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Synthesis and surface characterization of a chemically modified carbon paste electrode and its application in determination of Hg(II) ion in water, food and dental amalgam samples

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ABSTRACT

The development of an easy and affordable method for its determination in various samples is of major interest because the globe is affected by the toxicity of the environment caused by the presence of heavy metals, particularly mercuric ions. For the potentiometric measurement of Hg(II) ions in various materials, an unique carbon paste electrode was created using 1,3-Bis[2-(*N-morpholino*)*acetamidothiophenoxy*]propane (BMATPP) as a modifier. With a reaction time of six seconds, the electrode had a Nernstian slope of 30.01 ± 0.52 mV decade^{-1} over the concentration range of 5×10^{-9}-1×10^{-3} mol/L (SD of 5 replicates). It was discovered that the pH range for use was 2.2 to 4.5 and that it was thermally stable up to 60 °C. The selectivity of the suggested sensor towards the Hg(II) ion was investigated using the separate solution method (SSM) and fixed interference technique (FIM), and it demonstrated a satisfactory selectivity. The interaction between the target Hg(II) ions and modifier was demonstrated by scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray (EDX) and infrared (IR). The modifier's contact angle value demonstrated its lipophilicity, which is consistent with its stability and long life. With excellent F-test and *t*-test values obtained, the Hg(II) ion modified sensor was successfully used for potentiometric analysis of several real samples.

1. Introduction

Plastics, waste water, lead-mercury batteries, burning fossil fuels, mercury thermometers, and electronics are just a few examples of things that contain mercury and pose major risks to human life as well as environmental harm [1,2]. Due to its inability to decompose and persistence in toxic waste, mercury is poisonous. Because mercury may link to amino acids through the sulphur atom and cause function abnormalities, it can harm the kidneys and brain system of humans [3,4]. The American Environmental Protection Association (EPA) has set a limit of 10 nmol/L for the level of elemental mercury in drinking water [5]. The development of sensitive and selective mercuric ion measurement methods is of great significance for reducing mercury pollution in the environmental and scientific fields. Chromatography [6–8], atomic absorption [9–11], inductively coupled plasma (ICP) [12–14] and other conventional techniques for mercuric ions determination, however, these procedures are pricey, time-consuming, and labor-intensive. On the other hand, ion selective electrodes (ISEs), in particular carbon paste electrodes (CPEs), provide a number of benefits, including lack of predetermination procedures, rapid reaction, low cost, robustness, and renewability [15–19]. ISEs turn into a useful tool for measuring mercury ions in pollution caused by anthropogenic and natural sources of mercury. The development of a conventional ISE for the assessment of trace amounts of Hg(II) with good selectivity and sensitivity is particularly crucial, notwithstanding the enormous efforts that have been made to determine mercuric ions in environmental samples. Carbon powder is combined with a chemical modifier (ionophore) in carbon paste electrodes (CPEs) using plasticizing liquid [15–19,20]. The applied ionophore properties are primarily responsible for the functioning mechanism and response characteristics of the modified carbon paste electrode (MCPE). There are different electrochemical techniques utilizing ISEs for determination of target ions; potentiometric ($i = 0$) and amperometric ($i \neq 0$) methods of analysis. There are many reported amperometric techniques for determination of Hg(II) ions like stripping voltammetry [21–23], square wave voltammetry [24] and linear sweep voltammetry [25,26]. These methods exhibited accurate and sensitive

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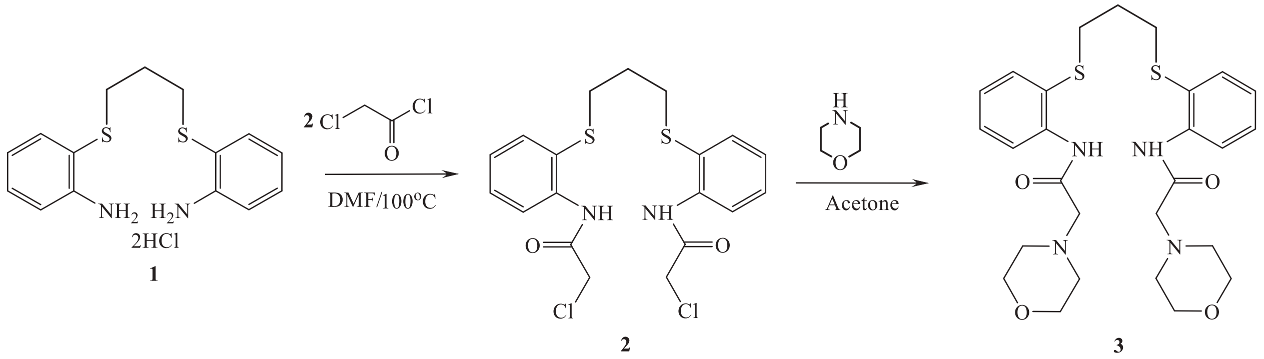


Scheme 1. Preparation of 1,3-bis[2-(*N-morpholino*)*acetamidothiophenoxy*]propane (BMATPP) novel ionophore (**3**).

determination of Hg(II) ion. However, potentiometric technique offers advantages over amperometric techniques like simple instrumentation, low cost and fast measurement.

Various chemical and inorganic substances were employed as ionophores for the selective detection of Hg(II) ions in the literature throughout the past few decades. Amines [27,28], oximes [29], crown ethers [30,31], calixarene derivatives [32], Schiff base derivatives [33], polyvinyl pyridine [34], thioureas [35] and dithio derivatives [36] have all been used as Hg(II) selective ionophores. However, many of these reported electrodes have some disadvantages like short lifetime, low sensitivity, long response time, serious interference from other metal ions, and a limited pH working range. Therefore, development of more effective sensors with enhanced features is a challenge and in turn it will improve the application of ISEs in routine analysis. Sulfur-containing modifiers work best to detect mercuric ions due to the fact that soft metal ions prefer soft ligands [37]; for ligands with “soft base” donor atoms, such as sulfur, mercury’s characteristic “soft acid” acceptor character displays a high affinity constant [10^{15}–10^{20} M]. Its affinity constants, on the other hand, are at least 10 orders of magnitude lower for “hard bases” like ligands containing oxygen or nitrogen, such as carboxylate or amide groups in peptides [38]. Therefore, the optimum option to be used in the potentiometric determination of Hg(II) ion efficiently was an ionophore containing sulfur atoms.

Hence, a carbon paste electrode modified with a freshly synthesized ionophore, 1,3-bis[2-(*N-morpholino*)*acetamidothiophenoxy*]propane was used to address the potentiometric measurement of mercuric ions (Hg (II)) in various genuine samples. It was researched and optimized how various parameters affected the electrode’s responsiveness to the target Hg(II) ions. The slope, linear range, detection limit, response time, isothermal coefficient, and selectivity of the resulting mercuric ion-selective electrode were detailed. Additionally, the proposed 1,3-Bis [2-(*N-morpholino*)*acetamidothiophenoxy*]propane-based Hg(II) sensor’s performance has been evaluated in comparison to that of those already published before.

2. Experimental

2.1. Materials

In this study, analytical sort reagents were used. Solutions were made from a stock solution of 0.1 mol/L Hg(II), which was made from enough mercuric chloride, which was provided by Merck, in bidistilled water, and buffered with the help of an acetate buffer, which had a pH of 4.5 and this stock solution was preserved in glass bottle in dark at 4 °C and can be used effectively for a month at this pH with reproducible results. After one month, the stock solution concentration was different and a new one was prepared and tested for reproducibility. Every day, the stock solution was properly diluted to create the working solutions. The analytical grade chloride salts that were acquired from the El Nasr firm were used to prepare all other solutions that were used in interference investigations. Fluka provided the *o*-nitrophenyloctyl ether (*o*-NPOE), while BDH provided the dioctyl phthalate (DOP) and dibutyl phthalate (DBP). Tricresyl phosphate (TCP), synthetic graphite powder (1–2 μm), and 2-fluorophenyl-2-nitrophenyl ether (FFNE) were provided by Sigma-Aldrich.

2.2. Apparatus

The produced graphite sensors were used with a double-junction reference electrode made of silver-silver chloride (HANNA, HI 5311) to monitor potential. Jenway 3505 pH meter was used to measure pH. For surface analysis, the National Research Center Quanta FEG250 scanning electron microscope and the energy dispersive X-ray analyzer (EDX), both from Egypt, were utilized. At the Microanalytical Center, Cairo University, Egypt, the FTIR spectra of potassium bromide pellets were measured using a Perkin-Elmer 1650 spectrometer (4000–400 cm-1). Biolin Scientific’s T 200 model contact angle analyzer was employed with the sessile drop method, 4 m droplet distilled water, and a 10-second evaluation period.

2.3. Procedures

2.3.1. Preparation and characterization of the used ionophore

The newly applied ionophore in this work namely 1,3-bis[2-(*N-morpholino)-acetamidothiophenoxy*]propane (BMATPP) was prepared in two steps (Scheme 1). Firstly, 1,3-bis[(2-*chloro-acetamido)thiophenoxy*] propane **(2)** was synthesized. A solution of each of **1** (5 mmol) in DMF (10 mL) was added to chloroacetyl chloride (10 mmol). The reaction mixture was stirred at 100 °C for 2 h. The reaction mixture was poured on crushed ice. The solid obtained was collected by filtration and crystallized from benzene as colorless crystals (yield 70 %) [39].

Secondly, a mixture of each of **(2)** (5 mmol) and excess, morpholine (12 mmol) and a few drops of triethylamine (TEA) in acetone (50 mL) was heated under reflux for 1 h, The solvent was then removed in vacuo. The oily product obtained was washed with cold water and keep in the refrigerators overnight. The solid obtained was collected by filtration and crystallized from ethanol as colorless crystals to give the desired ionophore **(3)** which has a melting point 108–110 °C (yield 72 %).

IR, ^{1}H NMR and CHN analyses confirmed the BMATPP structure. IR (ν, cm^{-1}, KBr): 3248 (NH), 1681 (C=O); ^{1}H NMR (δ, ppm, CDCl$_3$) 1.78 (quintet, $J = 6.9$ Hz, 2H, CH_2CH_2S), 2.60 (t, 8H, $J = 4.5$ Hz, CH_2N), 2.87 (t, 4H, $J = 6.9$ Hz, SCH_2), 3.16 (s, 4H, $COCH_2$), 3.75 (t, 8H, $J = 4.8$ Hz, OCH_2CH_2N), 7.00–8.49 (m, 8H, ArH s), 10.30 (s, 2H, NH). CHN: (Calcd. for $C_{27}H_{36}N_4O_4S_2$ (544.73 g/mol): C = 59.53 %; H = 6.66 %; N = 10.29 %. Found: C = 59.30 %; H = 6.70 %; N = 10.10 %.

2.3.2. Modified graphite electrodes preparation and calibration

The components for the graphitic paste—graphite powder, freshly manufactured electroactive material, and the appropriate amount of plasticizing liquid—were combined and appropriately smoothed in a

Table 1
Effect of composition of carbon paste on the electrode performance.

Electrode No.	Composition of various components in carbon pastes (amount in mg)			Electrode characteristics		
	BMATPP ionophore, mg	Plasticizer (100 mg)	Graphite, mg	Slope ± SD, mV decade^{-1}	Linear range, mol/L	Regression
1	0	TCP	250	10.5 ± 1.32	1×10^{-5}-1×10^{-2}	0.9682
2	5	TCP	250	24.32 ± 0.95	1×10^{-7}-1×10^{-3}	0.9981
3	10	TCP	250	27.95 ± 0.76	5×10^{-8}-1×10^{-3}	0.9990
4	**15**	**TCP**	**250**	**30.01 ± 0.52**	**5×10^{-9}-1×10^{-3}**	**0.9998**
5	20	TCP	250	26.92 ± 0.42	5×10^{-7}-1×10^{-2}	0.9987
6	15	*o*-NPOE	250	31.55 ± 0.96	1×10^{-8}-1×10^{-3}	0.9983
7	15	DBP	250	29.05 ± 0.72	5×10^{-8}-1×10^{-3}	0.9987
8	15	DOP	250	25.83 ± 1.32	1×10^{-6}-1×10^{-2}	0.9990
9	15	FFNE	250	26.52 ± 0.97	1×10^{-7}-1×10^{-3}	0.9991

mortar. In order to prevent air diffusion, the produced paste was carefully applied to the electrode Teflon body. In order to get a new shining side of the paste, the prepared electrode was polished on a smooth filter paper and condition for 24 h in distilled water [15–18,40]. The Hg(II) graphite selective electrode was calibrated by immersing it in a 25 mL beaker containing a 10 mL aliquot of buffered Hg(II) solution at pH = 4.5 with concentrations ranging from 5.0×10^{-9} to 1.0×10^{-3} mol/L, and applying steady stirring. For the study of unknown Hg(II) ion concentration, a plot of the acquired stabilised potentials at 25 °C ± 1 against -log [Hg(II)] was made and used.

2.3.3. *Selectivity determination*

According to reports from [18,40–43], the separate solution method (SSM) was used to perform selectivity analysis in separate solutions by connecting the potentials of the two solutions using the Debye-Huckel equation. The fixed interference approach was used to examine the study in a mixed solution environment (FIM). Here, the concentration of the Hg(II) ion was varied from 1.0×10^{-10} mol L^{-1} to 1.0×10^{-3} mol/L, and the modified Hg(II) sensor and reference electrode were placed in constant 1.0×10^{-3} mol/L concentration of interfering ion, as reported [15–18,40,41]. The coefficients of selectivity were estimated via detection limits of the obtained calibration plots.

3. Results and discussion

3.1. *Composition of carbon paste electrode*

It has been noted that a number of key components of the carbon paste electrode, including the binding liquid's characteristics, the ratio of binder to graphite powder, and the type and quantity of ionophore, have a significant impact on the sensitivity and selectivity of the ion-selective electrode [20,44,45]. In order to achieve this, various perspectives on the creation of a carbon paste electrode based on BMATPP were optimized. The outcomes are shown in Table 1. As can be seen, the electrode without the BMATPP modification responded to Hg(II) ions less potentiometrically (No. 1). This suggested that the most crucial component of the suggested Hg(II) ion sensor was BMATPP. The reaction became more Nernstian as the modifier dosage was increased, and it displayed more sensitivity up until 15 mg of BMATPP modifier was added and then deviation from Nernstian behaviour was caused by a shift in the ionic sites ratio [15,16]. The responsiveness and stability of the synthesized electrode are significantly influenced by the lipophilicity of the ionophore employed. The average contact angle used to study this lipophilicity was 130.67°, which is significantly larger than the 90° required to match the lipophilicity of the ionophore utilized [46].

The amount and type of the lipophilic additive (plasticizer) have been found to have a significant impact on how the ion-selective electrodes respond because they lower matrix resistance, enhance response quality, increase selectivity, and in some cases, increase sensor sensitivity by increasing the paste's ability to extract the desired ions [47]. TCP serves two purposes as a solvent mediator: it liquifies substances to enable paste homogeneity and modifies the ionophore distribution constant. TCP has all of the characteristics that make up an effective binder, including high conductivity and lipophilicity, a low tendency to leach from the paste matrix, a high capacity to dissolve the substrate and other paste additives, and non-volatility [20,48].

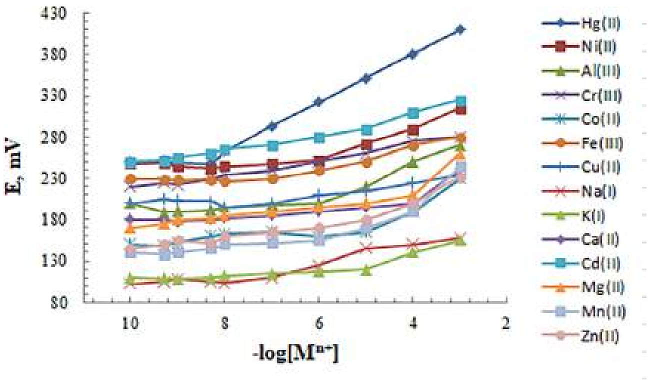


Fig. 1. Variation of potentials of sensor No. 4 for Hg(II) and different metal ions.

Table 1's findings demonstrate that the BMATPP is a superior ionophore for the Hg(II) ion. Additionally, the addition of TCP to the paste improved the electrode's slope, linear range, and regression.

3.2. *Selectivity studies*

An essential feature of a sensor is selectivity [49,50]. For the manufacture of carbon paste electrodes with the same composition as electrode (No. 4), listed in Table 1, the BMATPP modifier was used. The

Table 2
Selectivity coefficients of various interfering cations for sensor No. 4.

Foreign ion	$K^{SSM}_{Hg(II),\ B}$	$K^{FIM}_{Hg(II),\ B}$
Ni^{2+}	6.83×10^{-4}	8.73×10^{-4}
Pb^{2+}	4.03×10^{-4}	8.23×10^{-4}
Cd^{2+}	1.47×10^{-3}	5.72×10^{-3}
Co^{2+}	1.01×10^{-6}	1.32×10^{-4}
Cu^{2+}	1.47×10^{-6}	2.09×10^{-4}
Mn^{2+}	3.18×10^{-6}	4.25×10^{-5}
Zn^{2+}	1.17×10^{-6}	7.33×10^{-5}
Cr^{3+}	4.66×10^{-6}	5.22×10^{-5}
Al^{3+}	2.16×10^{-6}	8.12×10^{-5}
Fe^{3+}	4.66×10^{-6}	2.52×10^{-4}
Ca^{2+}	2.34×10^{-6}	5.02×10^{-5}
Mg^{2+}	1.00×10^{-5}	7.36×10^{-5}
Na^{+}	4.00×10^{-6}	5.00×10^{-3}
K^{+}	3.18×10^{-6}	8.51×10^{-3}
Ag^{+}	1.50×10^{-4}	2.63×10^{-3}

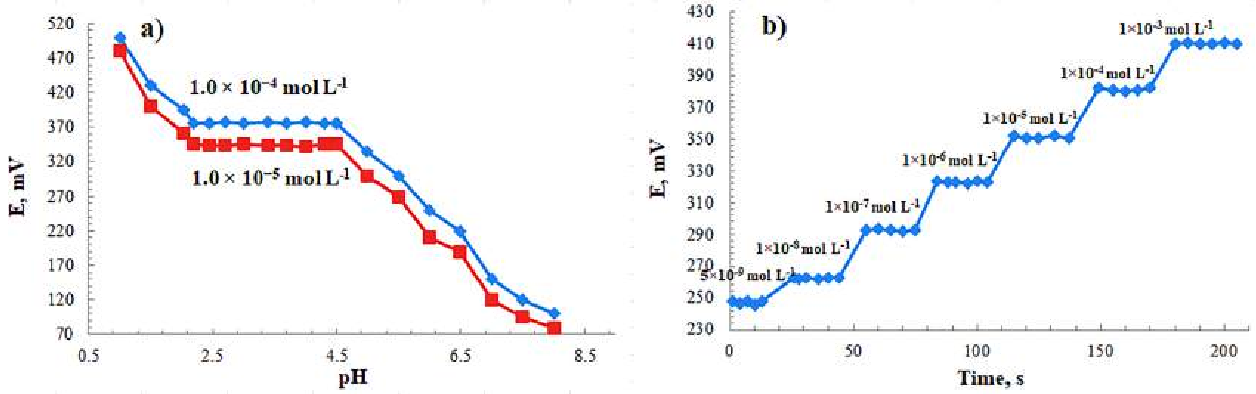


Fig. 2. Response characteristics of proposed Hg(II) sensor, a) Effect of pH and b) response time for step changes of Hg(II) ion concentration.

potential responses of the electrodes to various metal ions are depicted in Fig. 1. It was discovered that, among all examined cations, Hg(II) ion displayed the Nernstian potential response over a broad concentration range, in contrast to the majority of other examined metal ions. This can be attributed to Hg(II) selective behaviour, greater ionophore interaction, and rapid exchange kinetics [15,51].

Both the separate solution method (SSM) and the fixed interference technique (FIM) were used in this study to analyse the selectivity coefficients of the suggested electrode towards various cationic species ($M^{n+)}$ [52,53]. Hg(II) ion fixed concentrations and other interfering ions' potentials are evaluated independently in SSM. The interfering ion in FIM, on the other hand, had Hg(II) ions in changing amounts but at a stable concentration. The values of the selectivity coefficients are shown in Table 2. Equal response to primary and interfering ions is indicated by a selectivity coefficient value of 1.0. An identical reaction to primary and interfering ions is indicated by a selectivity coefficient value less than 1.0. This method yields a selectivity coefficient that is less than 1.0, showing that the present sensor (No. 4) is still selective even when exposed to a variety of monovalent, bivalent, and trivalent cations [54,55]. Bakhtiarzadeh *et al.* [34] and Júarez-Gómez *et al.* [36] found that their Hg(II) sensors interfere with Ag(I) and Fe(III) ions, respectively, while a neutral carrier polymeric based sensor reported by Gupta *et al.* [56] wasn't selective for Hg(II) ion in the presence of Ag(I), Pb(II) and Cu(II) ions. In addition, Rofouei *et al.* [57] found that Ag(I), Pb(II), Cd(II) and Cu(II) ions can cause interference in Hg(II) determination and Kaushal *et al.* [58] reported Hg(II) sensor suffer from interference from K (I) ion. Hence, the enhancement in selectivity of Hg(II) sensor is a goal and it was achieved in this work by applying BMATPP as an ionophore. The obtained selectivity coefficients for different trivalent, divalent and monovalent cations were less than 10^{-2} (Table 2) and this is a good addition to the existing list of Hg(II) ISEs.

3.3. Response characteristics of the proposed Hg(II) electrode

Using two different concentrations of Hg(II), 1.0×10^{-5} mol/L and 1.0×10^{-4} mol/L, the influence of pH on the performance of the most responsive electrode (No. 4) was investigated over the pH range of 1–8. The results are presented in Fig. 2a. The potential remained constant while the pH changed in the pH range of 2.2–4.5, and these results were consistent with those from other sensors that have been used to determine the Hg(II) ion potentiometrically [20,34,51,56,57]. With the help of 1.0 mol/L of HNO_3 and NaOH, the pH was changed. The large concentration of H_3O^+ ions that generated an interference may be responsible for the potential variation at pH 2.2 as H_3O^+ ions can exchange Hg (II) ions and cause interference by ligand protonation at such high concentration of hydrogen ions [20,56,57]. Conversely, variation of potential at pH > 4.5 is caused by the production of $Hg(OH)_2$ that can't react with the ionophore [20].

The average time needed for the specified electrode to reach a potential that is within 1 mV of the ultimate equilibrium value following multiple immersions in Hg(II) ion solutions, each with a 10-fold change in concentration, is a crucial component of any sensor. Hg(II) chloride solutions of varying concentrations (5.0×10^{-9} mol/L) to higher (1.0×10^{-3} mol/L) were used to monitor potential against time (Fig. 2b). In 5–7 s, the electrode finds equilibrium. The extended equilibration time was the cause of the reaction time increasing to 7 s when the concentration was reduced to 5.0×10^{-9} mol/L. Shorter response times are achieved at lower concentrations by quick exchange kinetics of the metal–ligand complexation-decomplexation at the surface of the paste [15,16]. However, compared to earlier reported sensors, this synthetic sensor had improved equilibration and exchange kinetics [20,51,56,57].

Calibration graphs encompassing the range of 10–70 °C were recorded at various temperatures to explore the influence of temperature on the used sensor. The electrode's reaction was discovered to be temperature independent up to 60 °C. The analyzed electrode was stable up to 60 °C without obviously deviating from the Nernstian behaviour, according to the calibration graphs of the proposed sensor, whose slope was in the Nernstian up to 60 °C and whose linear range remained unchanged. However, temperatures over 60 °C resulted in a large departure from the theoretical values, which can be attributed to an electrode surface degradation brought on by some ionophore leaching from the paste matrix, which reduced response and resulted in the departure [15]. Applying Antropov's equation, the isothermal coefficient $(dE/dt)_{cell}$ was obtained [42,59]. The measurement of 4.25×10^{-5} V $°C^{-1}$ indicated a good degree of thermal consistency.

Regarding the sensor's lifespan, steady and repeatable signals were acquired for three months (the sensor was heavily used for one hour each day), after which the sensor began to deviate from expected behaviour. The deterioration of the paste's mechanical stability with use may be the cause of the departure from Nernstian behaviour and decrease in sensitivity. However, the life of the electrode can be extended by many months if it is kept in distilled water while not in use.

3.4. Study of BMATPP ionophore and Hg(II) ion interaction

The kind of interaction between an ionophore and a metal ion may be explained by complex formation at the surface of the carbon paste during estimate as a result of the extraction of Hg(II) ions from the solution into the paste [15,16]. SEM along with EDX and IR tests were used to evaluate and confirm this produced complex. SEM, which is regarded as an important technique for illustrating the surface morphology of sensors [15–18,40,60,61], was used to relate surface morphology to the acquired response in an effort to tie the potentiometric response to surface morphology. The percentage of each element present on the surface was also provided by EDX.

The composition No. 4 carbon paste electrode was made, and it was

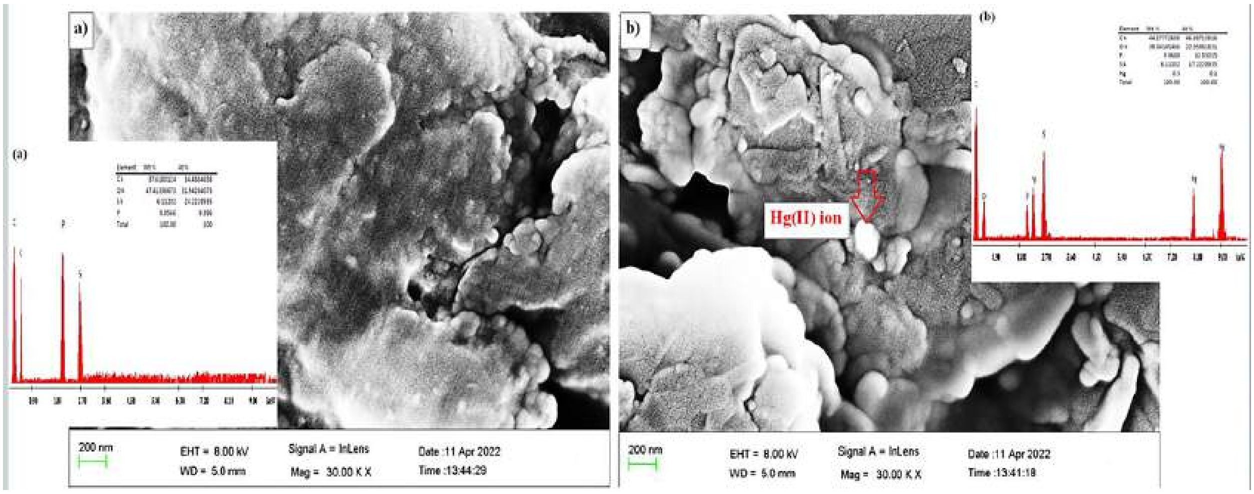
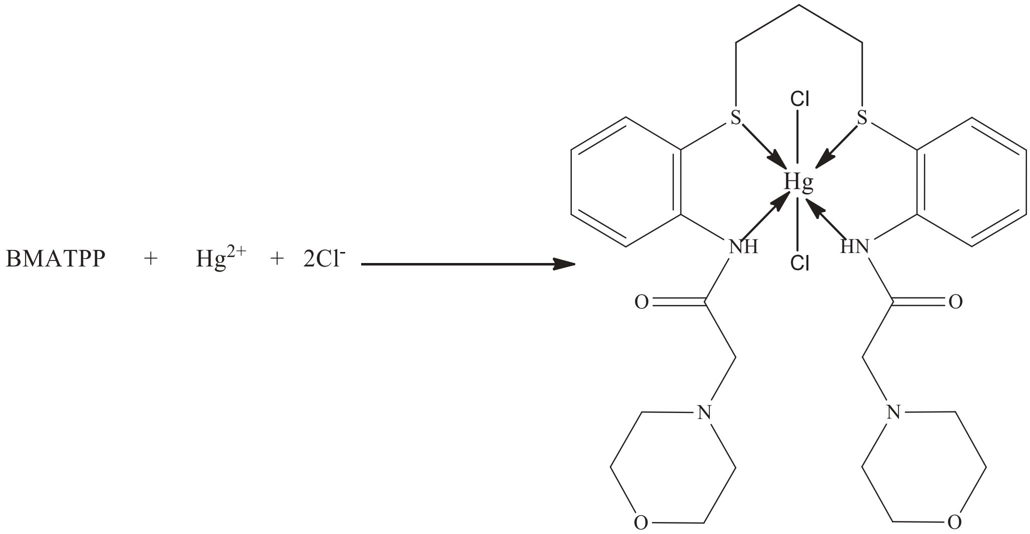


Fig. 3. SEM image and EDX chart for carbon paste surface (compostion No. 4) a) before soaking and b) after soaking in 1.0×10^{-3} mol/L of Hg(II) ion for 1 h.



Scheme 2. Mechanism of interaction between Hg(II) ion and the applied BMATPP modifier.

then immersed for an hour in 1×10^{-3} mol/L of Hg(II) ion. Fig. 3 illustrates the homogeneous and holey surface of the carbon paste, which helped the Hg(II) ions diffuse. This is demonstrated by the change in paste morphology and the appearance of lit-up marks between the carbon after soaking, which can be explained by complex formation between the Hg(II) ions and the used ionophore. Fig. 3's EDX charts show how Hg(II) ions entered the paste after soaking. IR spectra, which showed that the absorption (NH) band at 3430 cm^{-1} was moved to 3436 cm^{-1} and that its intensity was increased after soaking, also corroborated this mechanism. Additionally, following soaking in Hg(II) solution, the v(C—S) stretching vibration band that was observed at 1141 cm^{-1} in the unsoaked sample was moved to 1148 cm^{-1} while the other ionophore bands stayed the same. This change in band position was interpreted as proof that the BMATPP ligand bound to the Hg(II) ion via sulphur and nitrogen donating atoms, as shown in scheme 2 [16,62–64].

3.5. Sensitivity and reproducibility

According to IUPAC recommendations [65], For the purpose of validating an analytical method, particularly in the instance of determining impurities, the limits of detection (LOD) and quantification (LOQ) were evaluated. LOD, which is not always measured as an exact value, is the lowest concentration of the analyte in a sample that can be identified by it. The LOQ, on the other hand, is the lowest concentration of the analyte in a sample that can be quantified as an accurate number with the necessary accuracy and precision, and it is highly significant when the planned analytical method is for the identification of impurities. The point where the two linear components of a calibration curve connect, or the calibration plot's Nernstian and non-Nernstian portions, can be used to visually estimate LOD, while LOQ was determined according to the following equation (Eq. (1)):

$$\mathrm{LOQ} = 3.3\ \mathrm{LOD} \quad (1)$$

LOD was found to be 5.0×10^{-9} mol/L and limit of quantification was 1.65×10^{-8} mol/L of Hg(II) ion.

On the other hand, a series of 6 pastes with the ideal composition were created, and the responses of the prepared electrodes were evaluated at a Hg(II) ion concentration of 1.0×10^{-5} mol/L in order to assess the reproducibility of the Hg(II) ion selective electrode. The RSD% value of 2.05 indicated that the suggested electrodes had good repeatability. Furthermore, the intra- and inter-day investigations on a variety of sample concentrations revealed low RSD% values (0.9–2.76 %) and high recovery% values (97.05–101.4 %), indicating a satisfactory level of repeatability and accuracy for the suggested Hg(II) sensor.

Table 3
Analytical results for potentiometric assay of Hg(II) ion in real spiked water and fruit juice samples and dental amalgam at pH = 3.5.

Sample	Added, mol/L	Found(±*CL*)[a] mol/L		RSD%		Recovery%		F-test[b]	t-test[c]
		Sensor calibration	ICP	Sensor calibration	ICP	Sensor calibration	ICP		
River water	1.0×10^{-7}	$0.98(\pm 2.57) \times 10^{-7}$	$1.01(\pm 2.12) \times 10^{-7}$	1.85	1.25	98.0	101.0	1.920	0.031
	1.0×10^{-5}	$0.97(\pm 2.11) \times 10^{-5}$	$0.98(\pm 1.89) \times 10^{-5}$	1.34	1.06	97.0	98.0	1.566	0.013
Lab water	1.0×10^{-7}	$1.03(\pm 3.16) \times 10^{-7}$	$1.01(\pm 3.00) \times 10^{-7}$	2.36	2.25	103.0	101.0	1.144	0.014
	1.0×10^{-5}	$0.96(\pm 1.99) \times 10^{-5}$	$1.02(\pm 2.23) \times 10^{-5}$	1.22	1.35	96.0	102.0	0.723	0.077
Underground water	1.0×10^{-7}	$0.99(\pm 2.73) \times 10^{-7}$	$0.98(\pm 2.66) \times 10^{-7}$	2.01	1.95	99.0	98.0	1.084	0.008
	1.0×10^{-5}	$0.98(\pm 1.87) \times 10^{-5}$	$0.97(\pm 2.24) \times 10^{-5}$	1.04	1.49	98.0	97.0	0.497	0.013
Apple juice	1.0×10^{-7}	$1.02(\pm 2.85) \times 10^{-7}$	$0.97(\pm 2.73) \times 10^{-7}$	2.05	2.07	102.0	97.0	1.084	0.039
	1.0×10^{-5}	$0.98(\pm 2.15) \times 10^{-5}$	$0.99(\pm 2.25) \times 10^{-5}$	1.36	1.45	98.0	99.0	0.862	0.011
Mango juice	1.0×10^{-7}	$0.96(\pm 1.78) \times 10^{-7}$	$0.98(\pm 1.86) \times 10^{-7}$	0.98	1.03	96.0	98.0	0.869	0.033
	1.0×10^{-5}	$1.04(\pm 2.31) \times 10^{-5}$	$1.00(\pm 2.79) \times 10^{-5}$	1.39	2.04	104.0	100.0	0.502	0.052
Dental amalgam	–	$3.02(\pm 5.60) \times 10^{-2}$	$2.98(\pm 5.38) \times 10^{-2}$	0.98	0.92	–	–	1.165	0.022

[a] *CL* is the confidence limit and confidence interval value at 95% confidence level is 1.960.
[b] Tabulated F-test value at 95 % confidence level for n = 5 is 1.978.
[c] Tabulated *t*-test value at 95 % confidence level for n = 5 is 2.571.

Table 4
Comparison of proposed BMATPP based Hg(II) carbon paste electrode with Hg(II) ion-selective electrodes from literature.

Ref.	Slope, mV decade^{-1}	Linear range, mol/L	Detection limit, mol/L	pH range	Interfering ions, $K^{Pot}_{Hg(II),\ M^{n+}} > 10^{-2}$
[20]	29.3	5.0×10^{-9}-1.0×10^{-4}	2.5×10^{-9}	2.0–4.3	–
[33]	29.7	9.3×10^{-8}-3.9×10^{-3}	3.9×10^{-8}	3.0–7.0	–
[34]	30.0	1.0×10^{-7}-1.0×10^{-2}	5.0×10^{-8}	3.0–4.0	Ag(I)
[36]	29.8	1.0×10^{-9}-1.0×10^{-1}	9.1×10^{-10}	0.0–6.0	Fe(III)
[51]	32.6	1.0×10^{-6}- 1.0×10^{-1}	8.9×10^{-7}	1.0–4.0	–
	29.4	1.0×10^{-5}-1.0×10^{-1}	6.3×10^{-6}	1.0–4.0	–
[56]	30.0	7.0×10^{-8}-1.0×10^{-1}	4.4×10^{-8}	2.0–4.5	Ag(I), Pb(II) and Cu(II)
[57]	30.2	1.0×10^{-7}-1.0×10^{-2}	5.0×10^{-8}	2.6–4.2	Ag(I), Pb(II), Cd(II) and Cu(II)
[58]	28.0	1.0×10^{-7}-1.0×10^{-1}	7.1×10^{-8}	2.5–10.0	K(I)
This work	30.01	5.0×10^{-9}–1.0×10^{-3}	5.0×10^{-9}	2.2–4.5	–

3.6. Proposed electrode assay performance

Using the suggested electrode, the mercury concentration in various water samples—river water, lab water, and underground water was measured. Before usage, these water samples were first made acidic with HNO_3. Additionally, the sample of dental amalgam that contained mercury was examined, and it was treated as stated [51,66]. The suggested sensor was also used to measure Hg(II) ions in samples of fruit juice. These samples were first processed and digested as described in [67,68], after which the extract was spiked with various Hg(II) ion concentrations. For water samples, direct calibration method was applied, while standard addition approach (Eq. (2)) was utilized to evaluate Hg(II) ion concentration in food and dental amalgum samples to eliminate the difference between samples and standard solution matrix. Since the suggested sensor did not interfere with the other metal ions present in those samples, such as Zn^{2+}, Mn^{2+}, Mg^{2+}, Na^{+}, K^{+}, and Ca^{2+}, the data showed satisfactory RSD% and recovery% values demonstrating, respectively, the high precision and accuracy of the suggested sensor. The obtained data were contrasted with those from ICP, as shown in Table 3.

$$C_U = C_S x[V_S/(V_U + V_S)]/\left[\left(10^{(E2-E1)/m}\right) - (V_U/(V_U + V_S))\right] \quad (2)$$

where, C_U, concentration in the unknown sample, Cs, concentration in the standard, v_S volume of standard, V_U, volume of sample, E_1, electrode potential (mV) in the pure solution, E_2, electrode potential after the addition, m, the electrode slope.

3.7. Comparison with literature

The proposed carbon paste electrode based on 1,3-bis[2-(*N-morpholino*)-*acetamidothiophenoxy*]propane (BMATPP), which has been reported to be a major interfering ion in many of the studies compared, has been found to be better in terms of its wide linear range, lower detection limit, and improved selectivity with respect to the various secondary ions, especially the silver(I), which has been reported to be a major interfering (Table 4). Poor selectivity was a key issue for sensors used to detect Hg(II) ions in previous studies, especially when secondary ions like Fe(III) and Cd(II) were present. This issue is nearly completely resolved by the CPE suggested in this study.

4. Conclusion

The development of a new Hg(II) ion carbon paste electrode was made possible by the straightforward addition of the modifier 1,3-bis[2-(*N-morpholino*)*acetamido-thiophenoxy*]propane (BMATPP). In comparison to previously published Hg(II) ISEs, it was discovered that this sensor had a significant improvement in terms of sensitivity and selectivity toward Hg(II) ions. The operational pH, temperature, and response time ranges met requirements. With excellent agreement between the data acquired from the ICP method and the potentiometric detection of Hg(II) in samples, this sensor has been used successfully. Despite the presence of numerous other metal ions in these samples, the suggested sensor identified Hg(II) ions with great selectivity, which can be explained by the high affinity of the used soft ionophore towards soft Hg(II) ions.

CRediT authorship contribution statement

Aya E. Ali: Conceptualization, Data curation, Writing – original draft, Writing – review & editing. **Ashraf A. Abbas:** Data curation, Writing – original draft. **Gehad G. Mohamed:** Conceptualization, Data curation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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