

A New Fe (III)-Selective Membrane Electrode Based on Fe (II) Phthalocyanine

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ABSTRACT

A new miniaturized all solid-state contact Fe (III)-selective PVC membrane electrode based on Fe (II) phthalocyanine as a neutral carrier was described. The effects of the membrane composition and foreign ions on the electrode performance was investigated. The best performance was obtained with a membrane containing 32% poly (vinyl chloride), 64% dioctylsebacate, 3% Fe (II) phthalocyanine, and 1% potassium tetrakis (p-chlorophenyl) borate. The electrode showed near Nernstian response of 26.04 ± 0.95 mV/decade over the wide linear concentration range 1.0×10^{-6} to 1.0×10^{-1} M, and a very low limit of detection $1.8 \pm 0.5 \times 10^{-7}$ M. The potentiometric response of the developed electrode was independent at pH 3.5-5.7. The lifetime of the electrode was approximately 3 months and the response time was very short (< 7 s). It exhibited excellent selectivity towards Fe (III) over various cations. The miniaturized all solid-state contact Fe (III)-selective membrane electrode was successfully applied as an indicator electrode for the potentiometric titration of 1.0×10^{-3} M Fe (III) ions with a 1.0×10^{-2} M EDTA and the direct determination of Fe (III) ions in real water samples.

Keywords : PVC Membrane, Ion Selective Electrode, Fe (III), Phthalocyanine

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1. Introduction

Iron, which is the fourth most abundant element in the earth's crust, is essential for the cellular processes including electron transfer, the transportation of oxygen, transcriptional regulation [1,2]. Also, iron is a limiting nutrient for phytoplankton in southern oceans, and has important role in photosynthetic and respiratory electron transport, chlorophyll synthesis, and nitrate reduction [3,4]. Moreover, Fe (III) is present in various enzymes such as catalase, cytochrome C, aldolase, and takes place in the central nervous system as a cofactor. Since iron deficiency and accumulation in the body can result in various disorders such as Parkinson's, Huntington's, and Alzheimer's disease, hepatitis, hemochromatosis, cancer, heart disease, and diabetes, the concentration of iron in human body should be monitored [5-8]. Iron is a moderately toxic element among other transition

metals and may enter into watersheds as pollutant due to its numerous industrial applications in steel, water pipes, paints, plastic, and medical industry. Therefore, the quantitative detection of Fe (III) ions in clinical, biological and environmental samples has become important.

It has been reported that several analytical techniques such as chemiluminescence [9, 10], fluorescence [11], spectrometry [12], electrothermal atomic absorption spectrometry [13], inductively coupled plasma spectrometry [14], and inductively coupled optical emission spectrometry [15] have been deployed to determine aqueous iron concentration. Although these techniques provide accurate results, they are not suitable for routine and on-site analysis. Since they require sample pretreatments, sophisticated and expensive instruments, they are time-consuming and labor-intensive [16].

Phthalocyanines which is a π -conjugated metallo-macrocycles have many applications in modern science and technology such as sensors, oxidation catalysts and photocatalysis [17,18]. Metallophthalocyanines (MPc), 2-dimensional 18-electron aromatic porphyrin synthetic analogues with an electroactive

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metal center which is capable of binding transition heavy metals and are employed as electrical devices, solar cells and biosensors due to their superior electronic properties [19]. It has been showed that electroactive metals such as cobalt (Co) and iron (Fe) enhance the catalytic performance of MPcs towards heavy metal detection [20]. The studies about the phthalocyanines, including derivatives of Ag, Co, Cr, Fe, Mn, Re, Ru, etc., for which both the metal center and the macrocycle exhibited redox properties at electrodes [21].

A polymer matrix consisting of polyvinyl chloride plasticized with DOS or *o*-NPOE has been utilized for the fabrication of ion selective membranes since it has high hydrophobicity and good physical and mechanical properties to form thin membranes [22]. An ion selective membrane includes a hydrophobic ionophore and a hydrophobic ion exchanger which are dissolved in the polymer matrix. When the sample solution interact with the membrane, primary ions are carried to the membrane phase by forming a complex with the ionophore inside the membrane. The membrane potential which is generated by this interaction at the membrane interface can be measured against reference electrodes [23].

All solid-state contact ion selective electrodes (ISEs) are sensitive, miniaturized, rapid, low-cost, and portable devices allowing on-site measurements. In this study, Fe (II) phthalocyanine was used for fabrication an all solid-state contact Fe (III)-selective electrode for the first time. The fabricated electrode was successfully applied for the determination of Fe (III) ions in different water samples.

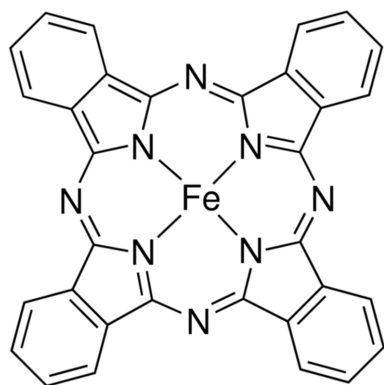


Fig. 1. The chemical structure of Fe (II) phthalocyanine

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade quality and were used as received. Tetrahydrofuran (THF), potassium tetrakis (p-chlorophenyl) borate (KTPClPB), graphite, Fe (II) phthalocyanine, high molecular weight poly(vinyl chloride) (PVC) and plasticizers, *o*-nitrophenyl octyl ether (NPOE), dioctylsebacate (DOS), dibutyl phthalate (DBP), dioctyl phthalate (DOP) were purchased from Fluka (Bucks, Switzerland). Epoxy (Macroplast Su 2227) and hardener (Desmodur RFE) were obtained from Henkel (Istanbul, Turkey) and Bayer AG (Darmstadt, Germany) respectively. All of the cationic solutions were prepared from their nitrate and chloride salt in doubly distilled water and, used without any further purification except for vacuum drying over P₂O₅. Fe (III) chloride hexahydrate (FeCl₃·6H₂O, >99.5%) was purchased from Merck. Ultrapure water (~18.2 MΩ·cm, 25°C) was acquired using the Water Purifying System. A stock solution of Fe (III) ion was prepared daily while working solutions were prepared with appropriate dilutions of the stock solution immediately before use. Other metal ion solutions were prepared from 1 M stock solutions after suitable dilutions.

2.2. Apparatus

The potentiometric measurements was performed by using a computer-controlled high-input impedance multi-channel potentiometric measurement system (sensitivity ± 0.1 mV) with a custom-made software program (Medisen Ar-Ge, Turkey). All electrode potentials were measured against an Ag/AgCl KCl (saturated) reference electrode (RE) (MF-2052 model, BASi). HI9126 (Hanna Instruments) waterproof portable pH/mV meter including the HI1230B double junction pH electrode was used to control the pH value of the solutions. The pH electrode was calibrated by using pH standard buffer solutions (Hanna Instruments) for pH 4, 7 and 10 before each experiment. Branson ultrasonic bath was used to homogenize solutions at their essential concentrations. Dissolved oxygen (DO) was measured using an Oakton DO 300 Series field meter; temperature, pH, and oxidation-reduction potential (ORP) were measured with Beckman U265 pH/Temp/mV meters; and an Oakton CON 400 series field meter

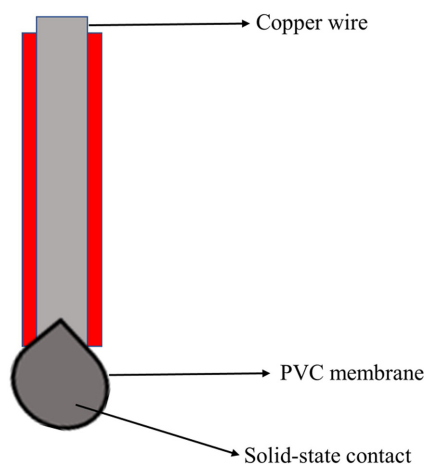


Fig. 2. Schematic illustration of the all solid-state contact electrode.

was used to measure conductivity. Inductively coupled plasma optical emission spectrometry (Optima 7300DV ICP-OES, Perkin Elmer, USA) was applied for analysis of environmental samples.

All glassware were cleaned by soaking overnight into a 3 M nitric acid solution. Then, they were further washed with tap water and deionized water. The glassware was then dried in an oven at 100°C for 1 h, cooled at room temperature and used for experimental work.

2.3. Preparation of the electrode

Details on the fabrication of micro-sized PVC membrane based electrode have been previously published [24]. A mixture of 32% PVC, 64% DOS, 3% Fe (II) phthalocyanine, and 1% KTpCIPB was dissolved in 5 mL THF. Then, this mixture was shaken. The solution was evaporated slowly until an oily concentrated solution was attained. After that, all solid-state contact electrode previously prepared was dipped into the concentrated membrane solution to obtain a transparent membrane film. The electrode membranes were allowed to dry overnight in the air and conditioned for 12 h in a 1.0×10^{-2} M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution.

2.4. Emf measurements

Potential difference between ISE and reference electrode was proportional to the logarithm of the ion activity based on Nernst-equation. The potential response values of the Fe (III) ion-selective mem-

brane electrode were measured at steady-state for different concentration of standard solutions of Fe (III) ions respectively. All potentiometric measurements with the all solid-state contact PVC membrane electrode were carried out under zero-current flow and at 25°C with cell of the type: Micro-sized Ag/AgCl RE | Test solution | PVC membrane | Cu wire surface.

An Ag/AgCl chloride reference electrode including a saturated solution of KCl was used throughout the emf measurements. Adequate increments of Fe (III) solution were added to 20 mL of 2×10^{-2} M acetate buffer solution (pH 4.0) to obtain the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M following by recording emf values after each addition. Then, calibration graphs were plotted by using the recorded potentials versus $\log [\text{Fe (III) ion}]$. The obtained graphs were evaluated in order to identify the response of the proposed electrode.

2.5. Assay of real waters for Fe (III) ion detection

After 10 mL of water samples were transferred to a 25 mL beaker, the pH of samples was adjusted to 4 by adding small amount of concentrated nitric acid. Potentiometric calibration of Fe (III) ion-selective electrode was used in order to determine Fe (III) ion content in water samples. The results were validated by analyzing of Fe (III) ions in the samples using ICP-MS to ensure the accuracy of the developed electrode.

3. Results and Discussion

All solid-state contact PVC membrane Fe (III)-selective electrodes were constructed in order to determine the suitability of ionophore in PVC membrane for various cations. After the electrodes were conditioned by soaking into the nitrate or chloride solution of each cation, the potentiometric responses of the electrodes were measured toward different cations. As shown in Fig. 3, the slopes of the corresponding potential versus $\text{p}[M^{n+}]$ plots were much lower than the expected Nernstian slopes except for Fe (III) ion. It was observed that the all solid-state contact PVC membrane electrode could be used for sensitive detection of Fe (III) ion over a wide concentration range due to higher affinity of Fe (II) phthalocyanine to trivalent iron ion over other ions. Thus, the Fe (II) phthalocyanine was chosen as ionophore for fabricating Fe (III) ion-selective membrane, and the

response characteristics of the developed all solid-state contact membrane electrode were investigated in further studies.

3.1. Optimization of membrane components

The membrane composition, the properties of plasticizers and additive used have impact on the sensitivity, selectivity and linearity of the potentiometric electrodes [25,26]. The plasticizers enhance the working concentration range, stability and life time of the electrode due to their nature [27,28,29]. Therefore, the effect of different membrane compositions as well as the nature and amount of the plasticizer (DOS, DBP, NPOE and DOP) on the response characteristics of the constructed Fe (III)-ion-selective electrode were analyzed (Table 1). It is obvious from Table 1 that the electrode displayed a very limited slope and linear range for lack of ionophore (no 6). After the ionophore was added, the linear range and slope of the electrode response were elevated. The results showed that the membrane containing DOS as plasticizer had the best sensitivity and linear range

among four different plasticizers (no 1). Moreover, a plasticizer/PVC ratio of 2 was used as the optimum amount in the PVC membrane [30]. KTpCIPB was used as an ionic additive in the membrane composition of the electrode. As can be seen in Table 1, the developed electrode did not exhibit Nernstian response characteristics (no. 5) in the absence of additive. The response behavior of the electrode can be enhanced because the presence of lipophilic additives in the membrane composition reduces the ohmic resistance [31]. The optimum amount of KTpCIPB was found to be 1 mg since additive improved the slope of the calibration curve to a near Nernstian slope of 26.04 mV/decade over a wide concentration range (no. 1). Thus, the membrane composition consisting of 32% PVC, 64% DOS, 3% ionophore, 1% KTpCIPB was selected as the membrane composition for the best potentiometric response of the electrode (Table 1, no 1).

3.2. The calibration curve, detection limit, and reproducibility of the Fe (III)-selective electrode

The Fe (III)-selective membrane electrode was conditioned by soaking into a 1×10^{-2} M Fe (III) ion solution for 12 h to assure the equilibrium at the membrane-water interface. Stable potentials were acquired when the conditioned electrodes were placed into Fe (III) ion solutions. A calibration curve (Fig. 4) for the optimized membrane electrode towards different Fe (III) ion concentrations was obtained. The limit of detection (LOD) was determined as $1.8 \pm 0.5 \times 10^{-7}$ M for Fe (III) ion according to IUPAC recommendations by crossing of two extrapolated segments of the calibration curve [32].

Four different electrodes with the same optimized compositions were used in order to examine the reproducibility of the proposed electrode. The rela-

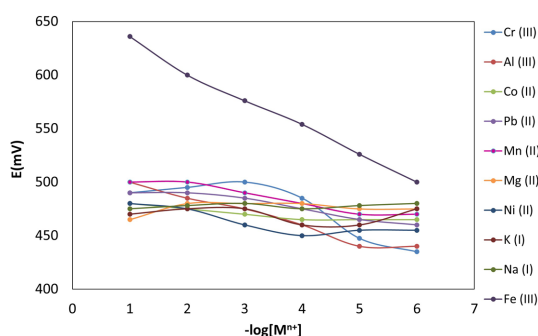


Fig. 3. The potential response of all solid-state contact PVC membrane Fe (III)-selective electrode against Fe (III) ion and some potential interferent ions.

Table 1. Composition and response characteristics of Fe (III) ion-selective electrode.

S. no.	Composition of the membrane % (w/w)				Linear range (M)	Slope (mV/decade)
	PVC	Plasticizer	KTpCIPB	Ionophore		
1	32	64 (DOS)	1	3	1.0×10^{-1} to 1.0×10^{-6}	26.04
2	32	64 (DBP)	1	3	1.0×10^{-3} to 1.0×10^{-5}	12.9
3	32	64 (DOP)	1	3	1.0×10^{-3} to 1.0×10^{-5}	9.5
4	32	64 (NPOE)	1	3	1.0×10^{-3} to 1.0×10^{-5}	29.80
5	32	64 (DOS)	0	4	-	-
6	33	66 (DOS)	1	0	1.0×10^{-3} to 1.0×10^{-5}	10.1

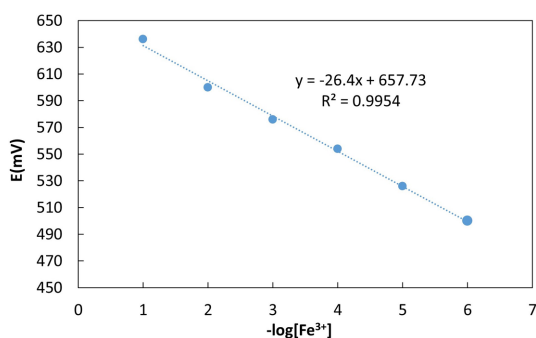


Fig. 4. Calibration curve of all solid-state contact PVC membrane Fe (III) ion-selective electrode.

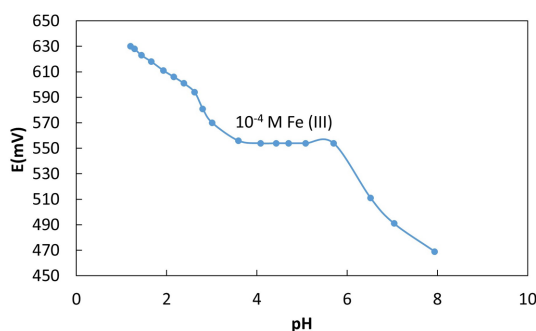


Fig. 5. Effect of pH on the potential response of the electrode in the presence of 1×10^{-4} M of Fe (III) ions.

tive standard deviation (RSD) for five measurements was attained as 3.1%. The repeatability of the electrode was also determined by five measurements with one electrode and the calculated RSD was 3.6%.

3.3. Effect of pH

The effect of pH on the potential response of the electrode was observed by adding suitable amount of HNO_3 and NaOH to 1.0×10^{-4} M Fe (III) ion solution over the pH range of 1.0-8.0. The potentials remained constant in the pH range of 3.5-5.7 (Fig. 5). Some hydroxyl complexes of Fe (III) ions could form at higher pH values ($\text{pH} > 5.7$) while resulting in the potential drift due to the reduced the free Fe (III) ion in the solution [33,24]. It was observed that the potentials increased at lower pH values because the membrane electrode may give response to hydrogen ions. Afterwards, the real sample pH values were adjusted at 4.0 by acetate buffer solution during Fe (III) ion determination.

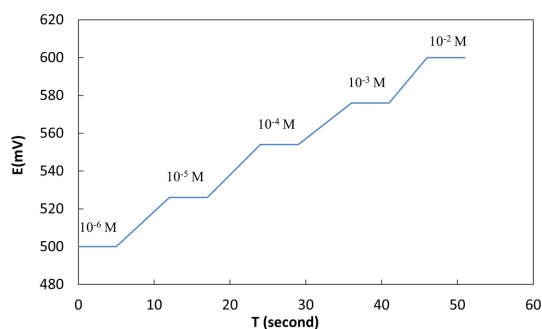


Fig. 6. Dynamic response time of the suggested electrode for step changes in the different concentration of Fe (III) ions.

3.4. Dynamic response time and lifetime of the electrode

Dynamic response time of the electrode was observed by measuring the average time required to achieve a 95% value of steady potential after the electrode was employed the diverse concentration of Fe (III) ion solution from lower (1.0×10^{-4} M) to higher (1.0×10^{-2} M). The attained results (Fig. 6) exhibit that the average response time for this Fe (III) ion-selective electrode is less than 7 s.

The potentiometric responses of the electrode in pH 4 were recorded over a period of 12 weeks to investigate the lifetime of the electrode. The electrode could be used without any significant divergence during this time. However, after 12 weeks small changes were observed in the slope (from 26.04 to 22.10 mV decade⁻¹). The lifetime of a polymeric membrane electrode in potentiometric measurements is confined due to the leakage of the membrane ingredients especially the ionophore into the working solutions.

3.5. Interference study

Selective detection of Fe (III), regarding to the ionophore used, might be attained from interactions between Fe (II)/ Fe (III) phthalocyanine complexes. Fe (II)-phthalocyanine is a four coordinated complex with a square planer structure. The Fe (II) centers are soft and it is capable for efficient and selective binding of soft Fe (III) ions [34]. Consequently, initial oxidation of the Fe (II) to Fe (III) followed in terms of an enhanced potential density that was observed when Fe (III) concentration increased. Different possible interfering species were evaluated for

Table 2. Selectivity coefficients of various ions (B) for the fabricated electrode.

interfering ions (j)	$\log K_{Fe(III), B}^{Pot}$
Cr ³⁺	-3.5
Al ³⁺	-3.2
Co ²⁺	-5.1
Pb ²⁺	-5.3
Cu ²⁺	-5.2
Mg ²⁺	-5.5
Mn ²⁺	-4.5
Ni ²⁺	-4.5
Zn ²⁺	-4.6
Fe ²⁺	-4.1
Na ⁺	-6.0
K ⁺	-5.8

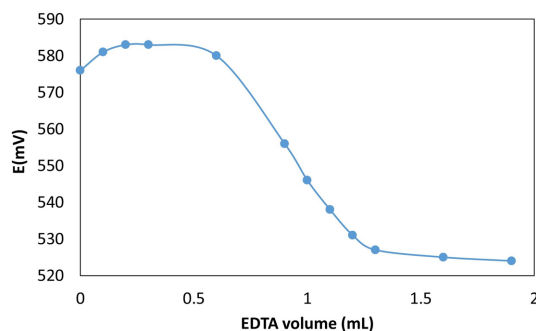
their possible effects on the detection of Fe (III) ions. The match potential method (MPM) recommended by IUPAC [35] was applied in order to assess selectivity behavior of the proposed electrode. A certain concentration of Fe (III) solution was added to a reference solution (1.0×10^{-4} M) and its potential was measured. After that, other cations solution was added to an identical reference solution until the attained potential response matched with the one obtained before adding Fe (III) ion. Then, the selectivity coefficient was calculated by the ratio of $\Delta\alpha_A$ (primary ion activity changes) to the α_B (interfering ion activity) which is expressed as:

$$K_{Fe(III), B}^{MPM} = \frac{\Delta\alpha_A}{\alpha_B}$$

Thus, the selectivity coefficients should be determined to investigate the analytical usefulness of the electrode in order to determine the target ions in real samples. The acquired selectivity coefficients for the developed electrode are listed in Table 2. The results show that the selectivity coefficients are of the order of $10^{-3.2}$ or smaller which indicate that the fabricated electrode exhibited a good selective response toward Fe (III) ions compared to the other ions.

3.6. Analytical applications

The constructed electrodes were used for the deter-

**Fig. 7.** Potentiometric titration of 10 mL of Fe (III) (1×10^{-3} M) with EDTA (1×10^{-2} M).

mination of Fe (III) ion concentration in tap water, mineral water and river water samples with using standard addition method as shown in (Table 3). The samples were prepared for analysis as mentioned in Section 2. The results obtained were also compared with those from ICP-OES analysis. It is obvious from the values in (Table 3) that there were a good agreement with those obtained by proposed electrodes and reported method. Hence, the electrodes can be successfully employed for the assessment of Fe (III) ions.

3.6.1. Potentiometric titration of Fe (III) using the developed electrode

The analytical utility of the fabricated Fe (III) ion-selective electrode was tested by employing it as an indicator electrode in the titration of 10 mL 1.0×10^{-3} M Fe (III) ion solution adjusted by acetate buffer in pH 4 with 1.0×10^{-2} M ethylenediaminetetraacetic acid (EDTA) solution. The resulting titration curve was shown in Fig. 7. As can be seen from Fig. 7, the potential values were reduced by adding EDTA to the solution due to forming complexation between Fe (III) ions with EDTA. Due to a 1:1 stoichiometry of the EDTA- Fe (III) ion complex, the potential response after the end point of the curve was constant. Thus, the developed electrode could be employed as an indicator electrode.

3.6.2. Determination of Fe (III) in water samples

The proposed electrode was applied to determine Fe (III) ion in tap water (Yildiz Technical University), mineral water (Kizilay mineral water, marketed in Turkey) and river water (Istanbul, Turkey) in order

Table 3. Determination of Fe³⁺ content in some real samples.

Samples	Added	The Value mg L ⁻¹ (ISE Method) ^a	The Value mg L ⁻¹ (ICP-OES) ^a	Recovery,%
Tap water	0	-	-	-
	20.0	20.5±0.4	20.1±0.2	101.9
River water	0	-	-	-
	30.0	30.8±0.5	30.3±0.4	101.6
Mineral water	0	-	-	-
	50.0	49.5±0.6	50.4±0.7	98.2

^a Average of six measurements

Table 4. Comparison study of the developed Fe (III) ion-selective electrode with other electrodes.

No	Ionophore	Linear Range (M)	Detection limit (M)	Response time (s)	pH range	Ref.
1	2-[(thiophen-2-yl)methyleneamino]isoindoline-1,3-dione	1.0×10 ⁻² - 1.0×10 ⁻⁶	5.0×10 ⁻⁷	10	2.3-4.8	[36]
2	2-methyl-6 (4methylenecyclohex-2-en-1-yl)hept-2-en-4-one	1.0×10 ⁻² - 4.3×10 ⁻⁷	4.3×10 ⁻⁷	10	1.5-6.0	[37]
3	Phosphorylated Calix-6-Arene Derivative	1.0×10 ⁻² -1.0×10 ⁻⁴	1.0×10 ⁻⁵	5	4.0-7.0	[38]
4	(E)-N'-((2-hydroxynaphthalen-3yl)methylene) benzohydrazide	1.0×10 ⁻² - 5.0×10 ⁻⁹	1.0×10 ⁻⁹	10	2.4-4.0	[39]
5	norfloxacin	1.0×10 ⁻¹ - 1.0×10 ⁻⁵	5.0×10 ⁻⁶	10	3.0-8.0	[40]
6	morin-Fe ²⁺ schiff-base complex	1.0×10 ⁻¹ - 1.0×10 ⁻⁶	4.5×10 ⁻⁷	<10	5.0-10.0	[24]
This work	Fe (II) Phthalocyanines	1.0×10 ⁻¹ - 1.0×10 ⁻⁶	1.8×10 ⁻⁷	<7	3.5-5.7	-

to investigate the applicability of the electrode. The Fe (III) concentrations in the samples were assessed by standard addition method.

3.7. Comparison between the proposed and other published Fe (III) ion-selective electrodes

The linear range, detection limit, response time and working pH range of the previous studies in detection of Fe (III) ions are compared with the proposed electrode in Table 4. Consequently, the novel all solid-state contact electrode for Fe (III) ion detection exhibits an excellent detection limit and wide linear dynamic range compared to previous works.

4. Conclusions

The all solid-state contact membrane Fe (III) ion-selective electrode based on Fe (II) phthalocyanine was fabricated and investigated for sensitive and selective Fe (III) ion determination under acidic pH conditions. The suggested electrode presented the

optimum sensitivity for Fe (III) ion over the range of 1.0 × 10⁻⁶ to 1.0 × 10⁻¹ M with a limit of detection 1.86±0.5×10⁻⁷ M. The electrode exhibited a selective response in the presence of various interferents. In addition, Fe (III) ion in water samples was determined in order to investigate its real potential.

Conflicts of Interest

The authors declare no conflicts of interest.

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