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Design and Evaluation of a Novel Bismuth Optical Sensor Using PC-ANN Application

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The characterization of and construction of a new optical sensor based on the immobilization of Pyrocatechol Violet on a triacetylcellulose membrane were described to determine bismuth(III) ions in real samples. The interaction between sensing membrane and bismuth(III) ions took place at pH 3.80 in acetate buffer solution, and the color changed from yellow to blue along with the appearance of a sharp peak at 613 nm. This optical sensor has a linear range of 4.98-47.60 µM with a detection limit of 0.853 µM. Bismuth(III) can be detected within 10 min. The working range was improved using a PC-ANN algorithm. The sensor could be regenerated with 0.1 M hydrochloric acid solution. This optical sensor is designed to determine bismuth(III) in the environmental and biological samples.

Keywords: Bismuth(III), ICP-AES, Optical sensor, PC-ANN, Pyrocatechol violet

INTRODUCTION

For a long time, bismuth compounds as a relatively rare element on the earth have been used in pharmaceutical industries for different medical purposes such as treatment of syphilis [1], Helicobacter pyloric-induced gastritis [2] and gas trointestinal tract disturbances [3]. They also appear in different areas of life such as semiconductors, alloys, cosmetics products, metallurgical additives and preparation and recycling of uranium in nuclear fuel [4]. Because of increasing the use of bismuth, possibility of exposure to this element has also increased that caused some toxic effects such as nephrotoxic, neurotoxic, and kidney damage symptoms in humans and other animals [5].

Bismuth has been determined by various methods such as flame atomic absorption spectrometry [6], cloud point extraction [7], molecular spectrophotometry [8], electro analytical methods [9], hydride generation-atomic fluorescence spectrometry (HG-AFS) [10] and inductively coupled plasma mass spectrometry (ICP-MS) [11]. However, each approach has some drawbacks such as the need for an apparatus and trained personnel, operational convenience, cost analysis, test speed and detection limit, *etc.*

On the other hand, optical sensing membranes as simple and selective tools have been successfully developed over the recent decades to provide fast determination methods for heavy metal ions [12]. The essential step in the fabrication of optical sensor is immobilization of indicators on the membrane [13]. Among the different immobilization methods such as physical entrapment [14], sol-gel [15] and multilayered membranes [16], chemical immobilization has a long lifetime, high reversibility that prevents leaching of reagent dyes [17].

Optical sensors show a sigmoidal response curve, therefore, they usually suffer from low sensitivity and narrow linear range [18]. In the last decade, the number of studies on the application of artificial neural network (ANN) for solving the problems of optical sensor technology has substantially increased [19]. ANN is defined as a data processing system that simulates the human's brain by building up the information that it learns [18]. ANN is used in signal processing, data reduction and optimization, interpretation, and prediction of spectra and calibration [20].

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It is possible to obtain accurate results by compressing the data into scores using the principal component analysis-artificial neural network (PC-ANN) [20].

The present research aims to describe the ability of a new simple, low cost and selective colorimetric optical sensor made by pyrocatechol violet as the sensing reagent (its possible structure is shown in Fig. 1a) immobilized on a triacetylcelloluse membrane and sheltered with methyltriocthylammoniumcholoride by forming an ion pair (Fig. 1b), for the determination of bismuth(III) ions. Furthermore, optimization of the main factors and application to the analysis of biological and environmental samples was studied in detail. The linear range of optical sensor was improved with a PC-ANN algorithm.

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EXPERIMENTAL

Reagents

All the reagents used were of chemical purity or analytical grade. Pyrocatechol violet as an indicator and ethylenediamine were obtained from Merck. Acetic acid/sodium acetate buffer solution was prepared from a mixture of 18 ml of acetic acid (0.2 M), 180 ml sodium acetate (0.2 M) and 200 ml of H_2O and the required pH was adjusted by a 0.5 M sodium hydroxide solution. A stock solution of 1.00×10^{-3} M of Bi(III) ion was prepared daily by dissolving 0.012 g of $Bi(NO_3)_3.5H_2O$ (Merck) in 25.0 ml of distilled water.

Apparatus and Software

UV-Vis spectra, obtained with a UV-Vis JASCO spectrophotometer, Model V-570, were used to report the visible spectral absorbance. A Metrohm 632 pH-meter was used for the pH measurements. Inductively Coupled Plasma -Atomic Emission Spectrometry (ICP-AES) (model VISTA-PRO) was used to determine Bi(III) ions in real sample solutions. The result of PC-ANN was obtained from an ANN toolbox of MATLAB (version 7.6).

Preparation of Optical Sensing Membranes

To supply the elucidation of the triacetylcellulose membrane, waste photographic membranes were used and then the colored gelatinous layer was removed with commercial sodium hypochlorite and distilled water. The sensing membranes were manually created by placing a clear solution of Pyrocatechol violet (0.02 g) and methyltrioctylammonumcholorid (0.02 g) in 5.0 ml ethylenediamine for 13 min at ambient temperature. To remove ethylenediamine and trapped indicator, the membranes were washed with distilled water and kept under distilled water when not in use [21].

General Procedure

The membrane was placed in acetic acid/sodium acetate buffer solution at pH 3.80 for 15 min. Then, the sensing membrane was put vertically inside the quartz cell implemented in the spectrophotometer to assess the optical response of the polymeric membranes. The sample was controlled by a blank membrane consisted of the prepared triacetylcellulose membrane without the indicator. 10.0 µl of standard or sample solutions over the concentration range of bismuth(IV) (from zero to 1×10^{-4} M) was injected into the solution. The sample solution was injected into a quartz cell using a microsyringe, and the absorbance spectrum of optical sensing membrane was measured at 613 nm after 5 min. This work was repeated to achieve a stable absorbance.

Real Sample Preparation

Tap and river water samples. 100.0 ml of the sample was placed into a glass beaker, and then the addition of 1.0 ml of concentrated nitric acid to the solution, and its contents were heated on a hot plate in 150 ºC for 3 h untill the solution becomes clarified from organic interferences. After filtration, the residue was transferred to a volumetric flask of 100 ml and was dissolved in 20.0 ml of acetate buffer solution at pH 3.80 and was kept in a refrigerator at 4 ºC.

Preparation of Bi(III)-containing Tablets

A Bi(III) -containing tablet was ground and homogenized by a mortar. Then, the sample was treated with 5.0 ml HNO_3 (0.1 M) to remove the Cl^- ions which interfere through formation of stable complexes with Bi(III). The resulting solution was evaporated nearly to dryness on a sand bath. The residue was dissolved in 100.0 ml of 0.1 M HNO_3 and filtered by a filter paper [3].

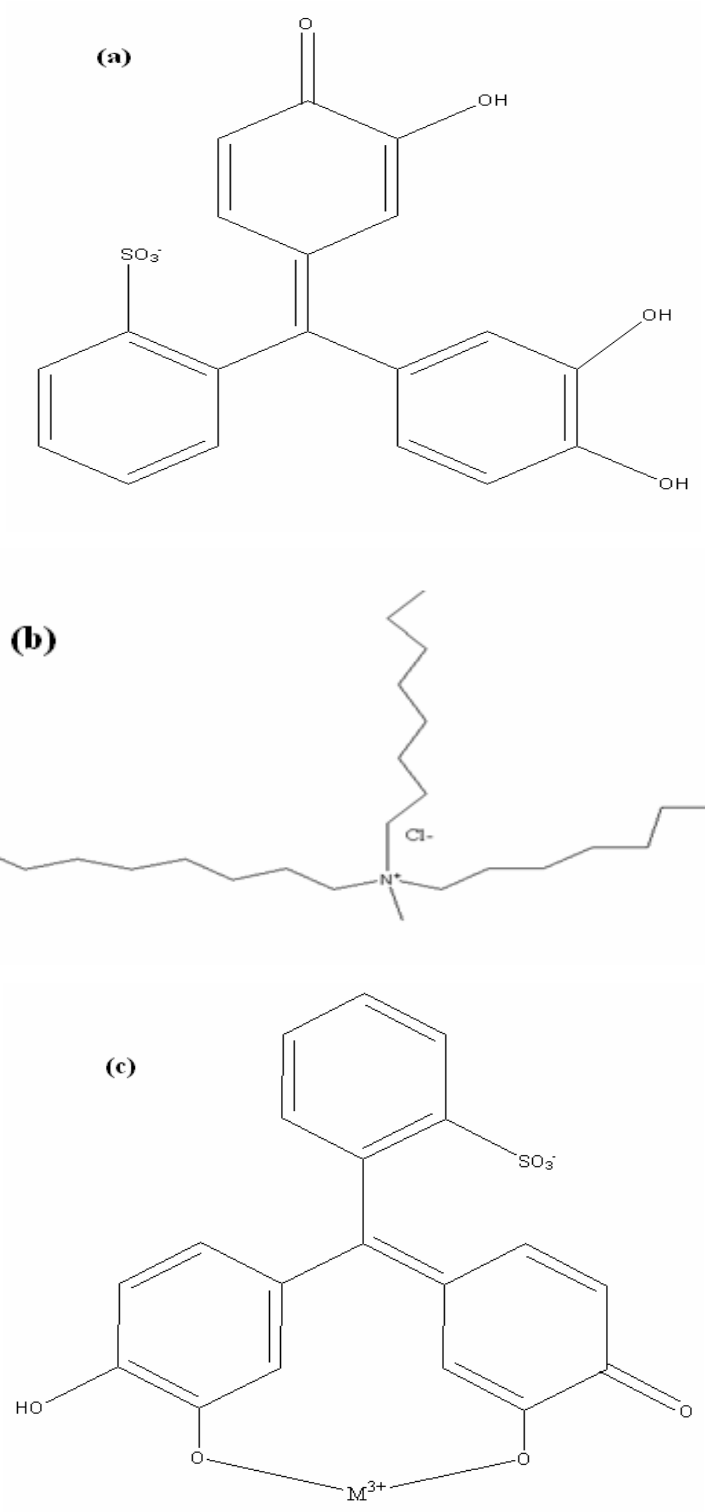

Fig. 1. (a)The possible structure of Pyrocatechol violet; (b) Molecular structure of methyltrioctyl-ammoniumchloride; (c) Complex of PCV with metal ions.

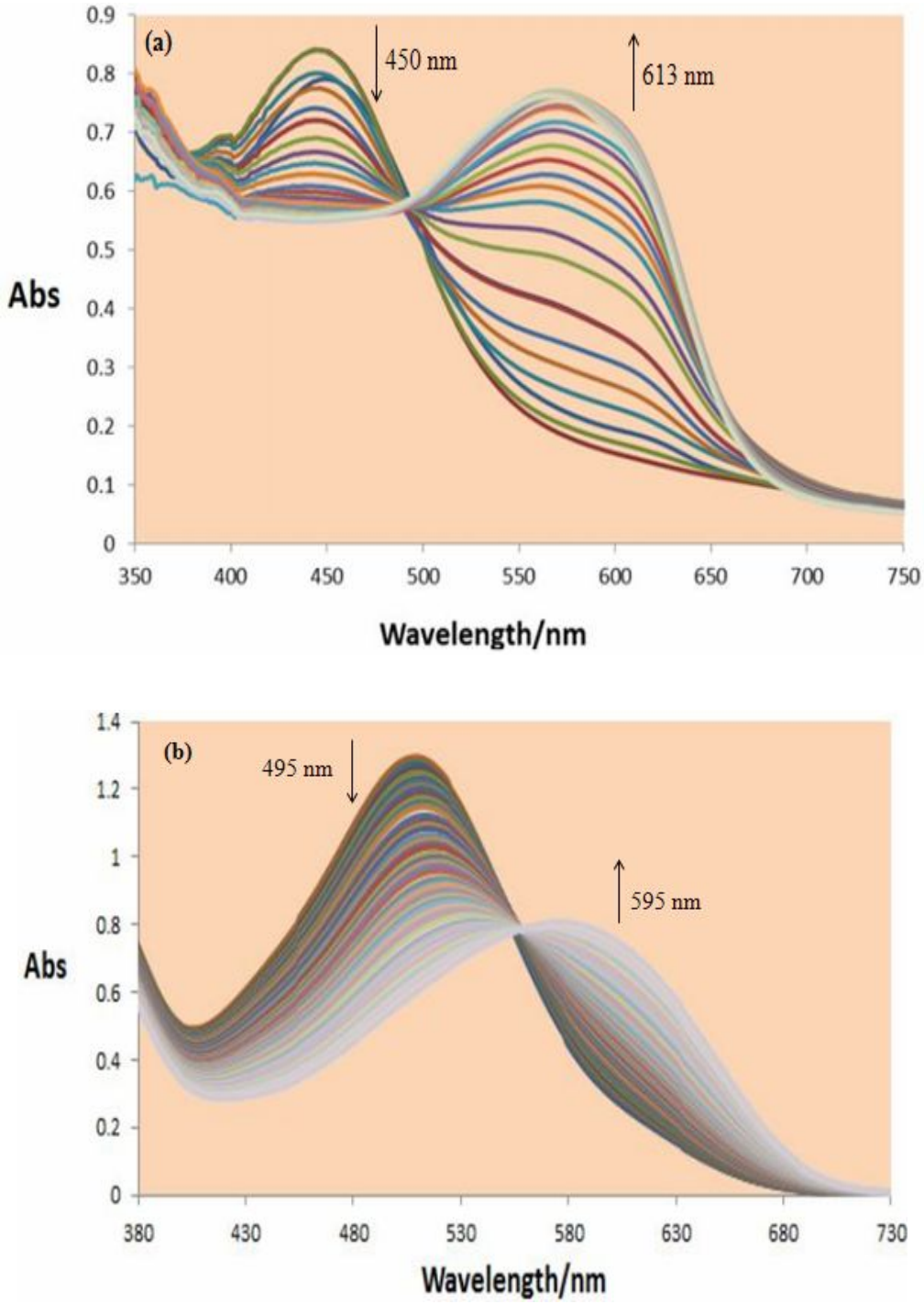

Fig. 2. (a) Absorption spectra of optical sensor membrane in the presence of 8.32×10^{-7}-7.54×10^{-5} M of Bi(III) at pH 3.80; (b) Absorption spectra of PCV solution in the range of 6.32×10^{-6}-4.70×10^{-5} M of Bi(III) at pH 3.80.

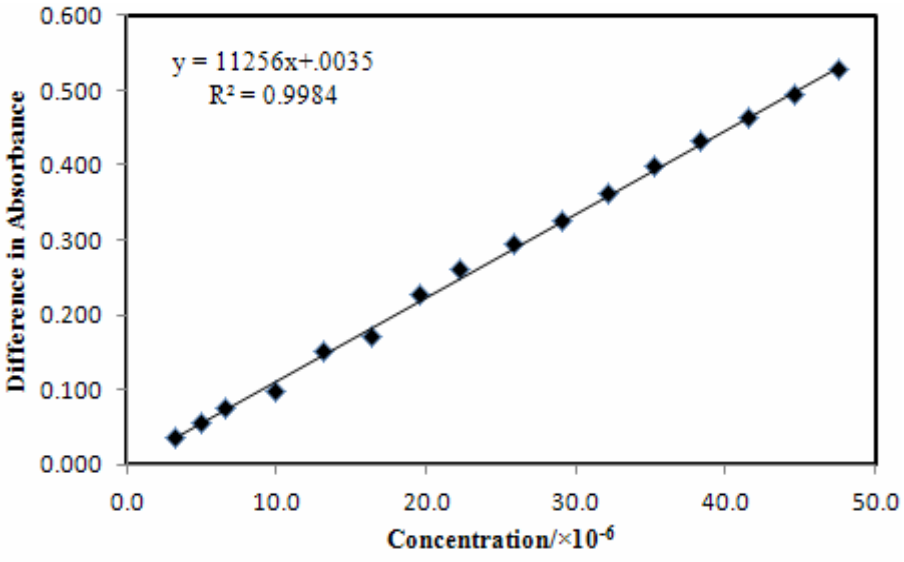

Fig. 3. Response of the optical sensor to Bi(III) ion concentrations in the range of 4.98×10^{-6}-4.76×10^{-5} M at pH 3.80.

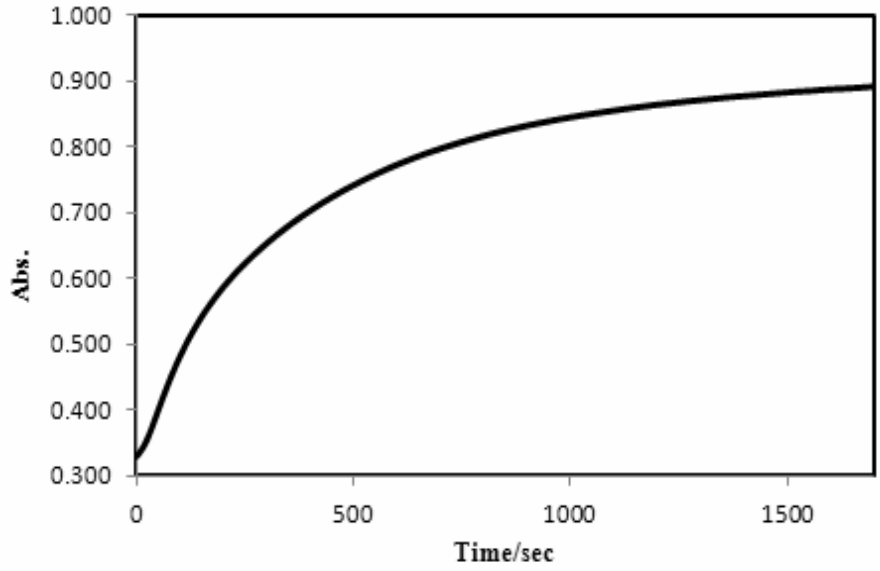

Fig. 4. The response of the sensor *vs*. conditioning time when the film was exposed to Bi(III).

RESULTS AND DISCUSSION

Spectral Characteristics

The absorption spectra of immobilized pyrocatechol violet, achieved after equilibration in buffer solution (pH 3.80) containing different concentrations of bismuth(III), is shown in Fig. 2a. By adding bismuth(III) ions with different concentrations, the absorbance was decreased at 450 nm

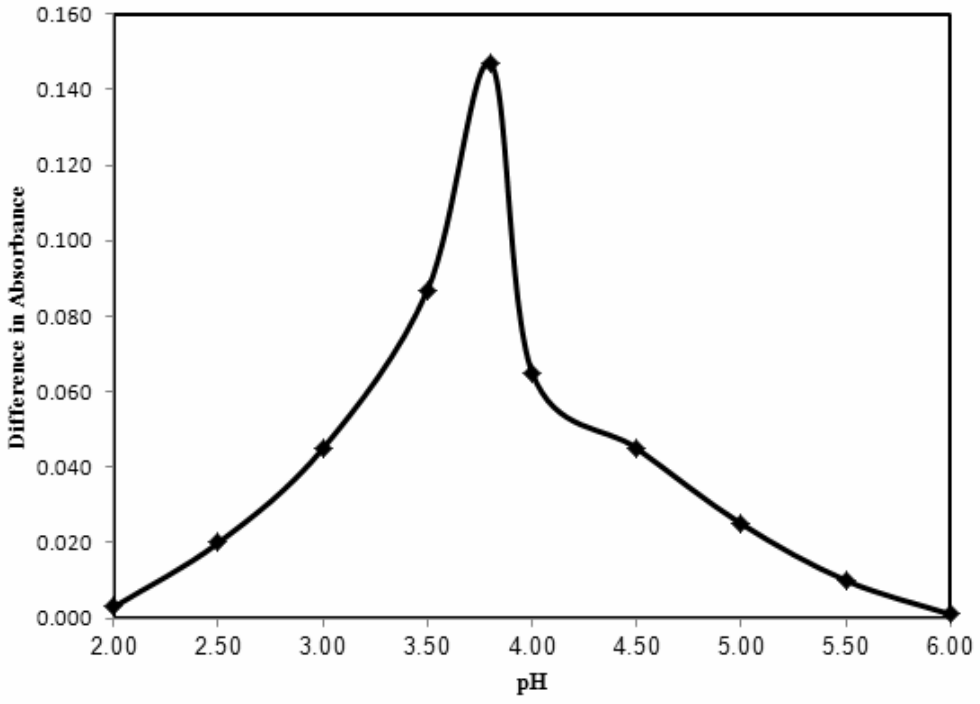

Fig. 5. The effect of pH on the response of optical sensor.

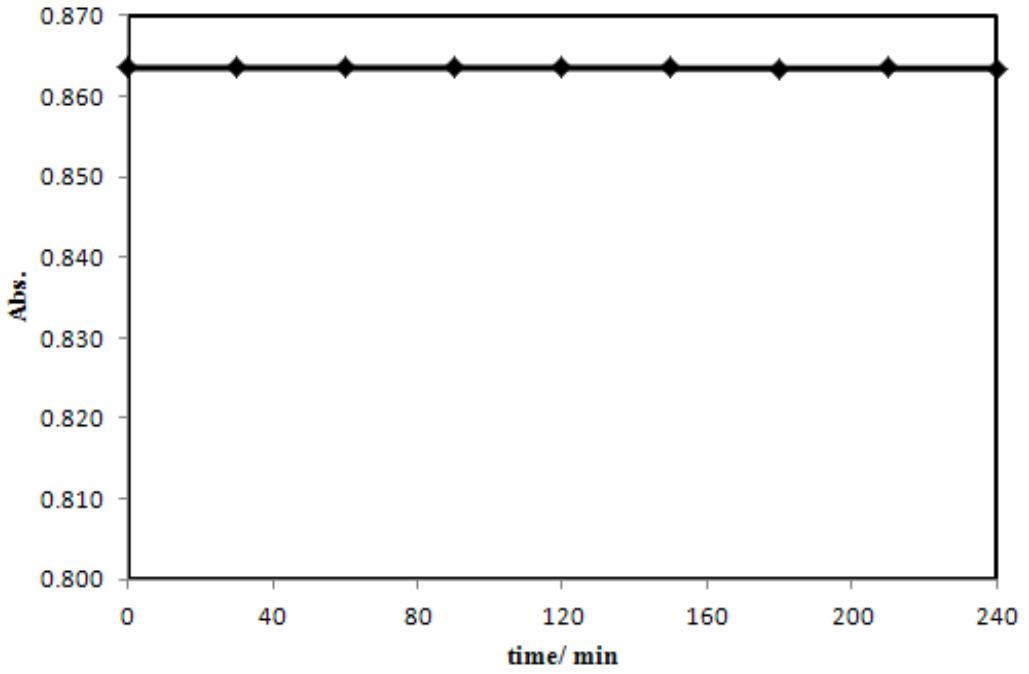

Fig. 6. The absorbance changes of the optical sensor membrane for four hour at 613 nm and pH = 3.80.

simultaneously with the appearance of a new absorption peak at 613 nm and a color change from yellow to blue. The wavelength of 613 nm was selected for further studies because of higher selectivity and sensitivity at this wavelength. Unlike a limited number of studies for the determination of Bi(III) in aqueous solutions [22-23], wide dynamic range and the low detection limit were achieved with an optical film sensor, as shown in Fig. 2. Besides, optical film sensor was comfortable in situ analysis.

In comparison with aqueous solutions, bathochromic shifts ranging from 5-15 nm were observed. This suggests that the structural conformation of the immobilized dye is more planar than that of its solution analogue [24].

Figure 3 shows the difference in absorbance signals from the optical sensor against Bi(III) ion concentrations. The calibration curve revealed a linear range of 4.98×10^{-6} - 4.76×10^{-5} M with the detection limit of 8.53×10^{-7} M. The required time for the reaction between sensing membrane and Bi(III) was 10 min, as shown in Fig. 4.

Influence of pH on the Optical Response

The equilibrium of the complexation reaction of immobilized pyrocatechol violet with Bi(III) is affected by the pH of the buffer. The effect of pH on the response of the optical sensor was studied in the pH range of 2.00-6.00 by changing the acetate buffer and injection of 2.60×10^{-5} M of the Bi(III) ion solution. As can be seen in Fig. 5, when the pH increases from 2.00 to 3.80, the value of the difference in absorbance increases. At pH values more than 3.80, the response decreases. At lower pH, the deprotonation of the ligand was slow, and the ligand did not have enough free position to react with Bi(III) ions. Therefore, the complex formed weakly. At higher pH, the hydroxide forms of Bi(III) were formed due to the hydrolysis of the Bi(III) ions in aqueous solutions. Therefore, pH 3.80 was selected for further studies.

Lifetime of Optical Sensor

To check the stability of the membrane, the signal was recorded at a maximum wavelength of 613 nm over a period of about four hours. During this time; the film was stable in acetate buffer solution at pH 3.80 with no indicator leaching and the relative standard deviation for nine absorbance measurements of the film was found 1.34% (Fig. 6).

Regeneration of the Optical Sensor

To have an optical sensor with a good performance, the color change must be reversible. Some complexing agents such as H_2SO_4, HNO_3, HCl, EDTA, H_3PO_4 and KI were used to reverse color of Bi(III) complex. Some complexing agents such as I^- and H_3PO_4 require prolonged time to remove the analyte from the film. Some of them, such as HNO_3, decomposed the indicator, and H_2SO_4 and EDTA formed new complexes with new colors and could not remove the analyte from the film. HCl was chosen as the best reagent with short regeneration time

The Repeatability and Reproducibility of the Optical Sensor

The repeatability of the response of the optical sensor was evaluated with repeatedly exposing the sensor membrane to the same solutions of Bi(III) ions (about 5.36×10^{-5} M) and 0.1 M hydrochloric acid. Four determinations were accomplished, and the coefficient of variation of the sensor response was 4.87%. Also, the reproducibility of five individual membranes with the same form was studied in the presence of the 2.00×10^{-5} M Bi(III) ions, and the variation coefficient of the responses between membranes was 4.32%. Figure 7 confirms that the precision of the response of the optical sensor is satisfied.

Interference Study

The sensing membrane was tested for the determination of 2.00×10^{-5} M Bi(III) ions in the presence of different metal ions (shown in Table 1) to determine the selectivity of the optical sensor membrane. To do so, samples containing a fixed concentration of Bi(III) ions and different concentrations of other metal ions were analyzed by the sensor. At the applied optimum pH, the main interferences were Fe(III) and Sn(II). Masking agents can be useful for reducing the interference of foreign metals. The interference from Fe(III) and Sn(II) can be eliminated using salicylic acid and triethanolamine, respectively [25-26].

Application

We examined two different water samples, including river water, tap water, and bismuth subcitrate tablets to evaluate the analytical applicability of the proposed method. The sensor was applied to analyze the treatment samples

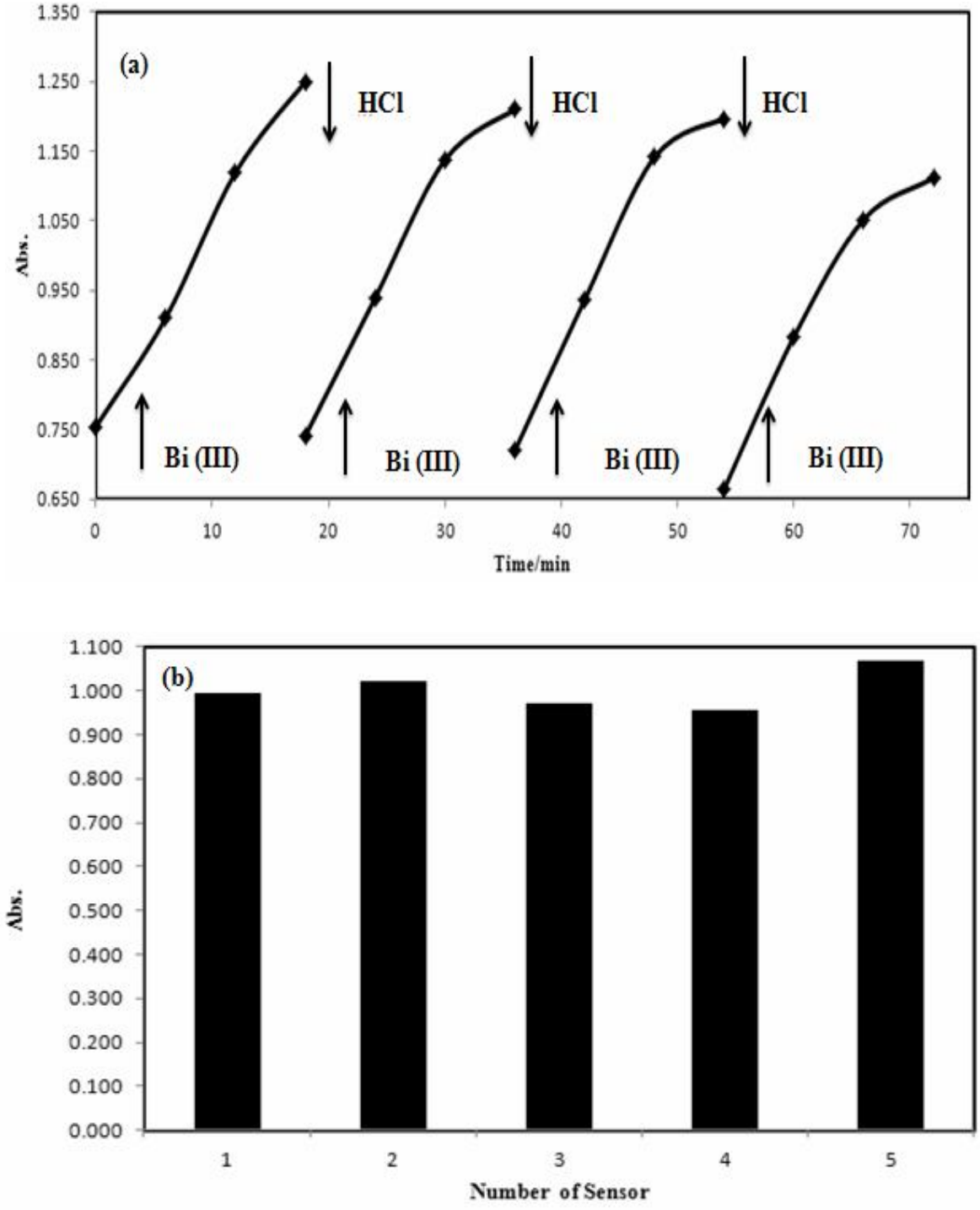

Fig. 7. Evaluation of the absorbance of the membrane at 613 nm with (a) reparative exposing into 5.36×10^{-5} M of Bi(III) ions and 0.1 M of hydrochloric acid and (b) the reproducibility of the response of different sensors for the determination of 2.00×10^{-5} M of Bi(III) ions.

Table 1. Effect of Foreign Ion on the Determination of 2.00×10^{-5} M Bi(III) Ion

Foreign ions	Tolerated ratio [interference]/[Bi(III)]
Ni^{2+}, Na^{+}, K^{+}, Be^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Cr^{2+}	1000
Mg^{2+}, Co^{2+}, Al^{3+}, Cu^{2+}	100
Zr^{2+}, Pb^{2+}, VO^{2+}, Fe^{2+}	50
Fe^{3+}, Sn^{2+}	1

Table 2. Analytical Results of Bi(III) in Real Samples

Sample	Bi(III) added (ppm)	Bi(III) content[a]		$t_{experimental}$[b]
		Proposed optode	ICP	
Tap water	-	Not found	Not found	-
Tap water	1.65	1.66 ± 0.035	1.64 ± 0.029	0.76
River water	-	Not found	Not found	-
River water	0.323	0.338 ± 0.136	0.332 ± 0.056	0.015
Devrom™ [c]	-	186.21 ± 1.25	189.39 ± 1.14	2.72

[a]Average of three determinations ± S.D. [b]The critical value for t (0.05, 2) is 4.30. [c]Deverom™ contains 200 mg of bismuth subgallate per tablet.

spiked with different amounts of Bi(III) ions, and the concentration was compared with inductively coupled plasma-atomic emission spectrometry (ICP-AES). The results show that the sensor is suitable for determination of Bi(III) concentrations in biological and environmental samples, indicating a well-correlation with the value of the same samples determined by ICP-AES, as shown in Table 2.

Neural Network Artificial and Optimization

The absorbance data obtained from experiments were processed by PC-ANN to extend useful measuring range and then improve sensitivity of the optical sensor. ANN is composed of many parallel processing elements, known as neurons, and consisted of an input layer, a hidden layer of neurons, and an output layer of one neuron [18]. A hidden layer consisted of neurons with sigmoid function and an output layer with one output for bismuth concentration. In this study, the principal components, which can explain more than 95% of total variances in the absorbance data [27], were chosen as input nodes for the input layer.

To investigate the effect of the PC-ANN algorithm on the working range of the response sensor, thirty spectra were employed in the training of the ANN. Twenty solutions made up training set, validation and test sets were prepared that involved 5,5 synthetic samples, respectively.

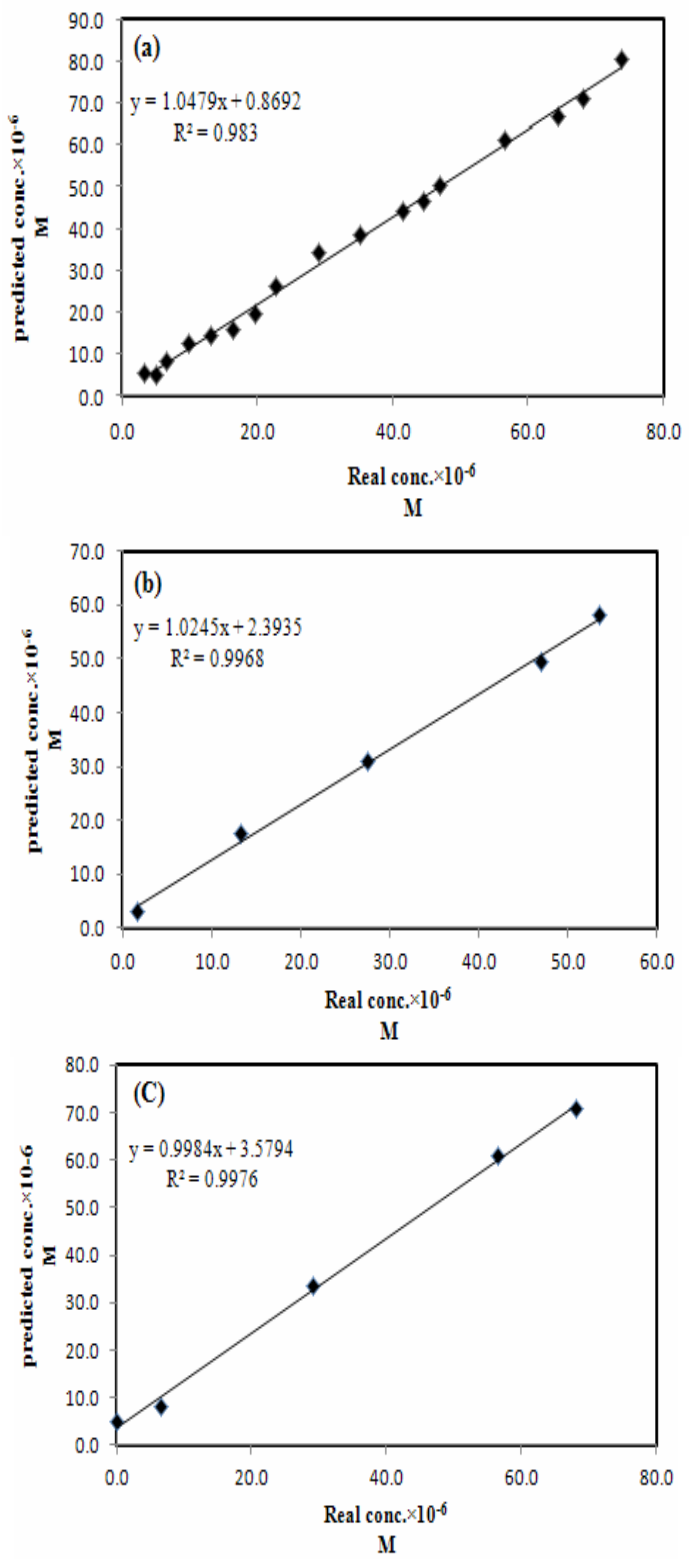

Fig. 8. Predicted *versus* true values of Bi(III) concentration in training (a), validation (b) and tests sets (c).

The optimum values of these parameters were as follow: Number of hidden layers: 2, Number of nodes in each hidden layer: 6 and 6, Learning rate: 0.05, Momentum: 0.03. Figure 8 shows the result of the optimized ANN algorithm with three principal components as input depicts.

According to Fig. 8c, there is a good correlation between predicted concentration generated by ANN and real concentration in the range of 8.66×10^{-7}-7.09×10^{-5} M, confirming an improvement in the dynamic range.

CONCLUSIONS

A simple, inexpensive optical sensor was developed for the determination of Bi(III) ions. The optical sensor exhibited a good linear range, long lifetime and reproducibility. The determination of Bi(III) ions with a sensing membrane caused a major color change from yellow color to blue color, which was clearly visible to the naked eye with a detection limit 1.01×10^{-7} M. The optical sensor provided a good selectivity for Bi(III) ions over other metal ions except for Fe(III) and Sn(II) which can be omitted by masking agents. By applying PC-ANN algorithm, the linear range was improved. Finally, the measurements of Bi(III) ions in some biological and environmental samples via the new naked eye sensor exhibited a good correlation with values obtained from the same samples using ICP-AES method.

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