyl sebacate (DMS), dibutyl phthalate (DBP), dibutylsebacate (DBS) were purchase from Fluka. All aqueous solutions were prepared with doubly distilled water. Adjustments of pH were made with dilute nitric acid or sodium hydroxide solution.

2.2. Synthesis of the ionophore 3

A mixture of (Z)-1-benzyl-3-(hydroxymethylene) indolin-2-one (0.50 g, 1.97 mmol) **1** and 4-(4-aminophenoxy) benzenamine (0.19 g, 0.98 mmol) **2** was refluxed in ethanol (20 mL) for 4 h. After cooling, a light orange solid product was filtered, washed with ethanol and dried in the air (Scheme 1). The characteristics of product **3** are as follows: (0.66 g, yield 95%); Mp: 148-150 °C; IR (KBr, cm^{-1}): 3433 (NH), 1674 (C=O); $^1\text{H-NMR}$ δ (ppm): 4.99 (CH_2 , s, 4H), 6.75–7.39 (ArH, m, 26H), 7.85 ($\text{CH}=\text{C}$, 2H, d, $J=12.5$), 10.65 (NH, 2H, d, $J=12.5$); $^{13}\text{C-NMR}$ δ (ppm): 43.2 (CH_2), 99.1, 108.8, 115.9, 117.5, 120.0, 121.3, 123.5, 124.3, 127.2, 127.4, 128.7, 135.7, 136.7, 137.1, 137.8, 153.6 (aromatic and alkene carbons), 168.9 (CO); Analysis calculated for $\text{C}_{44}\text{H}_{34}\text{N}_4\text{O}_3$: C, 79.26; H, 5.14; N, 8.40%. Found: C, 79.14; H, 5.08; N, 8.31%.



Scheme 1. The synthesis of ionophore 3

2.3. Apparatus and emf measurements

The coated membrane on polypyrrole modified stainless steel disk electrode was used as the measuring electrode in conjunction with a double salt bridge Ag/AgCl reference electrode. All measurements were performed at room temperature using a Metrohm pH/Ion meter (model 827).

The analytical performance of the electrode was investigated by measuring its potential response in mercury nitrate solutions, in the concentration range of 5.0×10^{-7} to 1.0×10^{-2} M by adding successive aliquots of known concentrations of metal ion to 25 mL of 0.1 M NaNO_3 solution. Constant concentration of NaNO_3 was used in order to maintain a constant ionic strength. The solutions were stirred and the potential readings were recorded when they reached a stable value. The data were plotted as observed potential versus the logarithm of Hg (II) activity. All measurements of emf were made by the following assembly:

Ag/AgCl, KCl (sat'd) // Hg^{2+} solution / membrane / polypyrrole/ stainless steel disk electrode. Usually the ion activities are calculated by the Deby-Hückle approximation, but

since in our experiment the ionic strength has been 0.01 M, we assumed that the activities are almost equal to their corresponding concentrations.

Electropolymerization of pyrrole (py) was accomplished using μ Autolab –type III. The software for this device was GPES version 4.9. The three-electrode system consists of the stainless steel disk electrode as working electrode, Ag/ AgCl /3 M KCl as a reference electrode and a Pt wire as a counter electrode were used.

IR spectra were recorded on Shimadzu FT-IR 8300 spectrophotometer. $^1\text{H-NMR}$ and ^{13}C NMR spectra were recorded in CDCl_3 using a Bruker Avance DPX instrument ($^1\text{H-NMR}$ 250 MHz, ^{13}C NMR 62.9 MHz). Chemical shift was reported in parts per million (δ) downfield from TMS. All of the coupling constants (J) are in hertz.

A780 Metrohm pH meter was used for pH measurements. SEM images were acquired by Philips XL30 at an accelerating voltage of 25 KV.

2.4. Pretreatment of MWCNT

The pristine MWCNT (OD=10–30 nm, ID=5–10 nm, length=0.5–500 μM , 95%) was purified and activated before use. For this purpose, the MWCNT was stirred in HNO_3 (2 M) for 24 h and was then filtered and washed several times with deionized water for complete removal of nitric acid. The resultant MWCNT was then dried at 80 $^\circ\text{C}$ in an oven overnight. Acid treatment removes the amorphous carbon and metal oxide impurities.

2.5. Electropolymerization of pyrrole

Electropolymerization of py was performed with the chronoamperometric technique in 0.5 M monomer and 0.5 M K_2EDTA solution. Electrochemical deposition on the working electrode was carried out by applying +1.5 V potential on it for 60.0 second. After polymerization, ppy film was rinsed with doubly distilled water, and then it was dried for one hour at room temperature.

2.6. Electrode preparation

Membrane cocktail mixture was prepared by mixing ionophore (4.0%); MWCNT (2.0%); o-NPOE (62.7%); and PVC (31.3%). A total weight of 200.0 mg of the mixture was dissolved in 5.0 cm^3 of dry freshly distilled THF and the mixture was homogenized with ultrasonication for 35 min in an ultrasonic bath. For coating process 10.0 μL of homogenized membrane was applied on to the stainless steel electrode with a micropipette, this electrode was previously covered with ppy film. Then the electrode kept at room temperature for 12 h until a thin membrane was formed on its surface. The electrode was finally conditioned for 24 h by soaking it in 1×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ solution.

3. RESULTS AND DISCUSSION

3.1. Response characteristics of mercury(II) selective electrode

Before any optimization the potential responses of solid contact Hg(II) selective electrode were obtained for a wide variety of cations. As shown in Fig. 1 this sensor has better response characteristics to activity of Hg(II) ion than the other cations under the same experimental conditions (overnight conditioning in a 0.001 M solution of each cations). The stainless steel coated electrode with optimum composition was exhibited a linear Nernstian response with a slope of 29.34 ± 0.2 over the concentration range of 5.0×10^{-7} to 1.0×10^{-2} M and a correlation coefficient of 0.999 ($n=6$).

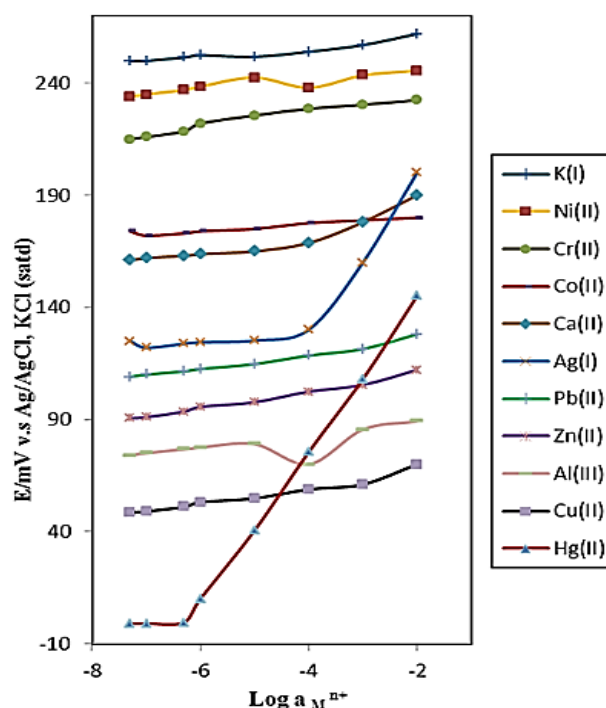


Fig. 1. The potential responses of various cations on the proposed electrode

3.2. IR and $^1\text{H-NMR}$ studies

To identify how Hg(II) interacts with the ionophore, IR and $^1\text{H-NMR}$ measurements were carried out. For this purpose, one mole of $\text{Hg}(\text{NO}_3)_2$ and one mole of the ionophore were refluxed in 10 mL ethanol for two hours. The color of the solution was changed from orange to yellow and then a yellow precipitate was formed. This precipitate was the complexation product of Hg(II) ion with the ionophore and was analyzed by IR and $^1\text{H-NMR}$ techniques.

As mentioned in section 2.2, $^1\text{H-NMR}$ of ionophore showed a doublet proton peak at 7.85 and 10.65 ppm for $-\text{CH}$ and $-\text{NH}$ respectively. The doublet at 7.85 for the $-\text{CH}$ group of the ionophore has been converted to a singlet at 8.0 ppm. This is certainly a confirmation of the

mercury ion interaction. Furthermore the disappearance of the -NH peak in $^1\text{H-NMR}$ approved the mentioned interaction. The IR spectrum of the Hg-ionophore complex (Fig. 2b) showed no -NH peak (which appears in Fig. 2a of the ionophore) due to the interaction of the -NH groups of ionophore with the Hg^{2+} . There was also a shift in the carbonyl group wavelength from 1674cm^{-1} to 1651cm^{-1} which also confirms the interaction of the electron pair of oxygen with the mercury ion. Based on these studies, the interaction of Hg (II) with ionophore is depicted in scheme 2.

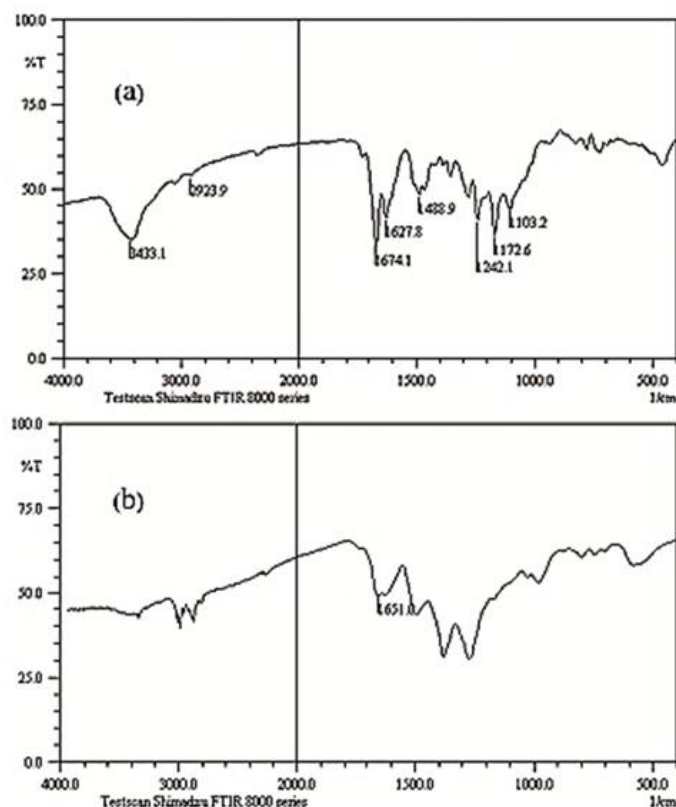
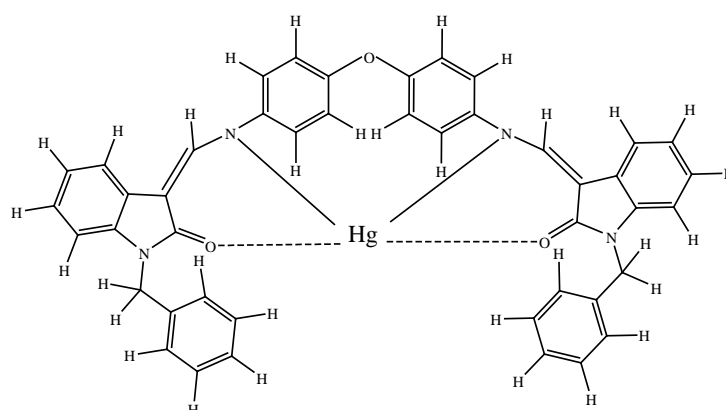


Fig. 2. (a) IR spectrum related to ionophore; (b) IR spectrum related to ionophore-analyte



Scheme 2. Structure of the ionophore-analyte interaction

3.3. Effect of conducting polymer

3.3.1. Effect of dopant in ppy film

The influence of the nature of dopants on the physical, mechanical, and electronic properties of the resulting ppy has been extensively studied [25,26]. The fact that a factor influences response performances of ppy could affect the properties of the corresponding SC-ISE. This persuaded us to study the effect of the nature of the doped anion into ppy film on the performance of Hg(II) selective electrode.

In the deposition of ppy film, the effect of several electrolytes with different anions (ClO_4^- , NO_3^- , SO_4^{2-} and EDTA^{2-}) was tested. The effects of the dopants on the potential response of sensors are shown in Table 1. As this Table shows Hg(II) sensors, whose sensing PVC membranes are the same, different response performance can be observed with various dopant anions. As it is clear from Table 1 indicates a suitable doping anion is EDTA^{2-} which its correspond SC-ISE has a wider linear range and better slope than SC-ISE with other doping anion.

Table 1. Effect of dopant on potential response of mercury ion selective electrode

ppy-film	Electrolyte	Slope(mV/decade)	Concentration range (M)
ppy- ClO_4	LiClO_4	17.64	1.0×10^{-7} to 1.0×10^{-4}
ppy- NO_3	NaNO_3	20.28	1.0×10^{-4} to 1.0×10^{-1}
ppy-EDTA	K_2EDTA	29.34	5.0×10^{-7} to 1.0×10^{-2}
ppy- SO_4	H_2SO_4	20.37	6.0×10^{-5} to 1.0×10^{-2}

3.3.2. Morphology of the electrode

To study the morphology of the mercury(II)-selective electrode SEM technique have been employed (Fig. 3). Comparing SEM images show that coated disk electrode modified with a ppy film has a smoother and more homogeneous surface than when there was no ppy. This has resulted to have a better and faster response.

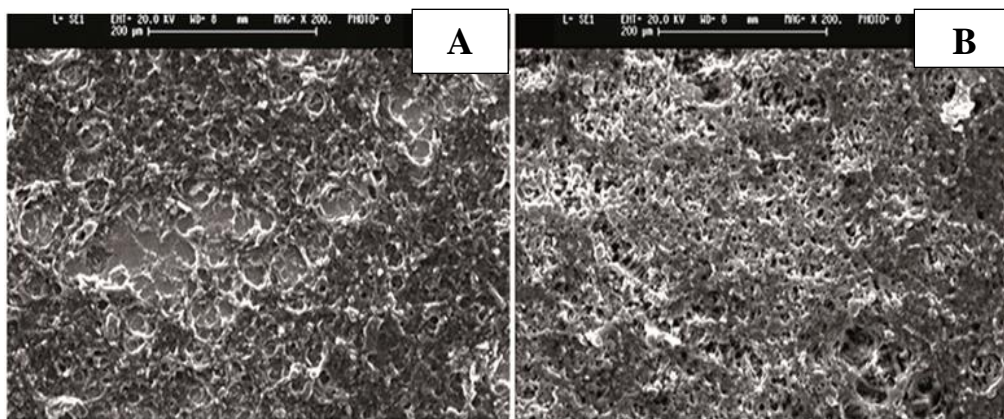


Fig. 3. SEM images of: (A) Nanocomposite modified stainless steel electrode; (B) PPy-Nano composite modified stainless steel electrode

3.4. Optimization of membrane composition

A plasticizer is a necessary membrane component which increases the flexibility, softness, workability of the polymer matrix. Several solvent mediators such as (*o*-NPOE, DBP, DBS, DMS) were tested as potential plasticizers for preparing the membrane. The mercury ion selective electrode based on *o*-NPOE exhibited a better Nernstian slope (29.3 mV/decade) and linear concentration range than DBP, DBS, and DMS (with a slope of 30.4, 29.1, and 27.5 mV/decade, respectively) as they are given in Table 2 in a wide concentration range 5.0×10^{-7} to 1.0×10^{-2} M of $\text{Hg}(\text{NO}_3)_2$. Therefore, *o*-NPOE was chosen as plasticizer in the rest of the experiments.

The performance of the membranes of different composition was investigated; the results are given in Table 2. It indicates the response of the electrode with only ppy film without the membrane (No. 9) exhibited sub-Nernstian slope of 20.8 mV/decade in a concentration range of 1.0×10^{-6} to 1.0×10^{-2} M. The electrode with 0.0% of ionophore (No. 7) showed a super-Nernstian slope of 34.6 mV/decade in a short concentration range of 1.0×10^{-5} to 1.0×10^{-2} M. The electrode which was coated with the composite containing 0.0% MWCNT (No.8) had a super Nernstian slope of 31.8 mV/decade in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M.

The response of the electrode in the absence and presence of ppy film on the surface of the solid contact was also tested. As shows in the Table 2 the electrode with ppy film (No.4) exhibited a Nernstian slope of 29.3 mV/decade with a concentration range of 5.0×10^{-7} to 1.0×10^{-2} M but the electrode with no ppy film (No. 10) had a sub-Nernstian slope of 24.3 mV/decade in a short concentration range of 7.5×10^{-6} to 1.0×10^{-2} M. Table 2 also compare the response of using of graphite powder instead of MWCNT (No. 12 and 14). As shown in Table 2. Nanocomposite membrane electrode exhibited a good Nernstian slope and wide concentration range with respect to the graphite membrane electrode.

It has been shown that using ppy-MWCNT composite improves the electrical conductivity as well as the mechanical properties such as stability of the electrode. It is clear from Table 2 that the dynamic range of this electrode not only influenced by the amount MWCNT but also effected the amount of the ionophore. The results obtained in this study also indicate that the electrodes show good sensitivity for mercury ions.

Table 2. Effect of various membrane compositions on potential response of mercury ion selective electrode

No.	Coating composition (%)									Slope (mV/decade)	r ²	Concentration range (M)
	ppy layer	DBS	o-NPOE	DMS	DBP	PVC	MWCNT ^a	GP ^b	Ligand ^c			
1	ppy-EDTA	62.67	-	-	-	31.33	2.0	-	4.0	29.1	0.993	1.0×10 ⁻⁵ to 1.0×10 ⁻²
2	ppy-EDTA	-	-	62.67	-	31.33	2.0	-	4.0	27.5	0.999	8.0×10 ⁻⁶ to 1.0×10 ⁻²
3	ppy-EDTA	-	-	-	62.67	31.33	2.0	-	4.0	30.4	0.987	2.5×10 ⁻⁵ to 1.0×10 ⁻²
4	ppy-EDTA	-	62.67	-	-	31.33	2.0	-	4.0	29.3	0.999	5.0×10⁻⁷ to 1.0×10⁻²
5	ppy-EDTA	-	63.33	-	-	31.67	2.0	-	3.0	26.7	0.971	1.0×10 ⁻⁶ to 1.0×10 ⁻²
6	ppy-EDTA	-	64.0	-	-	32.0	2.0	-	2.0	24.6	0.994	6.0×10 ⁻⁶ to 1.0×10 ⁻²
7	ppy-EDTA	-	65.33	-	-	32.67	2.0	-	-	34.6	0.997	1.0×10 ⁻⁵ to 1.0×10 ⁻²
8	ppy-EDTA	-	64.0	-	-	32.0	-	-	4.0	31.8	0.995	1.0×10 ⁻⁶ to 1.0×10 ⁻²
9	ppy-EDTA	-	-	-	-	-	-	-	-	20.8	0.997	1.0×10 ⁻⁶ to 1.0×10 ⁻²
10	-	-	62.67	-	-	31.33	2.0	-	4.0	24.3	0.932	7.5×10 ⁻⁶ to 1.0×10 ⁻²
11	ppy-EDTA	-	64.0	-	-	32.0	1.0	-	3.0	26.4	0.997	1.0×10 ⁻⁶ to 1.0×10 ⁻²
12	ppy-EDTA	-	62.67	-	-	31.33	-	3.0	3.0	13.6	0.992	1.0×10 ⁻⁷ to 1.0×10 ⁻²
13	ppy-EDTA	-	61.6	-	-	30.8	-	3.0	4.5	42.0	0.991	1.0×10 ⁻⁵ to 1.0×10 ⁻²
14	ppy-EDTA	-	61.6	-	-	30.8	-	4.5	3.0	26.6	0.995	1.0×10 ⁻⁷ to 1.0×10 ⁻²

^aMulti-walled carbon nanotube; ^bGraphite powder; ^c(Z)-1-benzyl-3-((4-(4-((Z)-(1-benzyl-oxindolylidene)methylamino)phenoxy)phenylamino)methylene)indolin-2-one

3.5. The effect of pH

The pH response profile of the proposed electrode for 1.0×10⁻⁴ and 1.0×10⁻⁵ M mercury solutions were investigated over the pH range of 2.0–12.0 (using HNO₃ or NaOH solutions for adjusting the pH). In the pH range of 3.6–5.0 this electrode shows nernstian response but at pH more than 5.0 (5.0–8.8) we have super nernstian response because of the presence of Hg²⁺ and [Hg(OH)]⁺ [27]. The observed drift at lower pH values could be due to the response of the electrode to H⁺ ions (or the ionophore would be protonated at lower pH). While, at higher pH the formation of some hydroxyl complexes of Hg²⁺ ions may cause a decrease in potential responses.

3.6. Figures of merit

The limit of detection, which is evaluated according to IUPAC recommendations [28] was 1.4×10^{-7} M of $\text{Hg}(\text{NO}_3)_2$.

Dynamic response time of the sensor was measured according to IUPAC definition [29], by changing the concentration of $\text{Hg}(\text{II})$ from 5.0×10^{-7} to 1.0×10^{-2} M. The resulting data depicted in Fig. 4 which shows that the time needed to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of Hg^{2+} ions (each having a tenfold difference in concentration). Response times were 13 and 5 s for Hg^{2+} concentrations lower and higher than 1.0×10^{-5} M respectively.

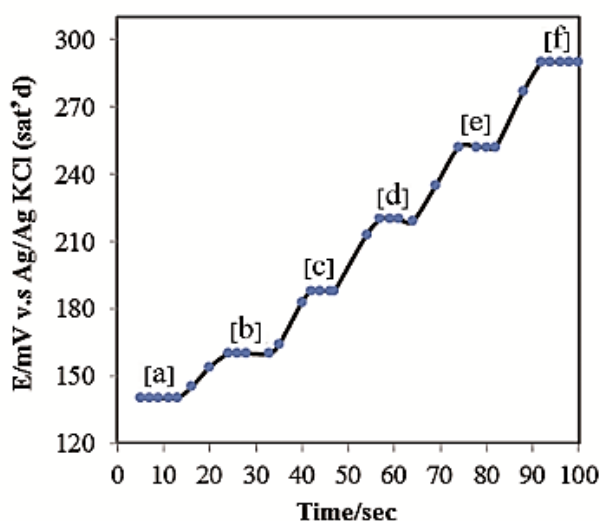


Fig. 4. Response time obtained with electrode. [a] 5.0×10^{-7} M Hg^{2+} , [b] 1.0×10^{-6} Hg^{2+} , [c] 1.0×10^{-5} Hg^{2+} , [d] 1.0×10^{-4} Hg^{2+} , [e] 1.0×10^{-3} Hg^{2+} , [f] 1.0×10^{-2} Hg^{2+}

The reproducibility was investigated by preparing seven similar electrodes at optimum membrane composition. Then the slope of each electrode was determined and the average slope with standard derivation was 29.45 ± 0.34 mV/decade (RSD=1.89%).

In repeatability study, the calibration curves of one electrode in seven times were obtained during seven days. The average slope with standard deviation was 29.25 ± 0.7 mV per decade (RSD=1.34%).

To investigate the lifetime of the electrode the calibration curves of mercury electrode at its optimized composition were periodically obtained for 60 days. After two months there was no considerable deviation in potential responses.

3.7. Selectivity coefficients of mercury selective electrode

A potentiometric selectivity coefficient defines the ability of ISE to distinguish one particular ion from others in the matrix of the sample. The selectivity coefficients for the

membrane electrode were determined by using both the fixed interference (FIM) [30] and matched potential methods (MPM).

Table 3. Selectivity coefficients measured by FIM and MPM

Interfering Ions	$K_{A,B}^{Pot}$	$K_{A,B}^{Pot}$
	FIM	MPM
Mg ²⁺	1.2×10 ⁻³	2.3×10 ⁻³
Na ⁺	1.8×10 ⁻³	3.1×10 ⁻³
Co ²⁺	1.4×10 ⁻²	6.5×10 ⁻³
Cu ²⁺	4.8×10 ⁻⁴	1.3×10 ⁻⁴
Zn ²⁺	1.6×10 ⁻³	5.0×10 ⁻⁴
Al ³⁺	1.2×10 ⁻³	2.7×10 ⁻³
K ⁺	1.0×10 ⁻²	2.2×10 ⁻²
Cr ³⁺	5.3×10 ⁻³	1.6×10 ⁻³
Ca ²⁺	7.5×10 ⁻³	3.4×10 ⁻³
Ag ⁺	2.5×10 ⁻²	1.2×10 ⁻²
Ni ²⁺	7.5×10 ⁻³	1.5×10 ⁻³
Cd ²⁺	2.6×10 ⁻³	5.6×10 ⁻³
Ga ³⁺	1.3×10 ⁻³	3.8×10 ⁻³
NH ₄ ⁺	1.0×10 ⁻³	4.6×10 ⁻³
Li ⁺	8.4×10 ⁻³	3.3×10 ⁻³
Ba ²⁺	1.2×10 ⁻³	8.1×10 ⁻⁴
Pb ²⁺	1.7×10 ⁻³	2.1×10 ⁻³
Fe ³⁺	6.7×10 ⁻³	2.4×10 ⁻²
Mn ²⁺	9.39×10 ⁻³	1.8×10 ⁻³

In the fixed interference method, the potential of a cell comprising an ISE and a reference electrode is measured with solutions of the constant level of interference, a_B , and varying activity of the primary ion, a_A . The potential values obtained are plotted vs. the activity of the primary ion. The intersection of the extrapolation of the linear portions of this curve will indicate the value of a_A which is to be used in calculation of $K_{A,B}^{Pot}$ from the following equation:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{\frac{Z_A}{Z_B}}}$$

Z_A and Z_B have the same positive or negative signs. Based on this equation selectivity coefficients of the mercury sensor were evaluated graphically with a fixed concentration of the interfering ions ($M^{n+}=1.0 \times 10^{-3}$ M) and varying amounts of the Hg²⁺ ions. The resulting values of the selectivity coefficients are summarized in Table 3.

In MPM, the selectivity coefficient defined as the activity ratio of the primary ion and the interfering ion that gives the same potential change in a reference solution. The concentration

of Hg^{2+} ions used as the primary ion in this study was 1.0×10^{-5} M. The resulting values of the selectivity coefficient for MPM were also summarized in Table 3. As Table 3 shows the proposed electrode exhibited a very good selectivity toward Hg (II) ion over a wide variety of metal ions.

3.8. Potentiometric titration

The proposed sensor was founded to work well under laboratory conditions. It was successfully applied as an indicator electrode in potentiometric titration of 25.0 mL of 1.0×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ by 1.0×10^{-1} M EDTA. A typical result of titration curve is shown in Fig. 5(A); it indicates the amount of Hg (II) ions in solution can be accurately determined with this electrode. In addition, this sensor also applied as a potentiometric indicator electrode in precipitation titration of 25.0 mL of 1.0×10^{-2} M of mixture of halide anions by 2.5×10^{-2} M $\text{Hg}(\text{NO}_3)_2$ solution. The resulted titration curve is shown in Fig. 5(B). As is shows, the halide anions can be accurately determined with this electrode.

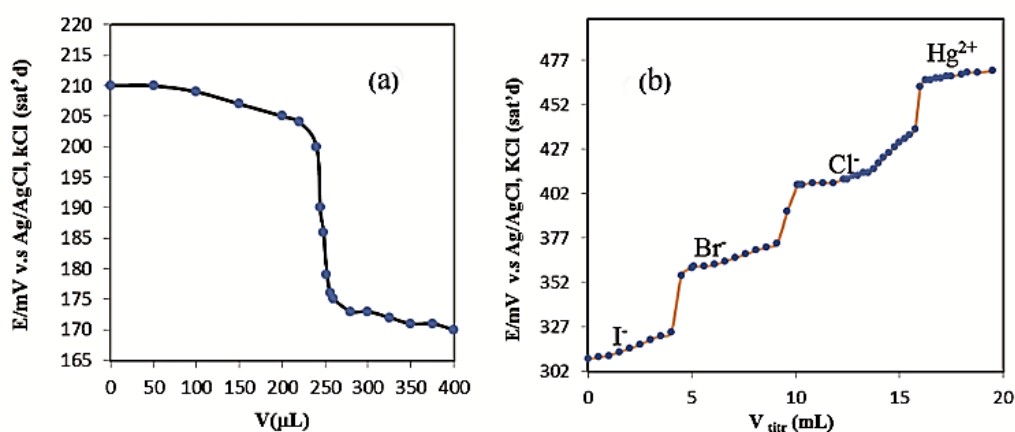


Fig. 5. (A) Potentiometric titration curve of 25.0 mL 1.0×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ by 1.0×10^{-1} M EDTA and (B) Potentiometric titration of the solution containing 25.0 mL, 1.0×10^{-2} M KI, KBr, KCl using 2.5×10^{-2} M $\text{Hg}(\text{NO}_3)_2$ as a titrant

3.9. Determination of mercury in water sample

Mercury is a high-priority pollutant and, like other trace elements of natural and/or anthropogenic origin, it is transported by rivers and transferred to the oceans and seas through coastal systems [31]. Therefore, proposed sensor was used for the determination of mercury in river water using the standard addition method. 48.3 ± 0.4 ppm of mercury was obtained by proposing sensor which is comparable with the amount determined by atomic absorption spectroscopy (48.9 ± 0.2 ppm).

3.10. Comparison of the proposed electrode with some other mercury electrodes

The characteristic responses to this and other mercury-selective electrodes are listed in Table 4. When the data was compared, it showed that the proposed sensor was superior to previously reported electrodes in most cases. This coated electrode had a reasonable detection limit and pH range compared to previous studies. In addition the response time of this electrode was short enough which made it more applicable for flow injection analysis methods.

Table 4. Comparing various reported mercury ion selective electrode with present work

Kind of electrode	pH range	Concentration range (M)	Slope (mV/decade)	Detection limit(M)	Lifetime (decay)	Response time (s)	Ref.
^a IS-ISE	2.6 - 4.2	1.0×10^{-7} – 1.0×10^{-2}	30.2±0.3	5.0×10^{-8}	-	15	[32]
^b CWE	3 - 4	1.0×10^{-7} – 1.0×10^{-2}	30.0±1	0.5×10^{-7}	120	25	[33]
IS-ISE	2.0 – 4.5	1.0×10^{-6} – 1.0×10^{-3}	30.0	7.0×10^{-7}	90	-	[34]
CWE	1.0 – 4.0	1.0×10^{-6} – 1.0×10^{-1}	32.6	8.9×10^{-7}	90	20	[35]
IS-ISE	2.0 – 4.3	5.0×10^{-9} – 1.0×10^{-4}	29.3 ± 0.2	2.5×10^{-9}	55	5	[36]
IS-ISE	6.6 – 9.3	1.25×10^{-5} – 1.0×10^{-1}	25 ± 0.1	8.9×10^{-6}	120	10	[27]
IS-ISE	2.5 – 5.0	1.4×10^{-6} – 1.0×10^{-1}	30.0	-	120	18	[37]
IS-ISE	3.0	1.0×10^{-6} – 1.0×10^{-1}	29.6	6.5×10^{-7}	30	45	[38]
IS-ISE	1.0 – 4.0	6.2×10^{-7} – 8.0×10^{-2}	29.6	5.0×10^{-7}	-	30	[39]
CWE	3.5 – 6.6	2.1×10^{-6} – 1.0×10^{-2}	58.8	7.3×10^{-7}	-	5-8	[40]
^c CDE	3.6 – 8.8	5.0×10^{-7} – 1.0×10^{-2}	29.3 ± 0.2	1.4×10^{-7}	60	5	This work

^aInternal solution-ion selective electrode, ^bCoated wire electrode, ^cCoated disk electrode

4. CONCLUSION

We have shown that the electrode prepared from polypyrrole-carbon nanocomposite can be used for analytical application. In this work, we used stainless steel as a working electrode which was a cheaper candidate with respect to platinum wire. The prepared electrode has many features such as easy to prepare, more economically sound, simple and inexpensive potentiometric equipment. The obtained results indicate that this electrode in most cases is better than to the previously reported mercury-selective electrodes.

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