ORIGINAL PAPER

Determination of bismuth ion in biological and water samples with a potentiometric sensor using carbon paste electrode as a straightforward and simple indicator electrode

Mahnaz Sanati[1] · Mahboubeh Masrournia[1] · Hossein Behmadi[1] · Ali Beyramabadi[1]

Abstract

Bismuth and its derivatives are important compounds that are used in various industries in alloy, laser, and semiconductor preparations, energy storage applications, thermoelectric applications, and pharmacological applications. In the study, a potentiometric sensor was prepared to measure Bi(III) ions in the real water and pharmacological samples using a carbon paste electrode (CPE) as an indicator electrode. Several components were chosen to prepare the best CPE, including graphite powder, a binder, carbon-based nanomaterials as a modifier agent, and an ionophore (synthetic Schiff base). For the selected best CPE composite, effects of three synthetic Schiff bases as the CPE ionophore, two binders (paraffin oil and an ionic liquid ([Bmim][BF$_4$])), and four carbon-based nanomaterials (graphene, multi-walled carbon nanotubes, amino-functionalized MWCNTs, and carboxyl-functionalized MWCNTs) were compared in the Bi(III) ion determination. Four CPE components, including graphite powder, ionic liquid ([Bmim][BF$_4$]), graphene, and a synthetic Schiff base were selected as the best CPE composite and their percentages were optimized using an experimental design. For this purpose, an optimal mixture design consisting of 20 runs was created to optimize the percentage of CPE components. Under the optimum percentage of CPE composite, the sensor displayed linearity in the range of 4.8×10^{-7}–1.0×10^{-2} M, a slope of 19.17 ± 0.57 mV decade^{-1}, a limit of detection of 1.45×10^{-7} M, a response time of 5 s, and a lifetime of 9 weeks to measure Bi(III) ions. The sensor selectivity was investigated based on the matched potential method (MPM), indicating the sensor has high selectivity toward Bi(III) ions in the presence of various interfering species. The application of the sensor to determine Bi(III) ions was evaluated by analyzing several real samples such as well water samples, river water samples, and pharmacological products. The relative recoveries for the real samples were in the range of 93.8–98.1% with a relative standard deviation between 0.71 and 1.98%, indicating that the sensor has an excellent ability to the routine measurement of Bi(III) ion in the pharmacological and water samples with a suitable linear range and fast response time.

Keywords Bismuth · Potentiometric sensor · Carbon paste electrode · Schiff bases · Biological samples · Water samples

Introduction

Bismuth (Bi) and its derivatives usually have relatively low toxicity with various industrial applications in alloy, laser and semiconductor preparations, energy storage and thermoelectric applications [1–6]. Bismuth compounds are employed for treating of Helicobacter pylori-induced gastritis, syphilis, tumor, and dermatological disorders in pharmaceutical applications [7]. They were also utilized as an anti-cancer, anti-microbial, and anti-leishmanial agent [8, 9]. Although bismuth compounds were generally known to be non-toxic drugs, their long-term use for treatment could have adverse effects on human organism. Therefore, providing new methods with low cost, rapid response with high accuracy and suitable sensitivity for determination of bismuth in biological and environmental samples is highly demanded [10–12].

A potentiometer sensor is a simple, fast, inexpensive, and efficient tool for determining the activities of various analytes in real samples. These sensors could be applied to measure analytes for 4–10 weeks without significant changes in their response depending on their type, stability

✉ Mahboubeh Masrournia
masrournia@yahoo.com; masrour@mshdiau.ac.ir

[1] Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

of sensor components and their storage conditions [13, 14]. The most critical component in potentiometric sensors is the indicator electrode so that sensor properties for the determination of analytes depend on its intrinsic properties. Carbon paste electrode (CPE) was widely utilized as an indicator electrode in potentiometric methods due to its excellent features including low cost, easy preparation, simple application, wide potential window, suitable thermal and chemical stability, fast response time, and long lifetime with a reasonable selectivity towards the analyte [15]. These proper properties of CPE were depended on the type and chemical properties of CPE components, especially ionophores, nanoparticles, and binders [16]. Mineral oils have been used as a critical component for connecting of graphite particles, ionophore, and nanoparticles mechanically. Essential features of mineral oils included high viscosity, low volatility, high chemical, mechanical and thermal stability, and low water solubility. Two main disadvantages of mineral oils for CPE preparation are their low conductivity and the difference in the type and percentage of their compounds as obtained from different refineries [17–19]. To overcome these limitations, ionic liquids (ILs) were employed as binders in the CPE preparation to increase the conductivity [20, 21]. In addition, nanoparticles were used as a modifier agent in the CPE composite to miniaturize the electrode, create excellent potential stability, and improve various external factors [22]. Ionophore is another critical component in CPE that determines the sensor's selectivity and sensitivity for analyte determination. Ionophore acts as a complexing agent to interact with an analyte on the electrode surface. The bond between the analyte and the ionophore is reversible so that it causes to faster analyte transfer to the electrode surface by increasing the concentration gradient in the diffusion layer [23, 24]. Since ionophore has an essential role in the selectivity and sensitivity of the prepared CPE to measure an analyte in a real sample [25–27]; therefore, synthesis and selection of new ionophores for the CPE preparation with high selectivity and sensitivity for potentiometric measurements of various analytes have received much attention. Schiff bases are a class of organic compounds, including the imine functional groups ($-RC=N-$) [28, 29]. Due to the their suitable properties, these compounds have found many applications in pharmacy, chemistry, and industry, such as the preparation of catalysts, pigments, corrosion inhibitors, and polymer stabilizers [30]. However, these compounds can be used as suitable ionophores for selectively interaction with analytes in the CPE composite due to their chemical structure and appropriate functional groups [31]. Alizadeh et al., in 2013 developed a highly selective and sensitive electrochemical sensor for Bi(III) determination based on nano-structured bismuth-imprinted polymer modified

carbon/carbon nanotube paste electrode. They reported that CPE exhibited a dynamic linear response range of 0.2–2 µmol L^{-1} and detection limit of 8.9 nmol L^{-1} for Bi(III) [7].

In this research, a potentiometric sensor was prepared to measure Bi(III) ions in the real water and pharmacological samples using a carbon paste electrode (CPE) as an indicator electrode. The effects of three synthetic Schiff bases as the CPE ionophore, two binders (paraffin oil and an ionic liquid ([Bmim][BF4])), and four carbon-based nanomaterials (graphene, multi-walled carbon nanotubes, amino-functionalized MWCNTs, and carboxyl-functionalized MWCNTs) were studied for determination of Bi(III) ion.

Experimental

Materials and instrument

Graphite powder with a particle size of 1–2 µm was obtained from Merck (Darmstadt, Germany). Paraffin oil and 1-butyl-3-methyl imidazolium tetrafluoroborate ([Bmim][BF$_4$]) were purchased from Sigma-Aldrich (USA). Graphene nanosheets ($\geq 99\%$ purity, 3.4–7 nm thickness, and 6–10 Layers), multi-walled carbon nanotubes, amino-functionalized multi-walled carbon nanotube, and carboxyl-functionalized multi-walled carbon nanotube were obtained from US Research Nanomaterials, Inc (USA). Other materials and organic solvents were analytical grade and purchased from Merck (Darmstadt, Germany). The stock solution of Bi(III) ion was prepared by dissolving of appropriate amounts of Bismuth(III) nitrate pentahydrate (Sigma-Aldrich, priority $\geq 99.99\%$) in nitric acid (1.0 mol L^{-1}). Benzaldehyde (priority $\geq 99\%$), 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol (priority $\geq 99\%$), 4-amino-3-methyl-1H-1,2,4-triazole-5(4H)-thione (priority $\geq 97\%$), and 2,4-dihydroxy benzaldehyde (priority $\geq 98\%$) were utilized to prepare Schiff bases and obtained from Sigma-Aldrich (USA). The sensor potential and pH of the sample solutions were determined using a pH meter (model 691, Metrohm, Switzerland). ^{1}H NMR spectrum of samples was determined by a Bruker 300 DRX instrument using DMSO-d_6 as solvent and tetramethylsilane as an internal standard and an AVATAR 370 instrument (Thermo Nicolet Company, USA) was used to record of Fourier Transform-Infrared spectrophotometer (FT-IR) spectrum. A saturated calomel electrode (Azar Electric Co., Iran) and the prepared CPE were selected as a reference electrode and indicator electrode, respectively, to measure the concentration of Bi(III) ion in the standard and real samples at a temperature of 23 ± 1 °C, according to the following potentiometric cell:

CPE|Sample solution of Bi(III)| | SCE

Schiff base synthesis

To prepare Schiff base No. 1 (L1) (presented in Fig. S1), two solutions containing 4-amino-3-methyl-1H-1,2,4-triazole-5(4H)-thione in ethanol (2.0 mL) and 2,4-dihydroxy benzaldehyde (0.138 g) in ethanol (2.0 mL) were individually prepared at ambient temperature (24 ± 2 °C). Then, two solutions were mixed and refluxed for 80 min under stirring. The light pink precipitation as Schiff base No. 1 was filtered and washed with ethanol before drying for 16 h in an oven at 50 °C [32]. ^{1}H NMR spectrum presented in Fig. S2 (DMSO-d_6), δ (ppm): 2.47 (s, 3H, –CH$_3$), 5.20 (s, 1H, –CH=N), 6.15 (d, 1H, $J = 7.2$ Hz, Ar–H), 7.54 (d, 1H, $J = 7.2$ Hz, Ar–H), 8.03 (s, 1H, Ar–H), 8.14 (s, 2H, 2 –OH), 10.46 (s, 1H, –NH), 13.9 (s, 1H, –SH). In addition, Fig. S3a shows the FT-IR spectrum of the synthesized Schiff Base No.1. The peaks at 3200–3400 cm^{-1}, 2800 cm^{-1}, 1600 cm^{-1}, 1350 cm^{-1} and 1020 cm^{-1} are related to the stretching vibration of O–H, C–H (methyl), C=C (aromatic ring), C–N aromatic ring and C–O, respectively.

To prepare Schiff base No. 2 (L2) (presented in Fig. S1), 0.5 g of 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol was dispersed in 20.0 mL of hydrochloric acid (1.0 M), followed by adding a solution containing 0.5 g of benzaldehyde in 5.0 ml of ethanol. The mixture was refluxed for 25 min and low-yellow precipitate as Schiff base No. 2 was separated and washed with water and ethanol [33]. ^{1}H NMR spectrum presented in Fig. S2b (DMSO-d_6), δ (ppm): 6.85 (s, 1H, –CH=N), 6.88–6.92 (m, 2H, Ar–H), 7.24 (t, 1H, $J = 7.2$ Hz, Ar–H), 7.42 (d, 1H, $J = 7.5$ Hz, Ar–H), 8.50 (s, 1H, –OH), 11.10 (b, 1H, –NH), 13.03 (b, 1H, –SH). In addition, Fig. S3b shows the FT-IR spectrum of the synthesized Schiff Base No. 2. The peaks at 3310 cm^{-1}, 1640 cm^{-1}, 1600 cm^{-1}, 1340 cm^{-1}, and 1280 cm^{-1} are related to the stretching vibration of N–H, N–H bending, C=C (aromatic ring), C–N aromatic ring and C–N, respectively.

To prepare Schiff base No. 3 (L3) (presented in Fig. S1), two solutions containing 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol (1.0 g) were dispersed in 20.0 mL of hydrochloric acid (1.0 M) and benzil (1.0 g) in 10.0 ml of ethanol was mixed at room temperature. The mixture was refluxed for 25 min and the precipitate as Schiff base No. 3 was separated and washed with water and ethanol [33]. ^{1}H NMR spectrum presented in Fig. S2c (DMSO-d_6), δ (ppm): 5.84 (b, 4H, 2 –NH$_2$), 7.31–7.62 (m, 10 H, Ar–H), 9.23 (s, 2H, 2 –NH), 12.95 (b, 2H, 2 –SH). In addition, Fig. S3c shows the FT-IR spectrum of the synthesized Schiff Base No. 1. The peaks at 3310 cm^{-1}, 1640 cm^{-1}, 1600 cm^{-1}, 1340 cm^{-1}, and 1280 cm^{-1} are related to the stretching vibration of N–H, N–H bending, C=C (aromatic ring), C–N aromatic ring and C–N, respectively.

CPE preparation

A CPE as an indicator electrode was prepared by mixing four CPE components, including graphene (0.354 g) as a modifier agent, graphite powder (1.674 g), ionic liquid (0.381 g) as a suitable binder, and Schiff base as an ionophore (0.588 g) in mortar for 40 min under optimization percentages of each component until a uniform paste (about 3 g) was obtained. The uniform paste was thoroughly filled into a metal rod (5 mm of ID and 3.0 cm of length) for preparing CPE. The carbon paste was well pressed inside the metal rod to prevent air bubbles and prevent its electrical resistance for increasing. A proper electrical connection was performed between the carbon paste in the metal rod and the pH meter by a Pt wire. Finally, CPE was thoroughly immersed into the aqueous solution of Bi (III) (1.0×10^{-2} M), followed by stirring at 300 rpm for 20 h.

Results and discussion

Type of ionophore

Three CPEs were prepared using graphite powder (65%), paraffin oil (10%), graphene (10%), and Schiff base L1–L3 (15%). For this purpose, three synthetic Schiff bases were chosen as ionophores in the CPE composites. The prepared CPEs were applied to determine Bi (III) ions in the concentration range of 1.0×10^{-7}–1.0×10^{-2} M at room temperature. The results presented in Table 1 indicated that the Schiff base (L2) has the best slope for the Bi (III) ion determination, and therefore, it was selected for further study.

Table 1 Effects of type of Schiff base and nanomaterials on the CPE slope

	Slope ± S	R^2
Type of Schiff base		
Schiff base no. 1	15.96 ± 0.91	0.8321
Schiff base no. 2	17.55 ± 0.87	0.9132
Schiff base no. 3	25.14 ± 1.26	0.8744
Type of nanomaterials		
Graphene	18.12 ± 0.78	0.9351
MWCNTs	17.56 ± 0.86	0.9131
NH$_2$-MWCNTs	24.5 ± 1.14	0.8976
COOH-MWCNTs	16.43 ± 1.08	0.8825

Type of nanomaterials

Four nanomaterials such as graphene nanosheets, multiwalled carbon nanotubes (MWCNTs), amine-functionalized MWCNTs, and carboxyl-functionalized MWCNTs, were selected as a modifier agent in the CPE composite for measuring Bi (III) ions in the concentration range of 1.0×10^{-7}–1.0×10^{-2} M at room temperature (Table 1). The obtained results indicated that graphene nanosheets provides better slope for the Bi (III) ion determination which may be related to the higher electrical conductivity and surface area of graphene nanosheets other than used nanomaterials.

Type of binder

Paraffin oil and an ionic liquid ([Bmim][BF$_4$]) were chosen as a binder in the CPE composite and their effects in the slope of CPE to determine Bi (III) ions in the concentration range of 1.0×10^{-7}–1.0×10^{-2} M were compared. The obtained CPE slopes were 18.12 ± 0.79 and 18.79 ± 0.63 using paraffin oil and [Bmim][BF$_4$], respectively, showing that the ionic liquid in the CPE composite provides better

CPE slope than paraffin oil which may be due to an increase in the CPE conductivity and higher purity of ionic liquid.

Optimization of CPE composite

The amounts of CPE components, including graphite powder, graphene, ionic liquid, and ionophore, for determining Bi (III) ions were optimized using an optimal mixture design. The experimental design includes 20 experimental runs. The experiments were performed in a random order to eliminate the effects of unknown and uncontrollable factors with three repetitions under similar conditions [34–36]. The CPE slopes were determined by drawing the calibration curve at a concentration range of 1.0×10^{-7}–1.0×10^{-1} M with each prepared CPE. The factors, provided design, obtained slopes are shown in Table 2. The results were evaluated using analysis of variance (ANOVA) at a 95% confidence level and presented in Table S1. The p value in the ANOVA Table was utilized to determine the significant factor on the CPE slope. According to the p value at a 95% confidence level, each factor is the significance when its p value is lower than 0.05 (p value $< \alpha$-level)[37]. Therefore,

Table 2 Factors and optimal mixture design for the optimization of CPE composite

Component	Name	Units	Minimum	Maximum
A	Graphite powder	g	0.500	0.600
B	Graphene nanosheets	g	0.100	0.150
C	Ionic liquid ([Bmim][BF$_4$])	g	0.100	0.150
D	Schiff base	g	0.150	0.200

Run	A	B	C	D	Slope
1	0.600	0.110	0.130	0.160	17.19
2	0.576	0.100	0.123	0.200	21.09
3	0.600	0.150	0.100	0.150	18.68
4	0.593	0.127	0.100	0.180	18.16
5	0.500	0.150	0.150	0.200	20.07
6	0.600	0.110	0.130	0.160	17.19
7	0.563	0.100	0.150	0.187	16.78
8	0.572	0.150	0.105	0.172	18.22
9	0.572	0.123	0.131	0.174	18.17
10	0.547	0.123	0.130	0.200	19.6
11	0.550	0.150	0.129	0.171	19.32
12	0.564	0.136	0.150	0.150	16.48
13	0.525	0.150	0.125	0.200	20.15
14	0.593	0.127	0.100	0.180	17.75
15	0.600	0.100	0.100	0.200	21.52
16	0.572	0.123	0.131	0.174	17.18
17	0.524	0.149	0.150	0.177	17.65
18	0.550	0.150	0.100	0.200	18.82
19	0.547	0.123	0.130	0.200	20.56
20	0.563	0.100	0.150	0.187	16.29

a linear mixture of components has a significant effect on the CPE slope to determine Bi(III) ions. Besides, all binary interactions of CPE components are meaningful parameters with significant impacts on the CPE slope, except for the interaction between ionic liquid and Schiff base (CD), which does not have a significant effect on the CPE slope (p value 0.1003). The quadratic model is selected by ANOVA as a significant model because the p value of the model is lower than 0.05 and the p value of the lack of fit (LOF) is higher than 0.05 (LOF is non-significance). The quadratic equation in terms of coded CPE components obtained to describe the relationship between the CPE components and their inter-actions with the CPE slope as presented in the following equation:

$$\begin{aligned} \text{Slope} = &+18.97\,A + 33.37\,B - 23.20\,C \\ &+ 50.37\,D - 22.59\,AB + 41.42\,AC - 35.83\,AD \\ &+ 56.46\,BC - 81.04\,BD + 21.93\,CD. \end{aligned}$$

$$(1)$$

A high amount of R-squared (0.9666) and adjusted R-squared (0.9366) calculated for the quadratic equation indicated that the provided equation is well fitted to describe the obtained results. Besides, the equation can predict

the results of future studies well due to a high-predicted R-squared (0.8909). The equation displayed that a critical component with a positive effect on the CPE slope is iono-phore (D). Obviously, the active sites of the CPE surface to interact with the analyte were increased by increasing the ionophore amount. Another component with a high and positive effect on the CPE slope is graphene as a modifier agent due to increasing the CPE conductivity and the CPE surface area to interact with Bi (III) ions. The interaction between graphene and ionophore is the crucial interaction with a negative effect on the CPE slope, indicating that the CPE slope was decreased with the simultaneous increase of both components. Interaction between graphene and ionic liquid (BC) is the next important interaction with a positive effect on the CPE slope, showing that the CPE slope was significantly increased with simultaneous increasing in the graphene and ionic liquid amounts into the CPE composite. Effects of simultaneous change in three critical components, including graphene, ionic liquid, and ionophore, on the CPE slope is represented in Fig. 1, which indicated that the CPE slope was dramatically changed with the simultaneous change of these three components in the range 16.29–21.52, where the amount of graphite is fixed at 0.581. The optimum
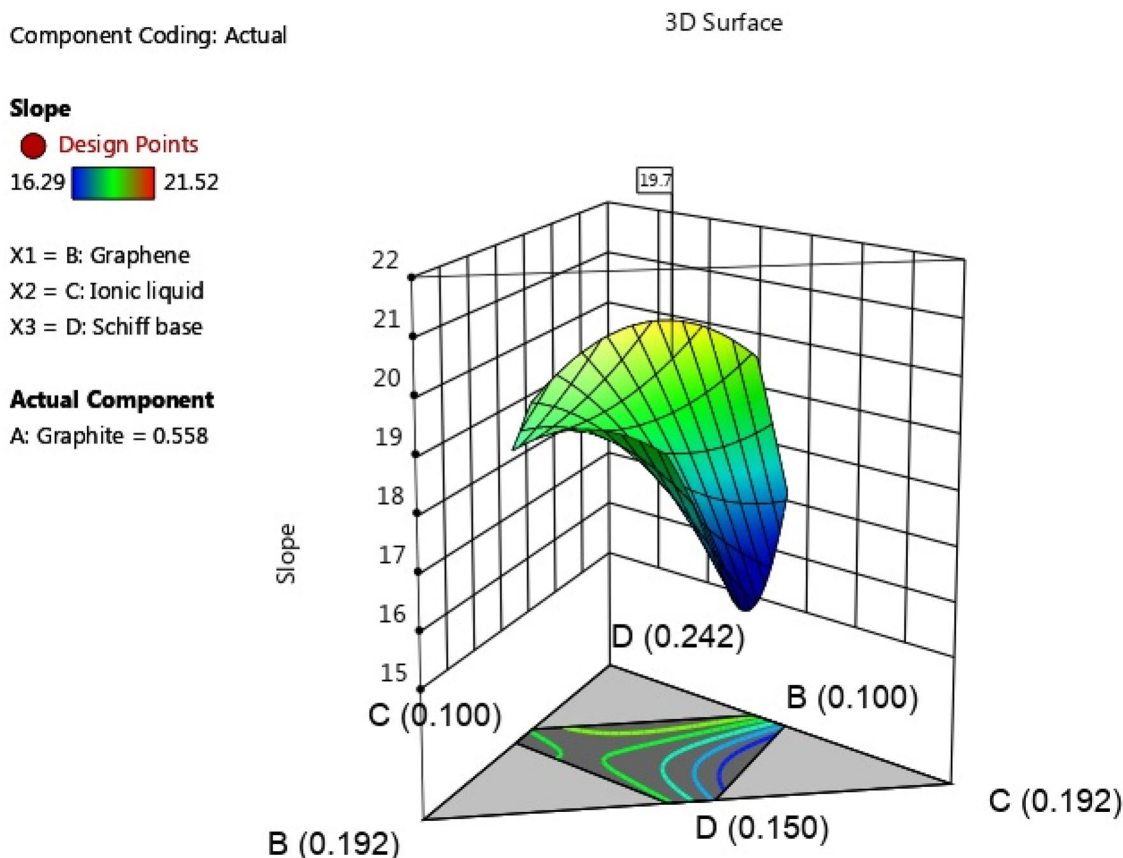

Fig. 1 Effects of simultaneous change in graphene, ionic liquid, and ionophore amounts on the CPE slope

amount of component was predicted based on the quadratic equation using the CPE slope of 19.7 as the target slope so that the optimum amount of graphite powder, graphene, ionic liquid, and ionophore were 0.558 g, 0.118 g, 0.127 g, and 0.196 g, respectively, to prepare 1.0 g of carbon paste electrode.

Figure of merit

A CPE was prepared based on the optimum amounts of the components and used for drawing the calibration curve for the Bi(III) determination. The standard solutions of Bi(III) ions at a concentration range of 1.0×10^{-8}–1.0×10^{-2} M were selected to draw the calibration curve and each standard solution was analyzed three times at similar conditions. The obtained results show that the calibration curve for determining of Bi(III) was linear in the concentration range of 4.8×10^{-7}–1.0×10^{-2} M with an R-squared of 0.9921 and a CPE slope of 19.17 ± 0.57 mV decade^{-1} at 24.5 ± 0.9 °C. Limit of quantitation (LOQs) and limit of detection (LODs) were calculated by determining the standard deviation of the blank sample (S_b) and the slops of calibration curves (m) based on 10 S_b/m and 3 S_b/m, were 1.45×10^{-7} M and 4.8×10^{-7} M, respectively [16]. Moreover, the relative standard deviation (RSD) was determined using a standard solution of Bi(III) ions (1.0×10^{-5} M) with five times repetition which equals to 0.82%.

pH effect

The pH of the sample solution as an important factor affected the CPE performance through a change in the polarity of the analyte in the sample solution and CPE components. The effect of pH on the prepared sensor was investigated in the pH range of 1.0–6.0 to determine Bi(III) ions (1.0×10^{-5} M). The pH of the sample solution was adjusted by adding the proper volume of sodium hydroxide (0.1 M) and nitric acid (0.1 M) solutions before using the sensor for Bi(III) ion determination. According to Fig. 2, the CPE potential for the Bi(III) ion measurement remains constant with a change of pH between 1.8 and 4.6, indicating the sensor is suitable for measuring Bi(III) ions in this pH range for analysis of real samples. Therefore, it could be concluded that in the pH range of 1.8–4.6, Bi(III) effectively interact with functional groups of Schiff Base L2 (N–S- and O-atoms of ionophore) that are bonded to the Bi(III)-nitrate species dominant in solution. However, the sensor potential was reduced at pH higher than 4.6 may be due to the presence of Bi(III)-hydroxide, the predominant species of Bi(III)ions in the sample solution, which cannot interact well with the ionophore at pH higher than 4.6. Obviously, the ionophore with the amine functional groups is neutral at pHs between 8 and 10 because the pKa of the 1,2,4-triazole-3-thione derivatives in the ionophore is usually lower than 10.3 [38].

Response time and lifetime

The response speed of a potentiometric sensor is a critical parameter in its commercial applications for analyte determination, which is evaluated based on response time. The IUPAC definition was usually utilized to determine the response time. Briefly, the prepared sensor was immersed in the standard solutions of Bi(III) ions with different concentrations varying from dilute to concentrated solution in the linear range of the sensor, respectively. The response time was determined as a time to reach 95% of the sensor

Fig. 2 Effects of pH on the sensor response for the Bi(III) ion determination
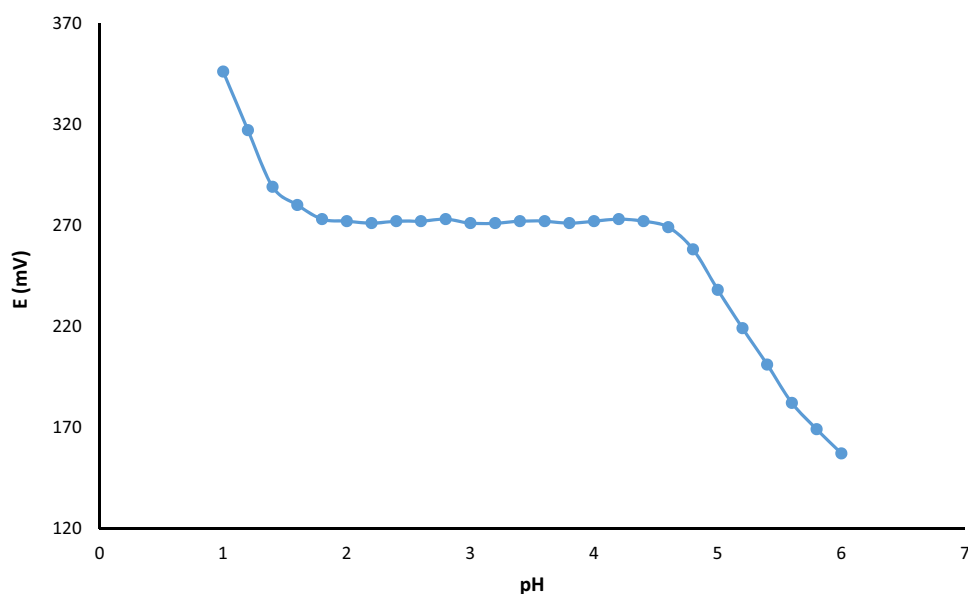
response (the sensor equilibrium potential). In the study, the Bi(III) ion concentration was chosen in the concentration range of 1.0×10^{-7}–1.0×10^{-2} M with a tenfold difference in concentration. The results are represented in Fig. 3, indicating that the sensor has a fast response and an excellent response time of 5 s to determine the Bi(III) ion concentration. Sensor lifetime is another crucial parameter that is commonly investigated to evaluate the stability of a potentiometric sensor over a period of about 2 months. For this purpose, the sensor was weekly utilized to determine Bi(III) ions in the concentration range of 1.0×10^{-7}–1.0×10^{-2} M. The sensor is then washed three times with distilled water and stored at room temperature in the dark place for reuse. The calibration curve is weekly plotted and its slope and R-squared are calculated (Table S2). The results showed that the slope of the sensor remained almost constant for 9 weeks and then significantly decreased which may be due to degradation or oxidation of CPE components, especially the ionophore or graphene nanosheets at room temperature. Therefore, the sensor can be applied to the Bi(III) ion determination for 9 weeks without significant changes in its slope.

CPE selectivity

Analyte measurement in real samples requires a high selectivity of the sensor in the presence of other ions. Therefore, the effects of different ions on the Bi (III) ion measurement were evaluated by calculating the selectivity coefficient ($K_{Bi.M}^{pot}$) according to the matched potential method (MPM) before analyzing the real samples[40]. The selectivity coefficient based on MPM was calculated using the following equation:

$$K_{MPM} = \frac{a_{analyte}}{a_x}, \tag{2}$$

where $a_{analyte}$ and a_x are the Bi (III) ion activity and the interfering ion activity, respectively.

In the study, the Bi (III) ion concentration was 1.0×10^{-4} M and the concentration of the other species was changed between 1.0×10^{-7} and 1.0×10^{-2} M to calculating the selectivity coefficient (Table S3). The obtained selectivity coefficients for the Bi(III) ion determination indicated that the sensor has an excellent selectivity toward Bi(III) and the presence of the studied interfering ions did not affect the Bi (III) ion measurement.

Potentiometric titration of Bi(III) ions

The prepared sensor was selected to determine the endpoint of the titration procedure. For this purpose, a Bi(III) ion solution (1.0×10^{-3} M, 10.0 mL) and a standard solution of EDTA (1.0×10^{-2} M) were used as titrant and titrant solution, respectively. The pH of the Bi(III) ion solution was adjusted to 2.5 before adding titrant (Fig. S4). The results show that the titration curve has a suitable slope and shape to determine the endpoint of Bi(III) ion titration, indicating that the prepared sensor can be well utilized for Bi (III) ion measurement with the potentiometric titration method.

Real sample analysis

Bismuth subcitrate tablet (120 mg) as a drug was obtained from Chemidarou Co. (Iran) and Tehrandarou Co. (Iran). Each tablet was dissolved in 10.0 mL of hot concentrated nitric acid and stirred for 30 min. The pH of the obtained solution was adjusted to 2.5, followed by diluting to 20.0 mL

Fig. 3 Response time of the sensor for the Bi(III) ion determination
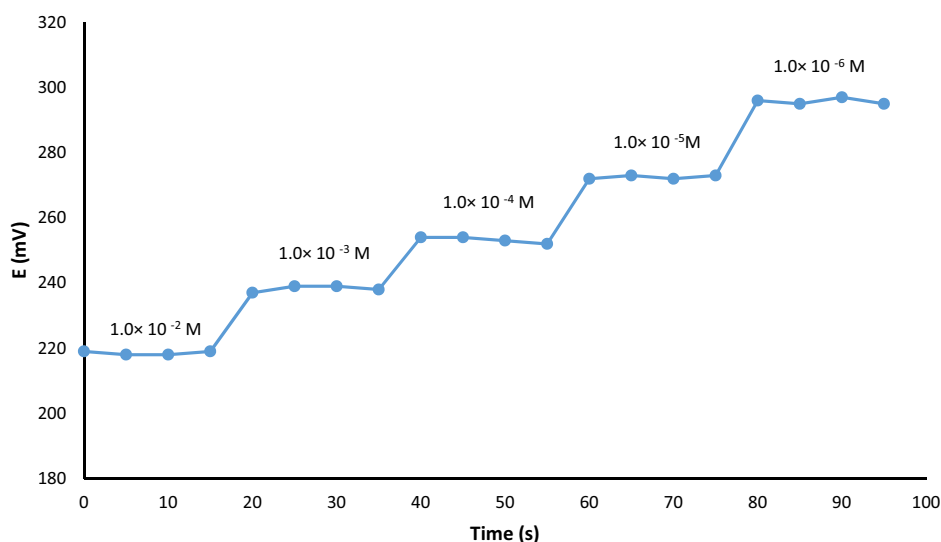
with distilled water. River and well water samples were obtained from the Mayan River (Torghabeh, Iran) and the outskirts of Mashhad (Iran). The pH of all water samples (50.0 mL) was adjusted to 2.5 using 0.1 M nitric acid. All real water and tablet samples were spiked with standard solutions of Bi(III) ions at two concentrations of 1.0×10^{-5} and 1.0×10^{-4} M. The pharmacological and water samples were analyzed by titration procedure with a standard solution of EDTA to determine Bi(III) ion content. Each analysis was performed for three replications under the same conditions. The results are presented in Table 3, indicating that the recoveries for the Bi(III) ion determination were in the range of 93.8–98.1% with a relative standard deviation between 0.71 and 1.98%. Therefore, the sensor has an excellent ability to measure Bi(III) ion in the pharmacological and water samples with a proper standard deviation and recoveries.

Comparison of the prepared sensor with other sensors

The proposed CPE was compared by other ion selective electrodes for determination of Bi(III) ion [41–44] as presented in Table 4. By comparison to other ion selective electrodes,

the prepared sensor has wide dynamic range and low RSD. In addition, other advantages such as low cost, fast response speed, suitable lifetime, and ease of use without the need for sophisticated tools makes it as an unique CPE for determination of Bi(III).

Conclusion

A potentiometric sensor was prepared using a carbon paste electrode as an indicator electrode for determining Bi(III) ion in real water and pharmacological samples. The carbon paste electrode contains four components including graphite powder, binder, nanomaterials, and ionophore. In this research, three synthetic Schiff bases were selected as ionophores in the CPE composite and the obtained results show that the synthetic Schiff base No. 2 provides the best slope with suitable R^2 for measuring of Bi(III) ions. Moreover, several carbon-based nanomaterials such as graphene, multi-walled carbon nanotubes (MWCNTs), NH_2-functionalized MWCNTs, and COOH-functionalized MWCNTs, were chosen as modifier agents in the CPE composite and based on the results graphene was selected as the best modifier agent

Table 3 Assay of the water and pharmacological samples using the potentiometric sensor ($n=3$)

Sample	Spike	Found ± SD	Recovery	RSD%
Tablet no. 1	0.0 mg	30.3 ± 0.6 mg	–	1.98
	50 mg	81.4 ± 1.6 mg	102.2	1.96
	100 mg	129.5 ± 2.5 mg	99.2	1.93
Tablet no. 2	0.0 mg	30.1 ± 0.5 mg	-	1.66
	50 mg	78.6 ± 1.6 mg	97.0	2.04
	100 mg	127.0 ± 2.9 mg	96.9	2.28
River water	0.0 M	ND[4]	–	–
	1.0×10^{-5} M	$(9.68 \pm 0.09) \times 10^{-6}$ M	96.8	0.93
	1.0×10^{-4} M	$(9.73 \pm 0.08) \times 10^{-7}$ M	97.3	0.82
Well water	0.0 M	ND	–	–
	1.0×10^{-5} M	$(9.64 \pm 0.08) \times 10^{-6}$ M	96.4	0.83
	1.0×10^{-4} M	$(9.81 \pm 0.07) \times 10^{-7}$ M	98.1	0.71

[1]Tablet (120 mg Bismuth subcitrate, 32.1 mg Bi(III) ion)

[2]Tablet (32.1 mg Bi(III) ion) and 50 mg bismuth nitrate pentahydrate (21.5 mg Bi(III) ion)

[3]Tablet (32.1 mg Bi(III) and 100 mg bismuth nitrate pentahydrate (43.0 mg Bi(III) ion)

[4]Not detected

Table 4 Comparison of the proposed method with other potentiometric method for determination of Bi

Method	LOD (M)	Linear range (M)	RSD (%)	References
Ion-selective electrode–bismuth sulfide NPs	8.1×10^{-9}	$1 \times 10^{-8} - 1 \times 10^{-4}$	1.3–1.5	[41]
PVC membrane ion selective electrode	–	$5 \times 10^{-7} - 1 \times 10^{-2}$	–	[42]
Bismuth(III) selective electrode	1.4×10^{-8}	$1 \times 10^{-7} - 1 \times 10^{-2}$	–	[43]
Ion-selective electrodes	3.98×10^{-7}	$5 \times 10^{-7} - 1 \times 10^{-1}$	–	[44]
Potentiometric method	1.45×10^{-7} M	$4.8 \times 10^{-7} - 1.0 \times 10^{-2}$ M	0.82	Present work

due to its higher conductivity than other selected carbon-based nanomaterials. In addition, the effect of two binders, paraffin oil and an ionic liquid ([Bmim][BF$_4$]), was compared and the results shown that ionic liquid is superior than paraffin oil in the CPE composite. Finally, the results of the analysis of real samples show that the prepared sensor has a very good recovery with proper standard deviation for determination of Bi(III) in different water and pharmacological samples.

References

1. A. Vega-Jiménez, A. Almaguer-Flores, M. Flores-Castañeda, E. Camps, M. Uribe-Ramírez, O. Aztatzi-Aguilar, A. De Vizcaya-Ruiz, Nanotechnology **28**, 435101 (2017)
2. K. Rudramamba, D.K. Reddy, T.S. Rao, S. Taherunnisa, N. Veeraiah, M.R. Reddy, Opt. Mater. **89**, 68 (2019)
3. A. Prasath, M. Athika, E. Duraisamy, A. Selva Sharma, V. Sankar Devi, P. Elumalai, ACS Omega **4**, 4943 (2019)
4. L. Torrisi, L. Silipigni, N. Restuccia, S. Cuzzocrea, M. Cutroneo, F. Barreca, B. Fazio, G. Di Marco, S. Guglielmino, J. Phys. Chem. Solids **119**, 62 (2018)
5. F. Li, T. Jiang, J. Zhai, B. Shen, H. Zeng, J. Mater. Chem. C **6**, 7976 (2018)
6. H. Mamur, M. Bhuiyan, F. Korkmaz, M. Nil, Renew. Sust. Energ. Rev. **82**, 4159 (2018)
7. T. Alizadeh, N. Hamidi, M.R. Ganjali, P. Nourozi, Sens. Actu. B Chem. **245**, 605 (2017)
8. D.M. Keogan, D.M. Griffith, Molecules **19**, 15258 (2014)
9. D.M. Griffith, H. Li, M.V. Werrett, P.C. Andrews, H. Sun, Chem. Soc. Rev. **50**, 12037–12069 (2021)
10. S. Vakilzadeh, M. Eftekhari, M. Chamsaz, F. Javedani-Asleh, Anal. Methods **7**, 7653–7658 (2015)
11. M. Alawadi, M. Eftekhari, M. Gheibi, F. Iranzad, M. Chamsaz, Chem. Pap. **73**, 2041–2051 (2019)
12. N.S. Gadhari, B.J. Sanghavi, S.P. Karna, A.K. Srivastava, Electrochim. Acta **56**, 627–635 (2010)
13. E. Shojaei, M. Masrournia, A. Beyramabadi, H. Behmadi, Eurasian. Chem. Commun. **2**, 750 (2020)
14. S. Shahraki, M. Masrournia, H. Karimi-Maleh, Chem. Methodol. **4**, 720 (2020)
15. S. Sharif Manesh, M. Masrournia, A. Beyram Abady, Anal. Bioanal. Electrochem. **12**, 180
16. S.S. Manesh, M. Masrournia, J. Iran. Chem. Soc. **18**, 1219–1229 (2021)
17. H. Bagheri, A. Afkhami, A. Shirzadmehr, H. Khoshsafar, H. Khoshsafar, H. Ghaedi, Int. J. Environ Anal. Chem. **93**, 578–591 (2013)
18. H. Bagheri, A. Shirzadmehr, M. Rezaei, Ionics **22**, 1241 (2016)
19. H. Khani, M.K. Rofouei, P. Arab, V.K. Gupta, Z. Vafaei, J. Hazard. Mater. **183**, 402 (2010)
20. J. Gębicki, A. Kloskowski, W. Chrzanowski, P. Stepnowski, J. Namiesnik, Crit. Rev. Anal. Chem. **46**, 122 (2016)
21. J. Narongthong, H.H. Le, A. Das, C. Sirisinha, S. Wießner, Compos. Sci. Technol. **174**, 202 (2019)
22. T. Yin, W. Qin, Trends Analyt. Chem. **51**, 79–86 (2013)
23. E. Luboch, M. Jeszke, M. Szarmach, N. Łukasik, J. Incl. Phenom. Macrocycl. Chem. **86**, 323–335 (2016)
24. O. Isildak, O. Özbek, M. Burcu Gürdere, J. Anal. Test. **4**, 273–280 (2020)
25. A. Rüütel, V. Yrjänä, S.A. Kadam, I. Saar, M. Ilisson, A. Darnell, K. Haav, T. Haljasorg, L. Toom, J. Bobacka, Beilstein J. Org. Chem. **16**, 1901 (2020)
26. Q. Hu, S. Chen, Z. Wang, Z. Zhang, Sens. Actu. B Chem. **328**, 128955 (2020)
27. M.S. Ferris, M.R. Behr, K.J. Cash, RSC Adv. **9**, 32821 (2019)
28. W. Al Zoubi, A.A.S. Al-Hamdani, M. Kaseem, Appl. Organomet. Chem. **30**, 810 (2016)
29. W. Al Zoubi, N. Al Mohanna, Spectrochim Acta. A Mol. Biomol. Spectrosc. **132**, 854–870 (2014)
30. A. Kajal, S. Bala, S. Kamboj, N. Sharma, V. Saini, J. Catal. **2013**, (2013).
31. G.I. Mohammed, A.L. Saber, H.A. El-Ghamry, J.T. Althakafy, H. Alessa, Arab. J. Chem. **14**, 103210 (2021)
32. H. Raouf, S.A. Beyramabadi, S. Allameh, A. Morsali, J. Mol. Struct. **1179**, 779 (2019)
33. R.G. Dickinson, N.W. Jacobsen, J. Chem. Soc. Perkin Trans. **1**, 975–979 (1975)
34. P. Mohammadi, M. Ghorbani, P. Mohammadi, M. Keshavarzi, A. Rastegar, M. Aghamohammadhassan, A. Saghafi, Microchem. J. **160**, 105680 (2021)
35. Z. Gordi, M. Ghorbani, M. Ahmadian K., Water Environ. Res. **92**, 1935 (2020)
36. M. Ghorbani, S. Ariavand, M. Aghamohammadhasan, O. Seyedin, J. Iran. Chem. Soc. **18**, 1947–1963 (2021)
37. M. Ghorbani, T. Pedramrad, M. Aghamohammadhasan, O. Seyedin, H. Akhlaghi, N.A. Lahoori, Microchem. J. **147**, 545 (2019)
38. V. Dimova, I. Jordanov, L. Dimitrov, J. Chil. Chem. Soc. **61**, 3071 (2016)
39. E. Bakker, E. Pretsch, Trends Anal. Chem. **24**, 199–207 (2005)
40. Y. Umezawa, P. Bühlmann, K. Umezawa, K. Tohda, S. Amemiya, Pure Appl. Chem. **72**, 1851 (2000)
41. L. Liu, L. Wang, H. Yin, Y. Li, X. He, Anal. Lett. **39**, 879–890 (2006)
42. H.X. Wang, Z.N. Yan, X.L. Wen, Y.X. Kang, S.Y. Zhang, Chin. Chem. Lett. **26**, 1147–1149 (2015)
43. Z. Yan, H. Zhang, R. Xing, X. Wen, B. Gu, Sens. Lett. **13**, 925–933 (2015)
44. R. Kumar Mahajan, R. Kumar Puri, G. Bhargava, M. Pal Mahajan, Anal. Lett. **42**, 2444–2459 (2009)