Sensor Review

New modified selective platinum electrode based on poly (ethylene glycol) for Iron (III) detection in real water

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Abstract

Purpose – This work aims to determine iron (III) in real water by using a new amperometric sensor on the basis of polyethylene glycol (PEG) to test and characterize a new modified selective platinum electrode.

Design/methodology/approach – In this review, the authors focus on testing and characterizing several polymeric membranes by using cyclic voltammetry and square-wave voltammetry (SWV) methods to differentiate the nature of plasticizers (2-Nitrophenyl octyl ether [NPOE], Di-n-octyl phthalate, Bis (2-ethylhexyl) sebacate, PEG. The authors have evaluated the possibility of using crown ether and three zeolite ionophore (faujasite [FAU], Chabazite and ZSM-5) matrixes as novel materials for the selective determination of iron (III) using SWV for the best membranes.

Findings – The results demonstrated that the modified platinum electrode presents linear dependence of amperometric signal with a wide linear range of 10^{-9} to 10^{-4} mol.L^{-1} for iron determination, revealing a detection limit of 10^{-10} mol.L^{-1} and amperometric sensibility of 58.58 μA/mol.L^{-1}. The slope of the membrane plasticized with PEG calibration curve is six times higher than that of the other membranes. It was noticed that when the crown ether and the three zeolite ionophores were used, as a new detective material for iron with the membrane plasticized with PEG, the expected results were highly proven. The modified platinum electrode showed high selectivity to iron (III) when the heavy metal ions such as Ni (II), Al (III), Zn (III), Cd (II), Gd (II) and Cu (II) were present.

Originality/value – The utility of the method and the efficiency of the best membrane sensor have been accurately tested by the determination of iron in real water samples of Hassi Messaoud, south of Algeria.

Keywords Amperometric sensor, Benzo-18-crown-6, Iron (III), Modified electrode, Polyethylene glycol (PEG), Polymeric membrane

Paper type Research paper

1. Introduction

Iron is an essential element for normal physiological functionality, and it plays an important role in many cellular processes including energy generation, oxygen transport and DNA synthesis (Lieu *et al.*, 2001). Compared with other transition metals, iron is considered as a moderate toxic element. Moreover, medical studies have shown that iron and its components can cause depression, rapid and shallow respiration, coma and cardiac arrest. To monitor Fe^{3+} ions from different samples (Baga *et al.*, 1998; Alemdaroğlu *et al.*, 2007), many iron (III) membrane sensors based on different noncyclical and macro-cyclic ionophores have been studied. Many plasticizers have been used in several chemical industries including pharmaceutical applications. Jinghua Yuan has analysed the use of polyethylene glycol (PEG) as a plasticizer with high elasticity. Kulinski *et al.* (2006) found that PEG exerts a plasticizing effect on poly-L-lactic acid, and the decrease in crystallinity is superior in polypropylene glycol, which modifies the permeability of CA films and the impact of PEG on morphology, thermomechanical properties and water vapor permeability of cellulose acetate-free films (Jinghua *et al.*, 2001). Honary *et al.* (2010) investigated the effect of plasticizer molecular weights and water concentrations and vapor permeability of hydroxyl propyl methyl cellulose films, whereas Fabien *et al.* (2013) examined the effect of types of plasticizers (different grades of PEG) on mechanical, thermal and permeability properties of a coating film. Thereupon, the results have shown that PEG with a higher

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molecular rate provides a better plasticizing effect for the film but it increases its water vapor permeability. We decided, after that, to evaluate the possibility of using zeolite ionophores. Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts (Kong and Toshinori, 2010; Weisenberger and Bucher, 2010). When heated rapidly, the material stilbite produces a large amount of vapour from the water that has been absorbed by the material (Hermann *et al.*, 2014). On the other hand, zeolites occur naturally, but these can be also be manufactured, on a large scale (Tanaka and Yoshida, 1989).

The use of ion-selective electrodes for iron (III) detection as a fast and low-cost method have also been reported in the past years. A sensor based on 5-(4-carboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin as carrier for the determination of iron (III), plasticized with bis(2-ethylhexyl)sebacate, in a concentration range of $1 \times 10^{-7} - 1 \times 10^{-1}$ M, with a super Nernstian slope of 21.6 mV/decade has been reported (Dana *et al.*, 2012).Mohammad*et al.*(2004) have developed a polyvinyl chloride (PVC) membrane sensors based 2-[(2-hydroxy-1-propenyl-buta- 1,3-dienylimino)-methyl]-4-p-tolylazo-phenol (HPDTP) as a suitable carrier with the best performances in the range of 3.5×10^{-6} to 4.0×10^{-2} M and a super Nernstian slope of 28.5 (±0.5) per decade, for the determination of iron (III) in the presence of iron (II). An iron (III) ion-selective sensor based on a 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one ligand was developed by Sasan *et al.* (2016). Using 1′-(iminobis (methan-1-yl-1-ylidene))dinaphtalen-2-ol as sensing material. Babakhaniana *et al.* (2010) have reported the fabrication of an iron (III)-selective sensor which works between $1.0 \times 10^{-7} - 1.0 \times 10^{-1}$ M with a Nernstian slope of 19.9 mV/decade. Sensitive sensors were applied for the detection of Fe^{3+} in real samples, in tap water samples (Mojtaba *et al.*, 2013), in pharmaceutical samples (Dana *et al.*, 2012), in synthetic leach liquors from spent lithium ion batteries (Ines *et al.*, 2008), in river and waste water samples (Zamani *et al.*, 2012) and in commercial tablet samples (Mohammad *et al.*, 2012).

Surface modification of platinum electrodes by macrocyclic ethers has been reported in the literature (Pedersen, 1967a, 1967b; Zhu *et al.*, 2000; Beer *et al.*, 1991; Wang and Bonakdar, 1988).

A multitude of crown ethers have been synthesized and modified since Pedersen's (1967a, 1967b) landmark paper to enhance the effectiveness of the crown ethers to complex with metal cations. So, Pedersen is widely regarded as the father of these important compounds. In most cases, metal cation–crown ether complexation processes can be explained by the multistep Eigen–Winkler (Eigen and Winkler, 1970) mechanism [equation (1)]:

$$M^+ + C \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} M^+ \ldots\ldots C \underset{k_{-2}}{\overset{k_2}{\Longleftrightarrow}} MC^+ \underset{k_{-3}}{\overset{k_3}{\Longleftrightarrow}} (MC)^+ \quad (1)$$

where M^+ is the solvated metal cation, C denotes the crown ether, $M^+ \ldots C$ is the solvent separated metal ion–crown ligand pair, MC^+ is a contact pair and $(MC)^+$ is the complication of the metal cation implanted in the crown ether cavity.

Moreover, several methods were developed for sensor application to detect species, chemical and electrochemical one, such as cyclic voltammetry, the current–voltage technique (I–V) and square wave voltammetry (SWV) (Ahmad *et al.*, 2015; Zhuo *et al.*, 2015). Among these various methods, SWV was used for simultaneous determination of trace iron (III). The modification of the electrode surface is a major area of interest in the present research in electrochemistry such as corrosion studies; it is the base of most investigations (Mohammad *et al.*, 2012).

This work is intended to study the effect of plasticization on the membrane of the PVC/electrolytes based on crown ether with modified platinum electrode plasticized together with PEG.

In this paper, a new modified selective platinum electrode based on PEG for iron (III) detection in real water was studied. Crown ether is presented as a neutral carrier encapsulated in a polymeric membrane electrode for iron (III) detection plasticized with PEG. In addition, crown ether and three zeolite ionophores (faujasite [FAU]), chabazite and ZSM-5) were used as new material for the selective determination of iron (III) by SWV. The square wave voltammograms showed a sharp peak around positive potentials +0.220 V. To detect iron, we put the square wave in 20-Hz frequency, a step potential of 40 mV, an amplitude of 40 mV and pH 2. By using the novel sensor, the amount of iron (III) in the real water samples was obtained.

2. Experimental

2.1 Reagents

PEG, 2-Nitrophenyl octyl ether (NPOE), tetrabutylammoniumtetraphenylborate (TBATPB), benzo-18-crown-6, Di-n-octyl phthalate, Bis(2-ethylhexyl) sebacate, Nafion, tetrahydrofuran (THF) and high relative molecular weight PVC, hydrochloric acid (HCl), iron (III) nitrate [$Fe(NO_3)_3$] were obtained from Sigma. Hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4) were purchased from MOLBASE (Shanghai, China) and Merck. We have arranged iron (III) solutions in 0.1M HCL to avoid its hydrolysis. Working solutions were daily prepared to prevent ageing and to keep the ionic strength constant – 0.1M sodium nitrate ($NaNO_3$) was used. FAU, chabazite and ZSM-5 were purchased from Zeolyst, Inc.

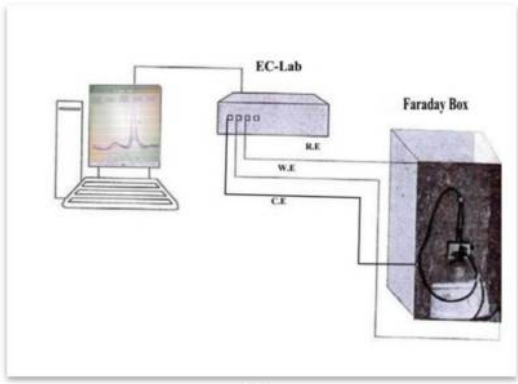
2.2 Apparatus and electrochemical measurements

A SP-300 Modular Research Grade potentiostat/galvanostat/FRA (Biological Science Instruments SAS, France) was used to perform electrochemical measurements, and the software EC-Lab was used for the acquisition of data and the control of the experiments. All electrochemical measurements were performed in a conventional three-electrode cell containing modified platinum plate as the working electrode; a platinum wire and Ag/AgCl/(KCl) were used as counter and reference electrode, respectively. The measurements were carried out in the solution of 0.1M $NaNO_3$ and 0.1M HCl (pH 2). All iron (III) solutions were prepared with $Fe(NO_3)_3$, the responses of all modified electrodes were measured at different iron (III) concentrations. The schematic diagram of the experimental setup (EC-Lab) and a photograph of the apparatus are shown in Figure 1.

2.3 Electrode cleaning and modification process

High purity metal electrode for voltammetry applications [type platinum plate (>99.99% purity grade) with a diameter of 8 mm, length of 120 mm (80 mm of underground joint) in the temperature range of (−10, −100°C)] was formed. The working electrodes were cleaned before each modification

Figure 1 (a) Schematic diagram of the experimental set-up (EC-Lab) and (b) photograph of the apparatus



(a)

(b)

step by use of chemical and electrochemical polishing methods. Chemical polishing included swirling the electrode in piranha solution (1/3 H_2O_2, 2/3 H_2SO_4) for 60 s followed by a 15-min ultrasonic rinse in H_2O. After three repetitions of chemical polishing, the electrode was subjected to an electrochemical polishing step. The working electrode was put in a 50-cycle potential sweep in 1.0M H_2SO_4 amid 1.50 V and −0.15 V, after the polishing step the working electrodes were rinsed with acetone, then with H_2O.

The modified electrode was prepared by dropping a mixture of PVC, plasticizers, ionic additive, and crown ether dissolved in 5 mL of fresh THF on its surface. The components of the various tested membranes are summarized in Table I.

3. Results and discussion

3.1 Electrochemical characterization of the platinum electrode

The characterization of the bare and the modified platinum electrode was realized by CV measurements in the presence of $Fe(CN)^{3-}{}_6/Fe(CN)^{4-}{}_6$ as a redox agent. The modified electrode was prepared by drop coating a membrane mixture on its surface. Figure 2 shows the cyclic voltammograms before and after the modification step of the platinum electrode in an aqueous solution.

The voltammograms of the redox reagents present a reversible behaviour. We observe a decrease in the peak current after the modification of the platinum electrode.

A larger peak separation for the modified electrode (E = 0.311 V) in comparison with the bare electrode (E = 0.261V) was observed. This behaviour indicates a decrease in the electron transfer owing to the effect of the layer deposited on the platinum electrode surface.

3.2 Effect of the membrane composition

It is well known that the composition of the polymeric membranes can naturally affect its characteristics (Ghaedi *et al.*, 2010; Huser *et al.*, 1991). Hence, some different compositions of the Fe^{3+} selective membrane were optimized, and the results (sensitivities of modified electrodes) are shown in Table I.

The prerequisite of plasticization is enhancing the conductivity of polymer electrolytes using low molecular weight and high dielectric constant additives (Gontard *et al.*, 1992). In fact, to overcome film brittleness, caused by high intermolecular forces, the addition of a plasticizer agent to an edible film is required.

Generally, plasticizers which are defined as small molecules increase not only flexibility but also water vapor and gas permeabilities, as illustrated by Sorbal *et al.* (2001), Baldwin and Robert (2002).

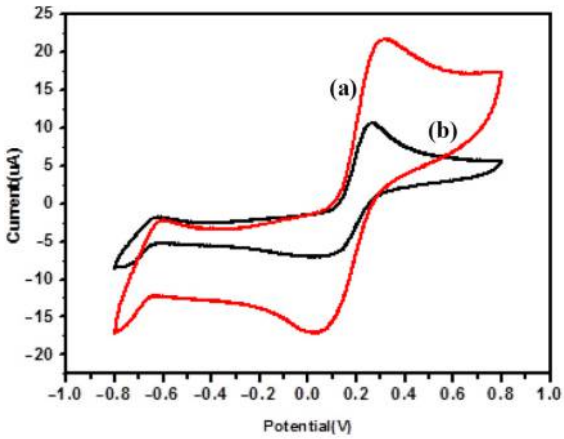
In this work, five polymeric membranes with a varying nature of plasticizers were prepared (Table I). It is noteworthy that the best membrane characteristics are obtained using plasticizer PEG (M4); as it is seen, by comparing the composition of M3 and M4, the sensitivity of the response of the membrane enhanced from 2.21 μA/mol.L^{-1} to 58.58 μA/mol.L^{-1}. A good response was obtained in a wide concentration range, from 10^{-4} to 10^{-9} mol.L^{-1}.

From Table I, we observe that the presence of PEG in the polymeric membrane induces stability and leads to the best response with optimized PVC, PEG, TBATPB and benzo-18-crown-6 Wt.% ratio of 29, 67, 2 and 2, respectively.

Table I Optimization of the membrane ingredients

Membrane No.	Composition of the membrane (%) PVC (mg)	Plasticizer (mg)	Additive (mg) (TBATPB)	Ionophore (mg)	Sensitivity (μA/mol.L^{-1})	Linear range (M)	R^2
M1	29	2-Nitrophenyl octyl ether (NPOE)	2	2(18-6 (crown ether))	7.24	5.10^{-7} to 10^{-2}	0.99
M2	29	Di-n-octyl phthalate	2	2(18-6 (crown ether))	2.33	10^{-8} to 10^{-3}	0.99
M3	29	Bis(2-ethylhexyl) sebacate	2	2(18-6 (crown ether))	2.21	10^{-9} to 10^{-6}	0.95
M4	29	Polyethylene glycol(PEG)	2	2(18-6 (crown ether))	58.58	10^{-9} to 10^{-4}	0.97
M5		100-μL de Nafion		2(18-6 (crown ether))	9.70	10^{-6} to 10^{-4}	0.90

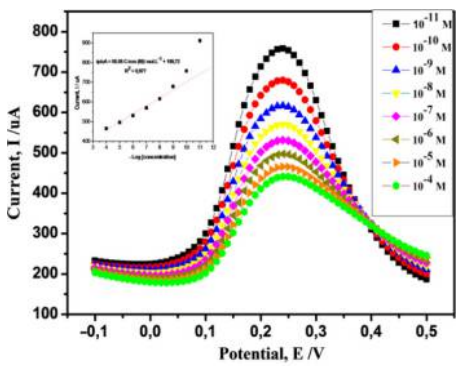
Figure 2 Cyclic voltammograms obtained on the bare platinum



Notes: (a) Modified platinum electrode; (b) after immersion in solution 0.1M $NaNO_3$ and 0.1M HCl (pH 2) containing 5mM de $Fe(CN)^{3-}_6/Fe(CN)^{4-}_6$: scan rate (0.100 V s^{-1})

Figure 3 depicts the SWV performance of iron (III) in 0.1M $NaNO_3$ and 0.1M HCl (pH 2). The significant pic of the sensor response signal to iron sensitivity was found to be around 0.22 V. A significant variation was observed for iron ions only, but no signal shift was observed for the other tested ions. The complexation phenomenon is based on the iron ionophore association which induce the pic signal intensity decreases at 0.22V. The peak currents were extracted and plotted against concentration (Figure 3). The related linear regression equation was:

Figure 3 Square wave voltammograms, obtained on platinum in $FeNO_3$ solutions (pH 2); inset shows calibration curve obtained from variation of the stripping peak current as a function of iron (III) concentrations



Notes: Stripping conditions: 0.1M $NaNO_3$ and 0.1M HCl solution (pH 2); potential step: 40 mV; amplitude: 40 mV; frequency: 20 Hz and calibration curve for Fe (III) selective electrode (2% crown ether; 29% PVC; 67% PEG; 2% TBATPB)

$$Ip/\mu A = 58.58\,C\,Fe\,(III)/mol.L^{-1} + 189,72 \quad (2)$$

The correlation coefficient was $R^2 = 0.977$. The detection limit of this electrode was 10^{-10} mol. L^{-1}.The proposed membrane sensor was prepared by incorporating the benzo-18-crown-6 ligand (L) in a plasticized polymeric membrane containing TBATPB, as a lipophilic anionic additive. The ligand binds to Fe^{3+} ions (M) under specific physiochemical interactions. The lipophilic anionic sites, TPB^-, furnish the optode membrane with the necessary ion-exchange properties, because the benzo-18-crown-6 crown ether cannot function as an ion exchanger but can act as a neutral ligand. Within the finest experimental conditions taking into account the formation of a 1:1 complex amid L and M in the organic phase, the reaction of the proposed optical system can be explained by the following ion-exchange pathway (Zamani *et al.*, 2008; Lakowicz, 1994; Pooyamanesh *et al.*, 2007 Bakker *et al.*,1997).

The observed relaxations have permanently been fitted satisfactorily by the Eigen–Winkler reaction mechanism (Eigen and Winkler, 1970), [equation (1)]:

$$\mathbf{L_{(org)} + TBA^{+}_{(org)} + TPB^{-}_{(org)} + Fe^{3+}} = \mathbf{[FeL]^{3+}_{(org)} + TPB^{-}_{(org)} + TBA^{+}_{(aq)}} \quad (3)$$

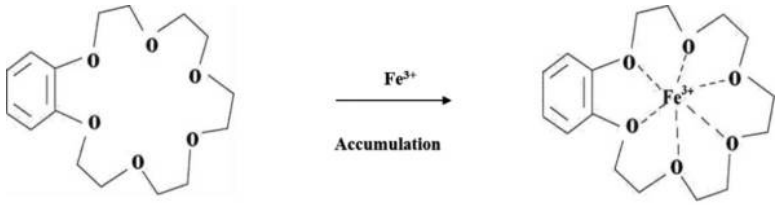
The aforementioned studies act as a guide for the complex formation between the cavity of the crown ether and the iron (III) ion used in this work. The formation of complexes by binding the cation is caused by an electrostatic ion-dipole interaction between the cation and the negatively charged six oxygen atoms in the crown ether ring (Ciampolini and Nardi, 1979). The following structural formula can be used for the complexes of 1:1 (ligand: metal). As shown in Figure 4. The stable 1:1 complexes are obtained according to the cation size which has an ionic diameter (Fe^{+3} = 1.28 Å) fitted to the cavity size of crown ether at B18C6 (2.6-3.2 Å) (MIzatt *et al.*, 1974).

3.3 Effect of zeolite ionophore on iron (III) detection

The working electrode was prepared by mixing 2-mg zeolite ionophore, 67-mg PEG, 29-mg PVC and 2-mg TBATPB. The mixtures in different weight quantities and sensitivities of modified electrodes in different compositions are shown in Table II.

Figure 5 shows the comparative response of zeolite ionophore contents on FAU, chabazite, ZSM5, crown sensors using PEG plasticizer. Linearized plots can be defined with the equations: Ip/uA = 11.85 C iron (III)/mol.L^{-1} + 480.1, R^2 = 0.92, Ip/uA = 11.44 C iron (III)/mol.L^{-1} + 398.297, R^2 = 0.99, Ip/uA = 08.025 C iron (III)/mol.L^{-1} + 245.253, R^2 = 0.95, Ip/uA = 58.58 C iron (III)/mol.L^{-1}+ 189, 72, R^2 = 0.97 for FAU, chabazite, ZSM5 and crown ether, respectively. The linearized plots reveal that, slope of the crown ether calibration curve is 5 times higher than the FAU, chabazite; ZSM5 calibrations curves. The results are displayed in Figure 5. It indicates that the crown ether has the best result for iron detection, mainly because of its high extractability of the formed ionophore – crown ether – in the electrode matrix. When this electrode is compared with formerly prepared ones (FAU, chabazite; ZSM5), it will be seen that most of them have smaller slopes.

Figure 4 Schematic illustration of iron (III) detection using PVC/PEG/modified platinum electrode



Source: Raed (2011)

Table II Effect of the membrane compositions prepared by mixing zeolite ionophore in 0.1M $NaNO_3$ and 0.1 M HCl (pH 2)

Electrode composition	Sensitivity (μA/mol.L^{-1})	Linear Range (M)	LOD (M)	R^2
2% Faujasite($(Na_2;Ca)$ $Al_2Si_4O_{12}$ $0.8H_2O$) + 29% PVC + 67% PEG + 2% TBATPB	11.85	10^{-8}-10^{-5}	10^{-8}	0.92
2% Chabazite $(Ca,K_2,Na_2)_2[Al_2Si_4O_{12}]_2 \cdot 12H_2O$ + 29% PVC + 67% PEG + 2% TBATPB	11.44	10^{-8}-10^{-4}	10^{-8}	0.99
2% ZSM-5 + 29% PVC + 67% PEG + 2% TBATPB	8.02	10^{-8}-10^{-4}	10^{-5}	0.95
2% Crown ether + 29% PVC + 67% PEG + 2% TBATPB	58.58	10^{-9}-10^{-4}	10^{-10}	0.97

Figure 5 Effect of zeolite ionophore contents on FAU, chabazite, ZSM5, crown sensors using PEG plasticizer

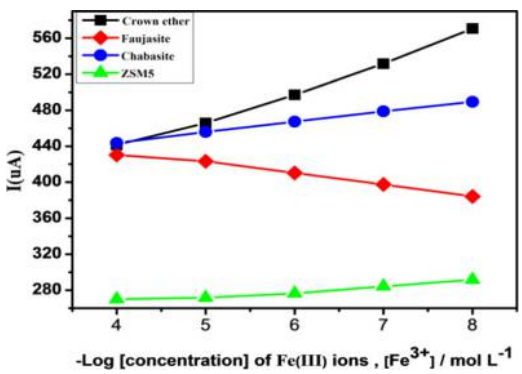
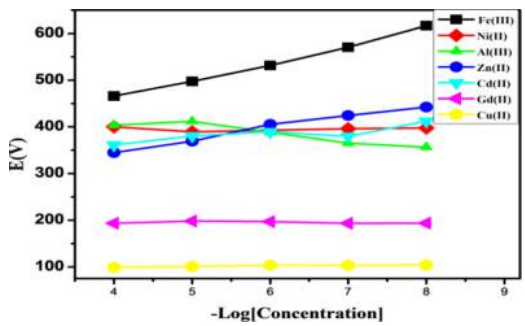


Figure 6 The response of platinum electrode having the optimum composition of the membrane M4 towards different metal ions



3.4 Interference study

The selectivity is an important factor for the iron-sensitive electrode. The procedure consists of measuring the sensor response to interfering substance addition: a calibration curve for each interfering substance is plotted and compared to the analyte calibration curve, under identical operating conditions. Selectivity is expressed as the ratio of the signal output with the analyte alone to that with the interfering substance alone, at the same concentration as that of the analyte. The iron sensor responses towards Ni (II), Al (III), Zn (III), Cd (II), Gd (II) and Cu (II) at pH 2 are studied by using SWV method to determine the selectivity of the modified electrode towards some heavy metal ions. The square wave voltammograms were recorded between −0.6 and 0.6 V with a pulse amplitude of 40 mV and a step frequency of 20 Hz. Concentration was achieved by dropping the modified electrode in a 5-mL cell containing Fe^{3+} ions at different concentrations under stirring for 5 min. Iron and interfering cations were prepared with the same conditions for the principal and different interfering ions with pH 2. The calibration curves (Figure 6) of the sensor for iron, nickel, aluminium, zinc, cadmium, gadolinium and copper ions were obtained from voltammetry responses. We show that the response of sensor for iron (III) is better than that for Ni (II), Al (III), Zn (III), Cd (II), Gd (II) and Cu (II). This result indicates that the electrochemical sensor has more selectivity towards iron (III) ions.

The limit of detection (LOD) of iron (III) sensor was studied and compared with values mentioned in the literature (Table III). As seen, our sensor shows better LOD of about 1.0×10^{-10} mol.L^{-1} with a linear range of 1.0×10^{-4} to 1.0×10^{-9} mol.L^{-1}

Table III LOD of the iron sensor compared with the literature values

Sample	Linear range C/mol.L^{-1}	LOD/mol.L^{-1}	References
1	1.25×10^{-6} to 2.68×10^{-5}	1.94×10^{-7}	Ines *et al.* (2008)
2	1.8×10^{-3} to 70×10^{-3}	1.2×10^{-3}	Diao and Katsuhiro (2010)
3	6.0×10^{-6} to 2.0×10^{-5}	2.4×10^{-6}	Zamani *et al.* (2012)
4	1.0×10^{-4} to 1.0×10^{-9}	1.0×10^{-10}	This work

Table IV Analytical application of the iron (III) sensor in industrial water

	Sample 1 – Balloons entry IGF/DGP before coagulation/flocculation	Sample 2 – Balloons out of IGF/DGP after coagulation/flocculation	Sample 3 – Enter the three-phase ball (water/oil/gas)	Sample 4 – The three-phase output tank (water/oil/gas)	Sample 5 –Settling pond
Iron (III) found by the Spectrophotometer (M)	0.93×10^{-5}	1.01×10^{-5}	1.02×10^{-4}	$1.06 \times 10 - 4$	1.03×10^{-4}
Iron (III) found by the electrode (M)	1.0×10^{-5}	1.0×10^{-5}	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
Linear correlation (R^2) was found	0.97	0.99	0.99	0.98	0.97
LOD (M)	1.0×10^{-9}	1.0×10^{-9}	1.0×10^{-8}	1.0×10^{-8}	1.0×10^{-8}
Dynamic range (M)	1.0×10^{-9} to 1.0×10^{-5}	1.0×10^{-9} to 1.0×10^{-5}	1.0×10^{-8} to 1.0×10^{-4}	1.0×10^{-8} to 1.0×10^{-4}	1.0×10^{-8} to 1.0×10^{-4}
Recovery (%) $\pm$ 1	93	101	102	106	103

towards Fe^{3+} compared with those reported by Mohammad *et al.* (2012) and Cleiton *et al.* (2008).

3.5 Real samples analysis

The developed sensor was applied to iron (III) analysis in real water samples. The obtained electrochemical results were correlated with those obtained by the spectrophotometric method. The spectrophotometric methods for water analysis are tested for the determination of iron (III) in real samples; five sampling waters were tested by the sensor at New Area North Industrial Complex Naili Abdelhamid (ZCINA) oil field of the SONATRACH company, located in the north of Hassi Messaoud City in Algeria. It is one of the largest oil fields in the Algerian Sahara. The solutions were decanted, filtered and centrifuged at a speed of 9,000 rpm. Then, the centrifuged solutions were diluted to 25 mL using distilled water in a calibrated flask. The iron determination is performed with a spectrophotometer at a fixed wavelength of 510 nm.

The results of iron (III) found by the spectrophotometric method (Hach Lange instrument) are given in Table IV. Electrochemical measurements were obtained using the sensor based on the PVC/PEG/TBATPB/benzo-18-crown-6 crown ether membrane for the detection of iron in real water samples. All samples were prepared in 0.1M $NaNO_3$ and 0.1M HCl. As can be seen from Table IV, the amounts of iron measured by the proposed sensor and those by the spectrophotometric method are in satisfactory agreement. The real water samples that were obtained via use of the novel sensor have shown that the sensor was successfully applied to the direct determination of iron content. In addition, a good recovery of the amount of iron (III) in the real water samples was also gotten by using the novel sensor.

4. Conclusions

Crown ether is a successful neutral carrier when it is used to detect the production of iron (III)-selective membrane electrodes. Among all tested sensing matrices, the membrane based on PVC/PEG/TBATPB/crown ether exhibits the best electrochemical performances in terms of sensitivity and stability. The modified electrode shows high stability in repetitive experiments owing to good adhesion and high affinity of the sensing membrane towards the iron (III) ions. This behaviour can be explained by the formation of complexes. The developed electrode showed an attractive candidate as an iron (III) sensor for practical analysis applications.

The optimized formulation of the membrane (i.e. 29-mg PVC, 67-mg PEG, 2-mg TBATPB, 2-mg benzo-18-crown-6) resulted in a linear concentration range of 10^{-9} to 10^{-4} $mol.L^{-1}$ with a slope of 58.58 $\mu A/mol.L^{-1}$ and an LOD of 10^{-10} $mol.L^{-1}$. These results could help us to choose the best plasticizer (PEG) with suitable concentration in real water.

As a result, the validity of the used electrochemical method and the applicability of the ion sensor were successfully tested by the determination of iron (III) ions in several real water samples of the ZCINA, located in the north of Hassi Messaoud, south of Algeria. The preparation of the electrode is simple, not expensive.

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