



Determination of Trace Amount of Cadmium by Modified Graphite Electrode in Aqueous Samples

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Abstract

In this study the 2,3- Dihydroquinazolin-4(1H)-one was used successfully as an ionophore in construction of modified graphite electrode for Cd (II) cation measurement in aqueous samples, which was formed from a thin layer by Sol-Gel method. The electrode response to Cd (II) cation was reported with a Nernstian slope of -28.9 mV/decade, dynamic range of 1.0×10^{-2} - 1.8×10^{-8} M and pH range of 5.0-6.5. The electrode response time was 45 sec and its detection limit was recorded as 8.6×10^{-9} M. The lifetime of electrode was about 40 days. The proposed electrode showed good selectivity for Cd^{2+} compared to many metal cations. Finally, the desired electrode was satisfactorily used as an indicator electrode in potentiometric titration with EDTA. Also, it was used to determination of Cd^{2+} in real samples and the results were compared with results of atomic absorption spectrophotometer.

Keyword: Cadmium, Ion-selective electrode, Sol-Gel, Ionophore.

1 Introduction

Cadmium can easily be dissolved and transported by water. As a result, the metal can easily enter the environment and the water cycle from various industries such as the rubber, painting, and battery industries. Permissible limit of cadmium content in drinking water is about 1.2 mg/Lit. Cadmium produces several complications such as anemia, bone, liver and kidney disease in the body [1-2]. Due to harmful cadmium poisoning effects, the ability of cadmium measurement in slight quantities is vital. Up To now, several methods have been used for measurement of Cd (II) cation such as: atomic absorption spectrometry (AAS) [3-4], inductively coupled plasma-optical emission spectroscopy (ICP-OES) [5] and chromatography [6]. These methods usually are expensive and need to an expert operator for their usage, so there is a serious demand for low cost, fast, simple and also precise measurement methods. An approach with noted features is potentiometric with using ion selective electrode. Selective electrodes are designed based on a Carrier ligand [6-8].

One of the methods used to modification and increase the electrode level is the sol-Gel method. The Sol-Gel method is based on the hydrolysis and concentrating of an alkoxide precursor and provides a new possibility for sensors modification, because the long range of organic, mineral and bio molecules could simply be duped with Sol-Gel texture [9-10]. For instant, this method could be used for modifying Carbone electrode since mineral silica polymers have profits like physical severity, low inflammation and chemical inactivity respect to organic

polymers [11-12]. Especially the mixture of Sol-Gel and Carbon has more stability in comparison with carbon and could be modified more adequately respect to organic compound electrode [13-14]. The modified electrode by Sol-Gel method could be used as indicator or reference electrode in Potentiometric and it can be used in the biosensor construction [15-17]. Isotonic Anhydride Compounds, which are part of the heterocyclic category, are used in the manufacture of many compounds as intermediates. Of these compounds, the two derivatives, namely quinazoline-4- (3-hydrogen) -1 and 3, 2-dihydroquinolin-4- (α -hydrogen) -1, are the most important ones. These compounds play a very important role in the synthesis of several batches of biological molecules, such as amino acids and peptides. In a recent study, the 2, 3- Dihydroquinazolin-4(1H)-one, one of the derivatives of the compounds above, was used as an ionophore in the construction of a graphite electrode [18-20].

2 Experimental

2.1 Reagents

Tetra ethoxy silane (TEOS), triton X-100, dimethylformamide (DMF), ethanol ($\text{C}_2\text{H}_5\text{OH}$), acetone ($(\text{CH}_3)_2\text{CO}$), sodium hydroxide (NaOH), (2, 3- Dihydroquinazolin-4(1H)-one, acid: Chloridric (HCl) Nitrate Salt of various metals and Buffer: citric acid/sodium nitrate. All above materials were purchased from Aldrich.

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2. 2. Apparatus

All potentiometric measurements were carried out at 25.0 ± 0.1 °C with a pH/mV meter (ZagShimi, Iran). A digital pH meter (Jenway pH-meter, UK 3020) was used for pH measurements. UV/VIS Spectrophotometer (UV-2100, JENUS, China). Saturated calomel electrode (SCE) and graphite electrode, were purchased from Azar electrode, Iran. Digital-Scale by 0.0001 accuracy (Shimadzu-AEL-200, Japan). Atomic absorption spectrometer (Shmadzu, AA-760, Japan) was used to determine metal ion under recommended conditions in the instrument manual.

2. 3 Procedures

2. 3. 1. Spectroscopic study

The spectrophotometry was used for ligand-metal cation reaction to do this. Samples with constant concentration of ligand (I) Fig. 1 were prepared and different amounts of Metal cations were added to them and solution absorption spectra was recorded. In this way, at first the back ground correction was done with 2 mL of solvent DMF. Then 100 micro liter of 0.01 M solution of ligand in solvent DMF was added to quartz cell and its absorption spectrum was recorded. In the next steps, different volumes of 0.01 M Metal cations were added to the cell, so the photometric titration spectra of these cations were plotted. Among these various metal cations, the cadmium cation ligand complex had high selectivity and other cations didn't have effective interaction with ligand.

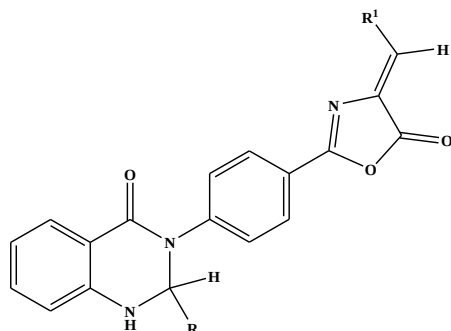


Fig. 1: The structure of ionophore 2,3- Dihydroquinazolin-4(1H)-one. (ligand I)

2.3.2 Preparation of Sol-Gel

Firstly different amounts of required reactants for cell preparation like ligand(I), DMF as a ligand solvent, TEOS, H₂O, ethanol, HCl and Triton X-100 were added to a poly ethylene vial. Then the reactants were mixed completely by magnetic stirrer in different temperatures diverse mixing times. With these conditions all needed processes for polymeric Sol-Gel network formation are accomplished.

3. 3 Electrode preparation

In this section, at first to prepare the electrode, modified by sol-gel, the graphite electrode was washed twice with distilled water several times. Then the tip of the electrode was placed in a sol-gel mixture for 60 seconds. The modified electrode was ready to use after 24 hours.

3.4 emf measurement

The modified Graphite electrode was used as an indicator electrode and saturated calomel electrode as a

reference electrode were used in Potentiometric method. All measurement was done in 25° C and the potensiometric cell was as: Hg/Hg₂Cl₂, KCl (satd.) | test solution | graphite electrode. The measurements started by placing modified graphite and calomel electrodes in 100 mL Beaker of dual distilled water. After that, to get the 1×10^{-1} - 1×10^{-10} M range of metal concentration, various volumes of standard Cd (II) nitrate solution was added with Hamilton micro liter syringe to the beaker. The magnet stirrer was used to make equal response and the solution potential was recorded after stirring in equilibrium condition. These steps were applied for different cations and modified graphite electrode potential was plotted versus calomel ones as a function of cations concentration. Fig. 2. (A and B). The experiments showed that the electrode response to Cd (II) cation was more than other cations considerably. According to the results of the experiments, the response of the modified electrode to Cd²⁺ was better than other reported metal cations significantly.

2.3.5 Optimization of Sol-Gel composition

It was optimized to increase sol in order to obtain the best response by the designed electrode, the proportions of the components used in the sol-gel should be optimized. Also, sol composition homogeneousness. In this way the amounts of ligand (I), DMF, (TEOS), H₂O, ethanol, HCl, and Triton X-100, also temperature and mixing times were changed to get optimal conditions. The results are shown in Table 1. According to the results, sol composition number 11 of Table 1. is the best one which is composed of 12 mg ligand, 1 mL DMF, 1.5 mL TEOS, 2 mL ethanol, 1 mL H₂O, 0.5 mL HCl and 2 drops of triton X-100. This mixture was stirred for 24 hr, with temperature of 25° C. Its Nernstian slope and linear range were -29.03 mV/decade and 1.0×10^{-2} - 1.8×10^{-8} M, respectively which were the best ones.

2.3.6 The effect of pH on the electrode response

One of the most important factors that can affect the response electrode is pH. To investigate the effect of pH on the electrode response, the 1.0×10^{-3} M Cd (II) nitrate solution was used and solution pH was adjusted by volumes of HNO₃ and NaOH. The plot of electrode potential versus pH in range of 2.0-10 is shown in Fig. 3. The electrode response was constant in pH range 4-7. By decreasing pH to lower than 5.0, the electrode potential increased which may was due to nitrogen atoms protonation in modifier. Also Cd (II) cation concentration decreased in pH higher than 6.5 due to Cd (II) complex formation with hydroxyl group then the electrode potential was decreased. According to the results, pH=6 was selected for next experiments.

2.3.7 Selectivity

To calculation the selectivity coefficients, which are describe as the Cd (II) concentrations in the presence of other cations, the fixed interference method (FIM) was applied [22]. To do this, the electrode potential was read for solutions of 0.1 M of interfering cation and 0.01×10^{-8} M of Cd (II). After potential record in each case, the plot of electrode potential versus the logarithm of main cation concentration was curved and main cation activity a_A , was obtained at intersection of plot's extrapolated linear sections.

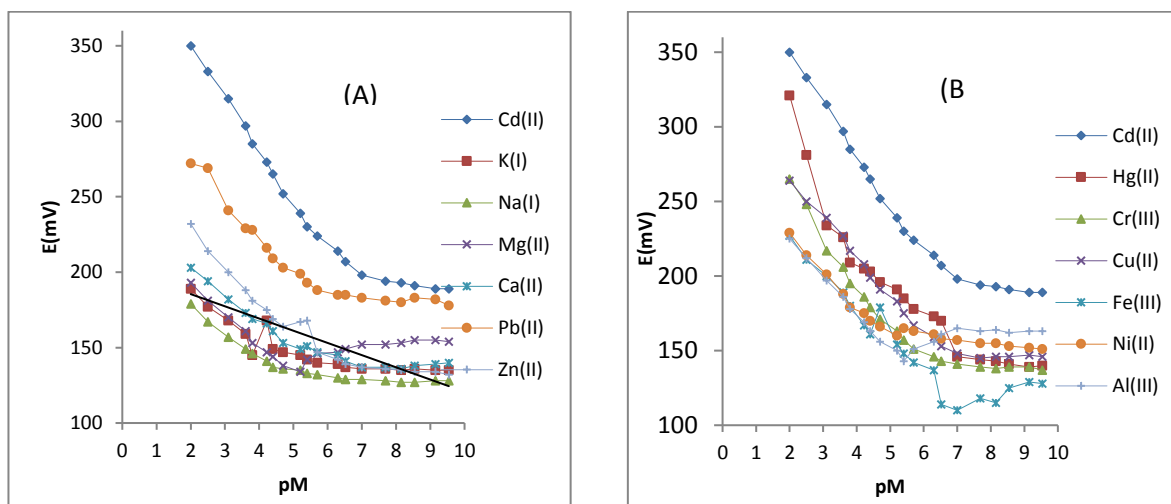
Fig. 2: Potential response of sol gel electrode for various cations (1×10^{-1} – 1×10^{-10} M).

Table 1: The composition and characteristics of several typical membranes for sol-gel electrodes

NO.	TEOS (mL)	Ethanol (mL)	H ₂ O (mL)	HCl(0.1M) (mL)	TX-100 (Drops)	DMF (mL)	Ligand (mg)	T (°C)	Stirrer Time(h)	Slope (mV/decade)	Linear range (-log C)
1	0.5	2.0	1.0	0.5	4	0.5	5	50	72	-27.94	2.0-6.7
2	1.0	2.0	1.0	0.5	3	0.5	10	50	72	-28.25	2.0-7.1
3	1.3	2.0	1.0	0.5	2	1	12	50	48	-28.2	2.0-7.5
4	1.5	2.0	1.0	0.5	2	1	12	40	48	-28.35	2.0-7.0
5	1.7	2.0	1.0	0.5	2	1	12	40	48	-28.63	2.0-7.5
6	2.0	2.0	1.5	0.5	2	1	12	40	24	-28.43	2.0-7.3
7	1.5	1.0	1.0	0.5	2	1	12	40	24	-27.74	2.0-7.6
8	1.5	2.5	1.5	0.5	2	1	12	30	24	-29.20	2.0-7.6
9	1.5	2.0	1.0	1.0	2	1	12	30	12	-28.11	2.0-7.6
10	1.5	2.0	1.0	0.7	1	1	12	30	12	-31.05	2.0-7.0
11*	1.5	2.0	1.0	0.5	2	1	12	25	24	-29.03	2.0-7.70
12	1.5	2.0	1.0	0.5	2	0.5	5	25	24	-27.93	2.0-6.50
13	1.5	2.0	1.0	0.5	2	0.5	9	25	12	-27.30	2.0-7.5
14	1.5	2.0	1.0	0.3	2	1.2	15	25	24	-30.85	2.0-7.6

Selectivity coefficient was calculated through, Nikolsi-Eizenman equation:

$$k_{A,B}^{\text{pot}} = \frac{a_A}{(Z_A/Z_B) a_B} \quad (1)$$

where Z_A , Z_B are respectively the charge of primary ion and interfering ion in the above equation, the results are listed in Table 2.

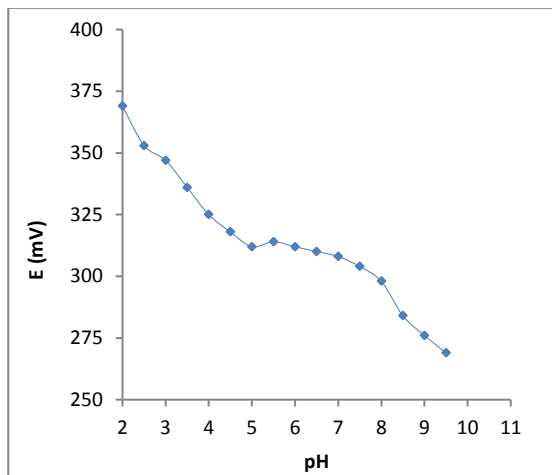


Fig. 3: pH effect of the test solutions on the potential response of the cadmium sensor (1.0×10^{-3} M Cd (II)).

Table 2: Selectivity coefficients of various interfering ions

M^{n+}	$K_{Cu,B}^{\text{pot}}$	M^{n+}	$K_{Cu,B}^{\text{pot}}$
Na^+	2.5×10^{-4}	Hg^{2+}	8.1×10^{-3}
K^+	3.7×10^{-4}	Pb^{2+}	4.8×10^{-3}
Ca^{2+}	3.0×10^{-3}	Cu^{2+}	3.3×10^{-3}
Mg^{2+}	6.1×10^{-4}	Cr^{3+}	2.7×10^{-3}
Ni^{2+}	1.7×10^{-3}	Fe^{3+}	1.2×10^{-3}
Zn^{2+}	1.9×10^{-3}	Al^{3+}	1.1×10^{-3}

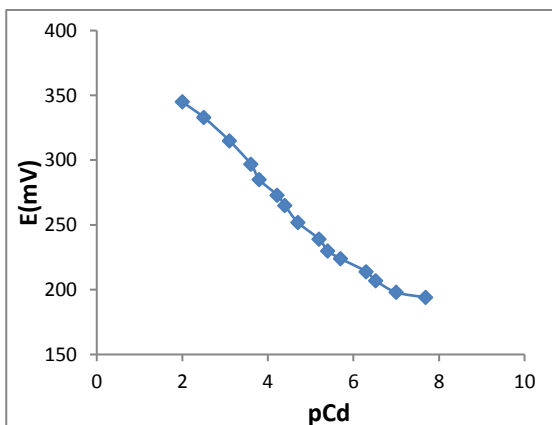


Fig. 4: Calibration curve of the cadmium electrode based on 2, 3-Dihydroquinazolin-4(1H)-one (1.0×10^{-2} - 0.36×10^{-10} M Cd (II) and pH=6)

2.3.9 Response time and electrode lifetime

In this study the response time was considered equal the IUPAC definition: response time is time at which the emf/time slope ($\Delta E/\Delta t$) of response potential curve of solution becomes equal to a limiting value, after change of main ion concentration in the solution. To calculate response time, the average time of whole procedure, from entering of electrode in 1.0×10^{-3} M Cd (II) solution until the response electrode became steady, was recorded. Then the plot of response potential electrode versus time was curved (Fig. 5.). The response time estimated about 35 seconds at intersection of two extrapolated linear sections of this curve. A modified graphite electrode was used daily for 40 days, to analysis the electrode lifetime. The used electrode performance was not changed considerably after 50 days.

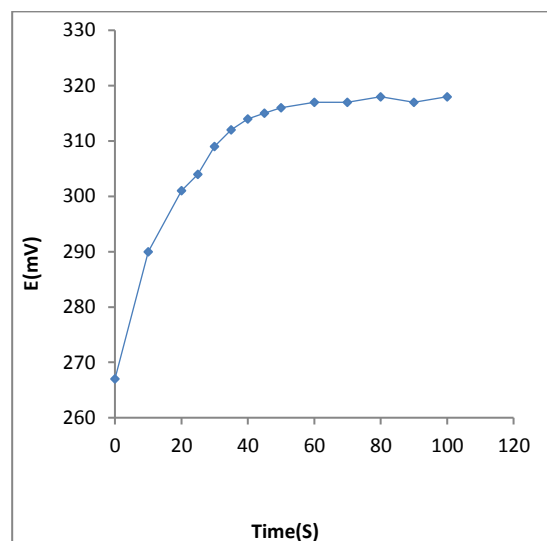


Fig. 5: Plot of optimum electrode response versus time (1.0×10^{-3} M Cd (II), pH=6).

2.3.10 Reversibility and Repeatability

Required reversibility of modified electrode was surveyed in the reaching to final equilibrium ± 1 mV potential. To do this, the noted electrode was immersed in two different solutions (1.0×10^{-2} and 1.0×10^{-4} M from Cd (II)) frequently and its potential was recorded. This measurement was repeated 8 times again regarding electrode response time (Fig. 6.). Relative standard deviation (RSD %) for low and high Cd (II) concentration (each 10 times measurement) RSD % was ± 0.15 for 1.0×10^{-2} M and ± 0.12 for 1.0×10^{-4} M concentration. The relative standard deviation showed that electrode behavior didn't change when potentials were recorded from high to low or inverse. For the obtained results, response repeatability was supported in each concentration.

2.3.8 Calibration curve, linear range and detection limit

To determine the curve slope, electrode potential of standard Cd (II) cation solution was recorded in different Cd (II) concentrations. The Nernstian slope of response potential curve in concentration range of 1.0×10^{-2} - 1.8×10^{-8} M was -28.9 mV/decade. Electrode detection limit was also estimated at intersection of two extrapolated linear sections in the lowest region of calibration curve about 8.6×10^{-9} M as it is shown in Fig. 4. Also characteristics of modified electrode in this study were contrasted with other works that were listed in Table 3.

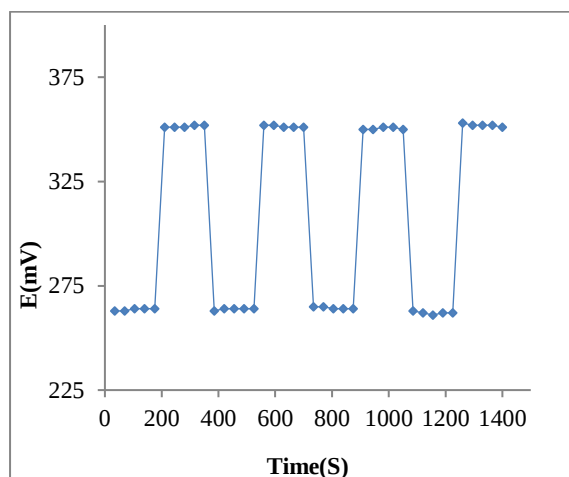


Fig. 6: Dynamic response time of the cadmium electrode for step changes in the concentration of Cd(II) (1.0×10^{-2} and 1.0×10^{-4} M and pH=6).

3 Analytical Application

The modified graphite electrode with ligand (I) was used to determine cadmium extent of 4 actual samples including soil, pipeline water, well water and river water. To preparation of soil sample, 20 mg of soil was mixed with 20 mL distilled water in a beaker. Then 12 mL of concentrated nitric acid and 3 mL of peroxide hydrogen were added dropwise to the mixture. Next, the beaker was heated to reduce volume mixture by half. After cooling and filtering the mixture, it was diluted to volume of 25 mL. At the end of the process of preparing soil sample, the pH was adjusted to 6 using a phosphate buffer [38]. After samples preparation (except for soil sample), the noted electrode was used to measure their Cd contents by method of standard addition. The obtained results with this electrode were compared by flame atomic absorption spectrophotometry (Table 3). According to Table 3, there is not meaningful difference between the results of two methods.

Table 3: Determination of cadmium ion in different samples using sol-gel electrode and AAS method

Sample	Real sample	Cd ²⁺ added (M)	Found: A (M) and B (W/W%)		RR(%)
			Proposed electrode	(AAS)	
A: pipeline water	N.D. ^a	1.0×10^{-6}	$1.5(\pm 0.27) \times 10^{-6}$	1.9×10^{-6}	103.0
A: Well water:	N.D. ^a	1.0×10^{-6}	$1.8 (\pm 0.12) \times 10^{-6}$	1.15×10^{-6}	109.0
A: River water:	N.D. ^a	1.0×10^{-6}	$1.8 (\pm 0.20) \times 10^{-6}$	1.6×10^{-6}	107.0
B: Soil	1.55×10^{-3} (w/w%)	-	$1.47 (\pm 0.18) \times 10^{-3}$	1.55×10^{-3}	94.7

^a Relative recovery

^b Not detected

Also the stability of this modified electrode for the actual sample (pipeline water) was evaluated. For this purpose, the measured solution with concentration of 1.0×10^{-6} and the electrode were kept at room temperature for 10 days. After which the electrode response did not change significantly (0.62%). After 40 days of holding the electrode at ambient temperature, the electrode response was changed to less than 8.12% of the percentage of the electrode's initial response. Therefore, these results indicate that proposed electrode has the potential to be used to measure cadmium ion (II) over a relatively long period of time (Table 4.).

Table 4: Inter-day precisions for real samples analysis (for pipeline water)

Day	Real amount (μM)	Measured value (μM)	Change %
1	1.6	1.6	-
10	1.6	1.59	0.62
20	1.6	1.58	1.25
30	1.6	1.55	3.12
40	1.6	1.51	5.6
45	1.6	1.47	8.12
50	1.6	1.43	10.62

4 Conclusion

The preparation Sol-Gel method of modified graphite electrode is simple and single stage with low cost. The presence of 2, 3- Dihydroquinazolin-4(1H)-one as an ionophore in the Sol-Gel matrix increases the affinity formation of Cd (II) cations. The noted electrode had suitable Nernstian slope, wide dynamic range and low detection limit respect to Cd (II) cation. Also this electrode

has remarkable selectivity for Cd (II) cation in the presence of wide range of alkali metals, alkaline earth metals and heavy cation metals. This electrode was used successfully in actual samples measurements.

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