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Rapid Determination of Cadmium: A Potentiometric Membrane Sensor based on Ninhydrin-Pyrogallol monoadduct as a New Ionophore

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Abstract- In this study, a Cd^{2+} potentiometric ion selective membrane sensor was prepared based on the selective complexation between 4b,6,7,9b-Tetrahydroxy-4bH-indeno[1,2-b]benzofuran-10(9bH)-one(ninhydrin-pyrogallol monoadduct) as ionophore and Cd^{2+} ion. The electrode exhibits a Nernstian response for Cd^{2+} ion over a concentration range of 1.0×10^{-1} to 1.0×10^{-4} mol L^{-1} with a slope of 28 mV per decade. The limit of detection of the sensor is 7.0×10^{-5} mol L^{-1}. The sensor has a relatively fast response time (~5 s) and a useful working pH range of 3.0–7.0. Interference of some cations was also evaluated. It was used as an indicator electrode in potentiometric titration of Cd^{2+} with EDTA and in direct determination of Cd^{2+} in water and wastewater samples. The results indicate that this electrode is sensitive for determination of Cd^{2+}.

Keywords- Ninhydrin-pyrogallol monoadduct, Cd^{2+}, Potentiometry, Membrane sensor

1. INTRODUCTION

Cadmium is a trace heavy metal with great importance in environmental protection since it is a highly toxic element [1]. Determination of cadmium in environment samples is important as this element exist as a contaminant originating from industrial or urban waste pollution. The most significant use of cadmium is in nickel/cadmium batteries, as

rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Other uses of cadmium are as pigments, stabilizers for PVC, in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products [2].

Cadmium is not biodegradable and, once absorbed by an organism, remains there for many years (over decades for humans) although it is eventually excreted. The long-term exposure is associated with renal dysfunction, obstructive lung diseases such as lung cancer. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. The average daily intake for humans is estimated as 0.15µg from air and 1µg from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4µg of cadmium, but levels may vary widely [3].

As a result of high toxicity even at low concentrations, and various matrix interferences in real samples, developing an accurate, precise and selective method for cadmium determination is necessary. Different instrumental methods such as flame atomic absorption spectrometry (FAAS) [4], graphite furnace atomic absorption spectrometry (GFAAS) [5], inductively coupled plasma atomic emission spectrometric (ICP-AES) [6], and electrochemical methods [7] have been used for cadmium determination. The most of the mentioned methods are elaborate and time consuming and involve sophisticated equipment that might not be available in most analytical laboratories. However, potentiometric ion sensors offer several advantages over other methods of analysis. The most attractive features of this technique are the speed with which samples can be analyzed, portability of the device, sample non-destruction, online monitoring, and cost effectiveness. The increasing use of ion sensors in the various fields has generated increasing interest in the development new sensors [8-22] to the fast and accurate determination of various species. Some commercialized sensors for alkali and alkaline earth metals, halides, etc. are available, however more efforts are required to develop ion-selective electrodes for heavy metal ions, which are toxic beyond a certain concentration level.

Therefore, in this work, we report a potentiometric method to cadmium determination by using a new liquid membrane ion selective electrode based on 4b,6,7,9b-Tetrahydroxy-4bH-indeno[1,2-b]benzofuran-10(9bH)-one (THIBF) which is ninhydrin-pyrogallol monoadduct as an excellent ionophore. To the best our knowledge, this is the first application of this ionophore for determination of cadmium ions.

2. EXPERIMENTAL SECTION

2.1. Apparatus

Melting point was obtained uncorrected using an Electrothermal-9100 apparatus. IR spectra were recorded with a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were

recorded with a Bruker Avance DRX-500 instrument using $(CD_3)_2SO$ as the deuterated solvent containing tetramethylsilane as internal standard, at 500 and 75 MHz, respectively, in parts per million, and *J* in hertz. Mass spectra were obtained with a Finnigan-MAT-8430 Electron impact ionization-mass spectrometer (70 eV) (in *m/z)*. Elemental analyses (C, H, N) were obtained with a Heraeus CHN-O-Rapid analyzer.

The glass cell, where the Cd^{2+}ion-selective electrode was placed, consisted of two Ag/AgCl reference electrodes (Azar electrode, Iran) as the internal and external reference electrodes. Both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ±0.1 mV precision

2.2. Reagents and Materials

Reagent grade dibutyl phthalate (DBP)**,** nitrobenzene (NB), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB) and tetrahydrofurane (THF) were purchased from Merck and used as received. Ninhydrin, pyrogallol and glacial acetic acid (AcOH) were obtained from Merck and were used without further purification. Nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout.

2.3. The preparation ofIonophore

4b,6,7,9b-Tetrahydroxy-4bH-indeno[1,2-b]benzofuran-10(9bH)-one(compound 3 in Fig. 1) was synthesized as follows:

A stirred mixture of ninhydrin monohydrate (356 mg, 2mmol) and pyrogallol (126 mg, 1mmol) in glacial AcOH (6 mL) was heated to 80–90°C for 3-4 h. During the reaction white solid was deposited in the reaction mixture. After cooling the reaction mixture to room temperature, solid materials were filtered and washed successively with cold AcOH and ether to afford the desired compound as a white solid, 271 mg (95%). Analytically pure sample was obtained by recrystallization from the mixture methanol/EtOAc/n-hexane and used as ionophore to preparation of electrode. 4b,6,7,9b-Tetrahydroxy-4bH-indeno[1,2-b]benzofuran-10(9bH)-one,Colorless crystals, m.p. 265-266°C; yield: 0.27g (95%). IR (KBr): 3387, 3324, 3200, 1713, 1635, 1603, 1225, 1138 cm^{-1}. ^1H NMR(DMSO): δ=6.31 (1 H, d, ^3J8.1, CH), 6.35 (1H, br-s, OH-alcoholic), 6.62 (1 H, d, ^3J8.1, CH), 7.57 (1 H, t, ^3J7.5, CH), 7.89 (1 H, d, ^3J7.5, CH), 7.79 (1H, br-s, OH-alcoholic), 7.82 (1 H, t, ^3J7.5, CH), 7.89 (1 H, d, ^3J7.5, CH), 8.53 (1H, br-s, OH-phenolic), 9.12 (1H, br-s, OH-phenolic)ppm. ^{13}C NMR (DMSO): δ 83.4 (C-OH), 105.5 (C-OH), 110.2 (CH), 112.6 (CH), 119.3 (C), 123.8 (CH), 126.2 (CH), 128.2 (CH), 128.9 (CH), 132.5 (C), 139.6 (C), 160.3 (C_{arom}-O), 164.2 (C_{arom}-OH), 169.8 (C_{arom}-OH), 199.8 (C=O) ppm.EI-MS: *m/z* (%)=286 (M^+,76), 268 (21), 184 (22), 153 (95), 126

(43), 104 (100), 76 (78). Anal. Calcd. for $C_{15}H_{10}O_6$ (286.0): C, 62.94; H, 3.52. Found: C, 62.22; H, 3.85.
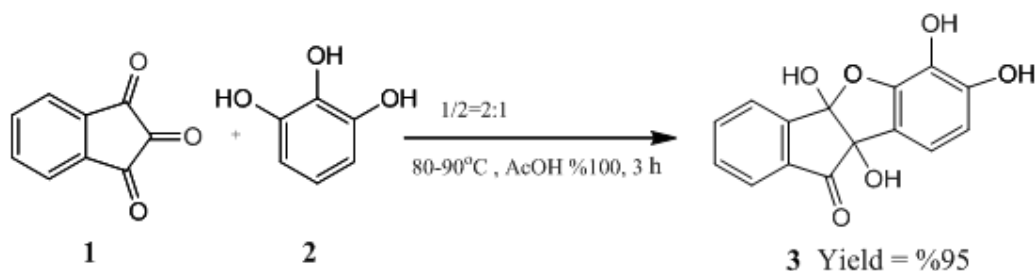

Fig. 1. The synthesis of ninhydrin-pyrogallolmonoadduct

2.4. Electrode Preparation

The general procedure to prepare the PVC membrane was as followed [23-26]: Different amounts of the ionophore (THIBF) along with appropriate amounts of additive (NaTPB) were weighed. Then, known amounts of PVC and plasticizer were added to the mixture. The mixture was dissolved in 3 mL of tetrahydrofuran (THF), and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3} mol L^{-1} Cd(NO$_3$)$_2$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} Cd(NO$_3$)$_2$solution.

2.5. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Ag–AgCl, KC1 (satd.) | internal solution, 1.0×10^{-3} mol L^{-1} Cd(NO$_3$)$_2$| PVC membrane | sample solution | Ag–AgCl, KC1 (satd.)

These measurements were preceded using calibration of the electrodes with several standard solutions. Activities were calculated according to the Debye- Hückel procedure.

3. RESULTS AND DISCUSSION

3.1. Membrane Composition Effect on the Potential Response of the Sensor

Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients, the influence of membrane composition on the potential

responses of the Cd^{2+} sensor was inspected [27,28]. In this study, different membrane compositions, as shown in Table 1, were tested. As can be seen, the membrane with the composition of 28% PVC, 5% ionophore, 3% NaTPB and 64% DBP (no. 4) was the optimum one in the development of this sensor.

The Cd^{2+} ion extraction into the liquid membrane is a result of the high concentration of the ligand in the membrane. From Table 1, it was obvious that in the absence of ionophore (no. 1,2), the response of the recommended electrode was low (slope of 8.9±0.6 and 10.3±0.7 mV per decade) which show significant effect of the ionophore. The sensitivity of the electrode response increases with increasing ionophore content until a value of 5% is reached. It shows the affinity of the THIBF toward Cd^{2+} ion. Further addition of ionophore will, however, result in diminished response of the sensor, most probably due to some inhomogeneities and possible saturation of the membrane [8].

The second factor which helps the extraction of the Cd^{2+} ion is plasticizer. After the evaluation of two solvent mediators (NB and DBP), it was observed that the DBP displays the better sensitivity than NB (no. 8 and 12, 10 and 13),because NB presented higher dielectric constant values than DBP, leading to the extraction of the polar interfering ions, which may have negative effects on the selectivity behavior of the sensor. This may seem to lead to the poorer extraction of Cd^{2+} ions, which have a high charge density, by the average polar solvent. But this seemed to be compensated by the selective complexation of THIBF with the Cd^{2+} ions.

The presence of lipophilic anions in a cation-selective membrane was also considered. Actually, the presence of such anions in a cation-selective membrane, which is based on a neutral carrier, decreases the Ohmic resistance and improves the response behavior and selectivity. Furthermore, when the extraction capability is poor, it increases the membrane electrode sensitivity [29-31]. Here, a NaTPB addition of 3% as an additive led to the slope increase of the potential sensor response from the sub-Nernstian value of 15.1±0.5mV per decade (no. 6) to the Nernstian value of 27.7±0.6mV per decade (no. 4). Addition of ionic additive to the membrane composition has improved the slope. In fact, it helps to the ion-exchange of the analyte from aqueous solution to organic layer of the membrane.

3.2. Internal Solution

The concentration of the internal solution $(Cd(NO_3)_2)$ of the electrode was changed from 1.0×10^{-2} mol L^{-1} to 1.0×10^{-4} mol L^{-1} and the potential response of the Cd^{2+} selective electrode was obtained (Fig. 2). It was found that the variation of concentration of the internal solution does not cause any significant differences in potential response, except for an expected change in the intercept of the resulting Nernstian plot. A 1.0×10^{-3} mol L^{-1} concentration $Cd(NO_3)_2$ solution is quite appropriate for smooth functioning of the electrode system.

Table 1. The optimization of the membrane ingredients

Membrane No.	Composition (%)				Slope (mV per decade)
	PVC (%wt.)	Plasticizer (%wt.)	Ionophore (%wt.)	NaTPB (%wt.)	
1	30	DBP, 70	----	-----	8.9±0.6
2	28	DBP, 69	----	3	10.3±0.7
3	30	DBP, 64	3	3	16.2±0.5
4	28	DBP, 64	5	3	27.7±0.6
5	27	DBP, 64	5	4	27.0±0.4
6	30	DBP, 65	5	---	15.1±0.5
7	29	DBP, 62	7	2	17.5±0.6
8	26	DBP, 64	7	3	19.8±0.6
9	26	DBP, 63	8	3	21.4±0.5
10	26	DBP, 62	9	3	21.0±0.4
11	26	DBP, 61	10	3	21.5±0.7
12	26	DBP, 58	13	3	19.4±0.6
13	27	NB, 62	8	3	19.5±0.4
14	26	NB, 61	10	3	18.9±0.5
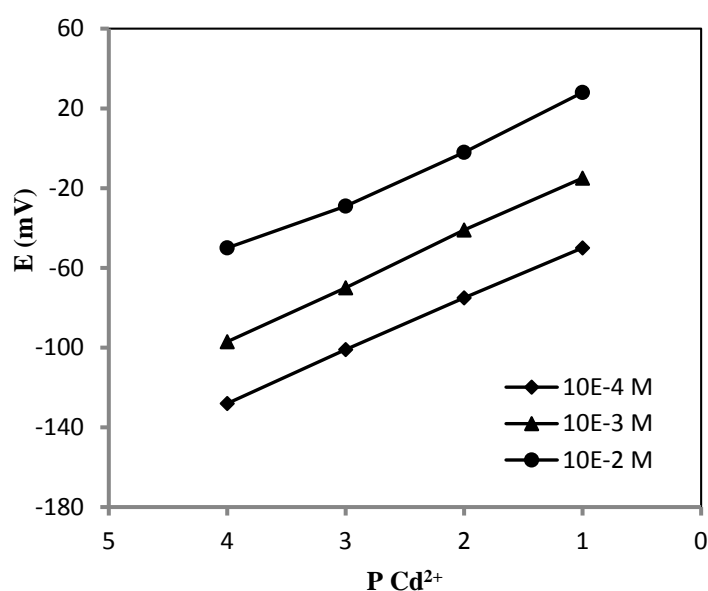
Fig. 2. The effect of internal reference solution concentration on the electrode response

3.3. pH Effect on the Electrode Response

The influence of the pH of the test solution on the potential response of Cd^{2+} sensor investigated at 1.0×10^{-3} mol L^{-1} Cd^{2+} ion concentration, in the pH value of 2.0 up to 10.0(concentrated NaOH or HCl solutions were employed for the pH adjustment). In agreement with the resulting data (Fig. 3), the potential remained constant despite the pH change in the range of 3.0 to 7.0, indicating the applicability of this electrode in this specific pH range.

On the contrary, relatively noteworthy fluctuations in the potential *vs.* pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 7.0 might be justified by the formation of the Cd^{2+} ion hydroxy complexes in the solution. On the other hand, the fluctuations below the pH value of 3.0 were attributed to the partial protonation of the employed ionophore. If H^+ concentration is much more than Cd^{2+}, then H^+ ions can compete with Cd^{2+} ions for making complex with ionophore. In pH between 3-7, H^+ concentration is not enough for competing with Cd^{2+} ions (because ionophore has more trend to Cd^{2+} ions in compare to H^+ ions), but in below pH of 3, H^+ concentration is enough to overcome on Cd^{2+} and employed ionophore can be protonated.
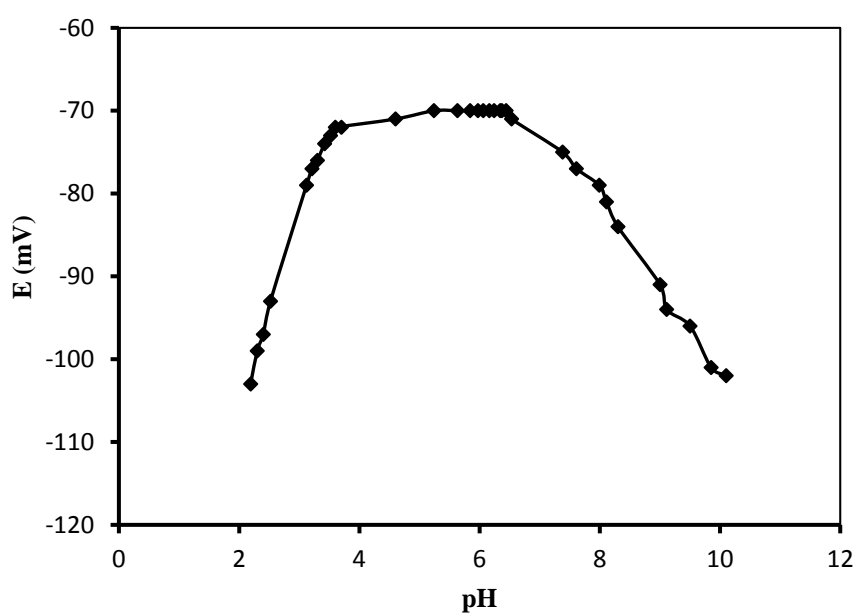

Fig. 3. The effect of the pH on the potential response of the Cadmium sensor

3.4. Response Time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ± 0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It

is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurements were performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effort on the experimental response time of a sensor [32].

In this work, dynamic response time was obtained by changing the Cd^{2+} concentration in solution, over a concentration range 1.0×10^{-4} to 1.0×10^{-1} mol L^{-1}. The actual potential versus time traces is shown in Fig. 4. As can be seen, in whole concentration range the electrode reaches its equilibrium response in a relatively short time ($\sim$5 s). This is most probably due to the fast exchange kinetics of complexation-decomplexation of Cd^{2+} ion with the ionophore at the test solution-membrane interface.
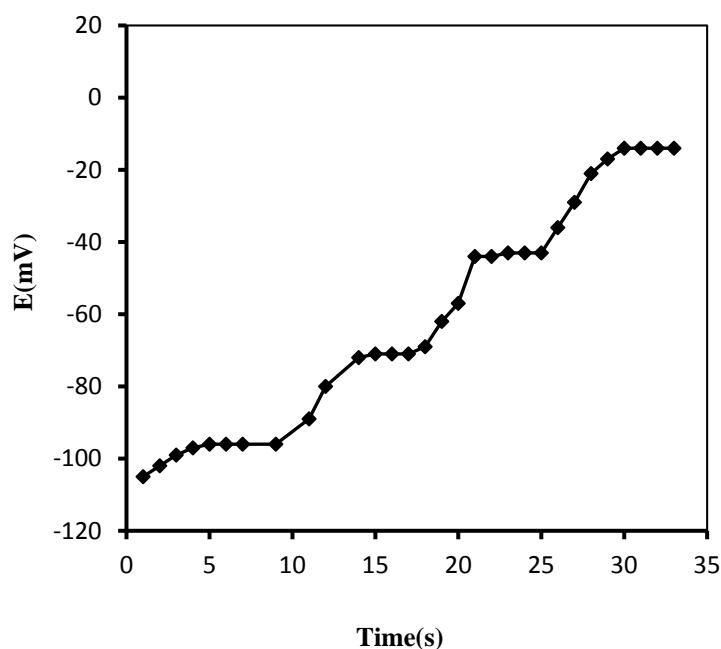

Fig. 4. Dynamic response time of cadmium ion electrode for step changes in concentration of Cd^{2+} over a concentration range from 1.0×10^{-4} to 1.0×10^{-1} mol L^{-1}

3.5. Measuring Range and Detection Limit

The measuring range of an ion-selective electrode includes the linear part of the calibration graph as shown in Fig. 5. The applicable measuring range of the proposed sensor is between 1×10^{-4} and 1×10^{-1} mol L^{-1}. In this work the detection limit of the proposed membrane sensor was 7.0×10^{-5} mol L^{-1} which was calculated by extrapolating the two segments of the calibration curve.
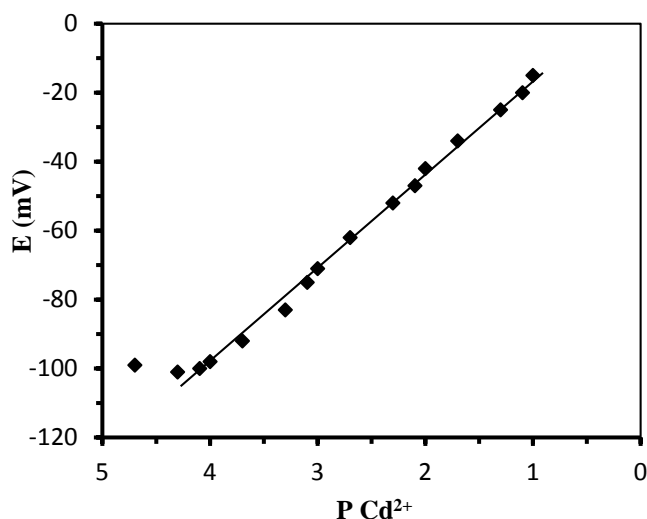
Fig. 5. The calibration curve of the Cd^{2+} membrane sensor

3.6. Selectivity

The potentiometric selectivity coefficients of the Cd^{2+} sensor were evaluated by the matched potential method (MPM) [33,34]. The calculated selectivity coefficient (K_{MPM}) values are given in Table 2. A value of $K_{MPM}=1.0$ indicates equal response to primary and interfering ions. Further, the smaller the value of the selectivity coefficient, the higher is the selectivity of the sensor. It is seen from the table that the selectivity coefficient values are much smaller than 1.0 indicating that they exhibit sufficient selectivity towards Cd^{2+} over all the interfering ions studied.

Table 2. The selectivity coefficients of various interfering cations for the membrane

Ion	K_{MPM}
Na^+	1.1×10^{-3}
Mg^{2+}	4.2×10^{-3}
Mn^{2+}	6.8×10^{-4}
Ca^{2+}	9.0×10^{-4}
Co^{2+}	7.4×10^{-3}
Pb^{2+}	2.2×10^{-2}
Ni^{2+}	8.9×10^{-3}
Cu^{2+}	3.8×10^{-2}
Zn^{2+}	0.5×10^{-3}
Ag^+	1.3×10^{-3}
Cr^{3+}	1.1×10^{-3}

3.7. Lifetime

It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors. The average lifetime for most of the reported ion-selective sensors is in the range of 4–10 weeks. The average lifetime of this sensors was investigated by monitoring thechanges in sensor slope with time. The sensors were tested for 16 weeks, during which time the electrodes were used extensively (one hour per day). Fig. 6 shows the changes in the slope of this sensor with time. The proposed sensors can be used for 13 weeks. There is a slight gradual decrease in the slopes (from 27.98 to 25.70 mV per decade) .
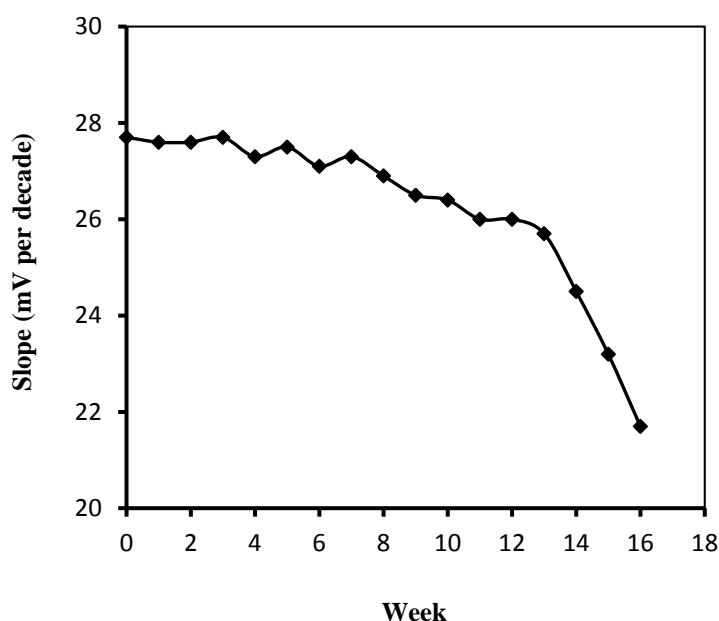

Fig. 6. The lifetime of the Cd^{2+} membrane ion electrode

3.8. Analytical Application

Ion-selective electrodes tend to be; low in cost, simple to use, rapid in determination, with low interferences from the matrix and can be applied to small volumes. These characteristics make them an ideal choice for environmental measurements.

The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 50.0 mL of 1.0×10^{-4} mol L^{-1} of Cd^{2+} solution with EDTA 1.0×10^{-2} mol L^{-1}. The resulting titration curve is shown in Fig. 7. As can be seen, the amount of Cd^{2+} ions in solution can be accurately determined with the electrode.

To assess the applicability of proposed electrode in real samples an attempt was made to determine Cd^{2+} ions in water and wastewater sample. At first, the proposed method was applied to the determination of Cd^{2+} in Well water samples. The samples were filtered using a 0.45-μm pore size membrane filter to remove suspended particulate matter. To the some

sample solutions, different amount of the Cd^{2+} ions were added and to some of the solutions were added nothing and the concentration of Cd^{2+} ions were determined by proposed electrode. Also, the electrode was applied to the direct measurement of Cd^{2+} ions in Islamic Azad university of Yadegar-e-Imam Khomeini (RAH) laboratory wastewater samples. Wastewater samples were filtered using a 0.45-µm pore size membrane filter. One aliquot of the wastewater sample was adjusted to pH of about 6 and their potentials were measured by direct potentiometry. The real concentration of Cd^{2+} ions in wastewater sample, after filtration and dilution, was determined by the standard addition calibration procedure by flame atomic adsorption spectrometry (FAAS) method. All of the results are given in Table 3. As seen, the agreement is good and we conclude that the membrane electrode may have applications in the environmental monitoring of cadmium ions.
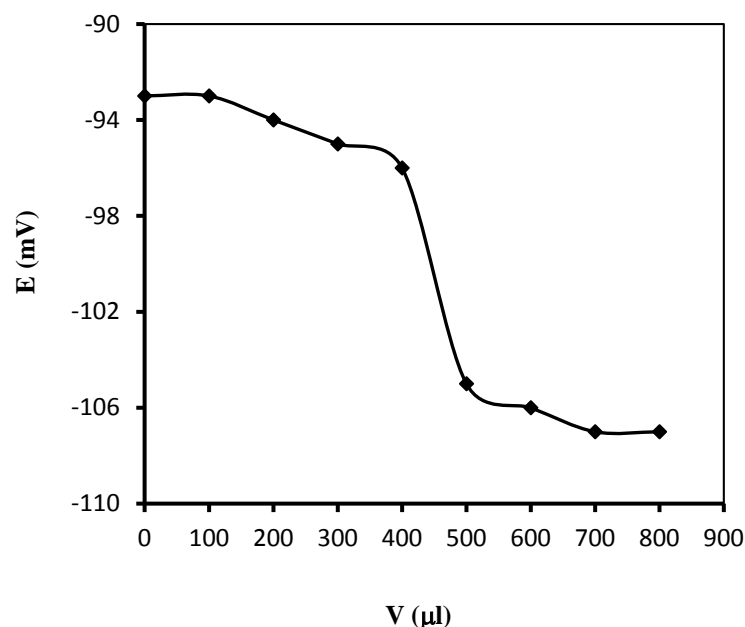

Fig. 7. Potentiometric titration curve of 50 mL 1.0×10^{-4} mol L^{-1} Cd^{2+} with 1.0×10^{-2} mol L^{-1} EDTA, using the proposed sensor as an indicator electrode

Table 3. Determination results of Cd^{2+} ions in various samples

Sample	Added amount	Measured with proposed sensor	Measured with FAAS
Wastewater	0	147 (mg L^{-1})	145 (mg L^{-1})
Well water	0	< LOD	----
	1.0×10^{-3} (mol L^{-1})	1.1×10^{-3} (mol L^{-1})	----
	1.0×10^{-2} (mol L^{-1})	0.9×10^{-2} (mol L^{-1})	----

[a] % RSD based on three replicate analysis

3.9. Comparison of the proposed Cd^{2+} sensor and some of the best previously reports

The Nernstian slope, linearity range, working pH range, life time and response time of proposed Cd^{2+} sensor with some of the best previously reports are compared in Table 4. As is obvious, the results clearly indicate that the proposed sensor is superior to the previously reported ones in: response time and lifetime [35-42]. These two are the most important characters on construction of ion selective electrodes. Proposed sensor has the shortest response time (5 s) and the longest lifetime (13 weeks) between them. Also, it should be mentioned that it is found to perform satisfactorily over a relatively large range of pH values (3.0 to 7.0). In Nernstian slope, proposed sensor is closed to the previously reports.

Table 4. Comparison of the proposed Cd^{2+}ion sensor and the some previously reports

Ionophore	Slope (mV/decade)	Linear range (mol L^{-1})	pH	Life time (Week)	Response time (s)	Ref.
N,N′-[bis(pyridin-2-yl)formylidene]butane-1,4-diamine	29	7.9×10^{-8}-1×10^{-1}	2.0–8.0	8	10	[35]
N′-p-[1-(2-furyl)methylidene]-2-furohydrazide	29	1×10^{-6}-1×10^{-1}	2.8-8.6	9	10	[36]
5-[((4-Methyl phenyl) azo)-N-(6-amino-2-pyridin) salicylaldimine], and 5-[((4-methyl phenyl) azo)-N-(2-diamino-2-cyano-1-ethyl cyanide) salicylaldehyde]	28 22	7.5×10^{-7}-1.5×10^{-1} 4.0×10^{-7}-2.0×10^{-1}	3.5-9.0	12	----	[37]
Benzilbis(carbohydrazone)	30	1.0×10^{-7}-1.0×10^{-1}	2.0-9.0	----	8	[38]
p-tert-butylcalix[4]arene	29	1.6×10^{-6}-1×10^{-2}	6.0-9.0	1	10	[39]
1, 2-bis(quinoline-2-Carboxamido)-4-chlorobenzene	30	1.0×10^{-6}-1.0×10^{-1}	2.4-9.0	8	10	[40]
(13E)-N-benzylidene-2-(3-((E)-2-(benzylideneamino)ethyl)-2-phenylimidazolidin-1-yl)ethanamine	29	1.0×10^{-6}-1.0×10^{-1}	3.5-7.9	13	35	[41]
4-hydroxy salophen	30	1.0×10^{-6}-1.0×10^{-1}	2.8-8.1	8	20	[42]
4b,6,7,9b-Tetrahydroxy-4bH-indeno[1,2-b]benzofuran-10(9bH)-one	28	1.0×10^{-4}-1.0×10^{-1}	3.0-7.0	13	5	This work

4. CONCLUSIONS

In order to simple, low cost, accurate and rapid determination of Cd^{2+} ions, the Cd^{2+} potentiometric membrane ion selective electrode was constructed by 4b,6,7,9b-Tetrahydroxy-4bH-indeno[1,2-b]benzofuran-10(9bH)-one as new ionophore. The electrode exhibits a Nernstian response for Cd^{2+} over a concentration range (1.0×10^{-4} to 1.0×10^{-1} mol L^{-1}) with a slope of 28 mV per decade. This electrode was shown a fast response time (~5 s), pH

independent potential responses across the wide range of 3.0–7.0 and long lifetime (13 weeks). Its selectivity towards the Cadmium ions was not influenced by the presence of the common alkali, alkaline earth, or transition and heavy metal ions, since the interference of these substances was low. It was used as an indicator electrode in potentiometric titration of Cd^{2+} ion with EDTA and in direct determination of Cd^{2+} ion in water and wastewater samples.

Acknowledgments

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