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Bio-Mimetic Cadmium Ion Imprinted Polymer Based Potentiometric Nano-Composite Sensor

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A novel cadmium nano-composite carbon paste electrode based on biomimetic ion imprinted polymer (IIP) is constructed. The IIP was prepared by using vinyl pyridine and quinaldic acid as functional monomer and complexing agent, respectively. The nano-composite paste were made of cadmium imprinted polymer (IIP) as a sensing element, multi-walled carbon nanotube (MWCNT), nanosilica (NS), graphite powder, and room temperature ionic liquid (RTIL). The best response of the nano-composite sensor were obtained from the electrode composition of 5% MWCNT, 1% NS, 20% IIP, 20% RTIL, and 54% graphite powder. The proposed sensor shows a Nernstian response (29.2±0.3 mV decade^{-1}) in the range of 1.0×10^{-7}-1.0×10^{-2} M with detection limit of 1.0×10^{-7} M. The response of the sensor is independent of pH in the range of 3.5-8.0. The nano-composite based Cd(II) sensor displayed very good selectivity, fast response time, and long lifetime.

Keywords: Cadmium, Ion selective electrode, Ion Imprinted Polymer (IIP), Sensor, Potentiometry, Multi-walled carbon nanotube (MWCNT), Nanosilica (NS), Ionic Liquids (IL)

1. INTRODUCTION

Cadmium is a soft; bluish-white metal which is chemically similar to two other stable metals in group 12, zinc and mercury. Similar to zinc, it prefers oxidation state of +2 in most of its compounds and similar to mercury it shows a low melting point compared to other transition metals. Cadmium compounds were used to stabilize plastic. With the exception of its use in nickel–cadmium batteries and cadmium telluride solar panels, the use of cadmium is generally decreasing in its other applications. These declines have been because of cadmium toxicity in certain forms and concentration [1].

Cadmium ion shows no definite indication of being an essential trace element in biological processes; on the contrary, it is highly toxic to a wide variety of living organisms, including man [2]. Ionic cadmium causes genotoxic effects in a variety of types of eukaryotic cells, including human cells. There is some evidence relating cadmium exposure to prostate cancer in men and animal studies [3]. An accumulation of cadmium in many tissues and a particularly long half-life, 10–30 years, has been reported for muscles, kidneys and liver [4]. Cadmium and its derivatives are also found as industrial waste because of its growing area in production of some batteries, cameras, and have been used as a catalyst. Hence, monitoring cadmium levels in our environments is important.

Common instrumental methods for cadmium analysis are flame atomic absorption spectrometry [5] and inductively coupled plasma (ICP) [6]. These methods involve expensive instrumentation and sample pretreatment, which is time consuming and inconvenient. In contrast, potentiometric detection based on ion-selective electrodes (ISEs), offers advantages of speed and ease of procedures, simple instrumentation, relatively fast response time, wide dynamic range, reasonable selectivity, and low cost [7-19].

Thus, the development of a selective sensor for Cd(II) has been a subject of investigation to analytical chemists. Several organic and inorganic compounds have been tested as sensing materials in producing cadmium ISEs. Those ISEs have a short lifetime, and interfered by a number of metal ions such as silver, iron, and mercury ions. However, here, a new synthesized ion imprinted polymer (IIP) is introduced as a very selective carrier for Cd(II) ion.

Biological recognition elements such as antibodies, enzymes and aptamers have been used as specific receptors to a target molecule in a wide variety of sensors. However, they have many difficulties for their practical uses such as lack of stability, reusability, cost and not easy to obtain. During recent years, a new approach has been used to synthesis the hosts which possess a structure capable of binding complementary guests to develop specific recognition materials. Moleculary imprinted polymers (MIP) technology is the synthesis of specific recognition sites which has been accomplished by coordinating functional monomers around a target molecule, and then cross-linking to position functional monomers around the target molecule. Since MIPs can behave specifically, and mimic bio-receptors; so, they are called “biomimetic recognition elements”. This technology can also be used for preparation of the polymers containing inorganic cation selective sites as ion imprinted polymers (IIP) [20-24].

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell in which carbon paste electrode was placed into contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode and Cd^{2+} CPE as an indicator electrode. Both electrodes were connected to a mili-voltmeter.

The following cell was assembled for the conduction of the EMF (electromotive force) measurements:

Carbon paste electrode | sample Cd^{2+} ion solution | Ag/AgCl–KCl (satd.)

2.2. Reagents and materials

The multi-wall carbon nanotubes (MWCNTs) (10-40 nm diameters, 1-25 μm length, SBET: 40-600 m^2/g and with 95% purity were purchased from local company in Iran. Graphite powder with a 1–2 μm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for preparation of the carbon pastes. The ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and chloride and nitrate salts of the cations were all purchased from Merck Co.

In order to prepare Cd(II) imprinted polymer, 1 mmol of $Cd(NO_3)_2$ and 1 mmol of quinaldic acid were dissolved in 20 mL of DMSO and then 4 mmol of 4-vinyl pyridine was added to the solution. The solution was allowed to be at this condition for 1 h in order to ensure the equilibration of the complexation reaction. Finally, 0.15 g of initiator (2,20-azobisisobutyronitrile) and 20 mmol of cross-linker (EGDMA), dissolved in 3 mL of DMSO, was mixed with previous solution and followed by purging with N_2 gas for 10 min. The polymerization was carried out in a water bath at 70 °C for 24 h. The obtained polymer was grounded in a mortar and wet-sieved. The particles were firstly washed with ethanol and then washed with HCl solution (2 M). Finally, the particles were washed with distilled water and dried at 60 °C [24].

2.3. Preparation of the sensors

General procedure for preparation of the carbon paste electrode was as follows: various amounts of IIP along with appropriate amount of graphite powder, paraffin oil or IL, nano-silica and MWCNTs were thoroughly mixed. After homogenization of the mixture, the resulting paste was transferred into a plastic tube with 6 mm o.d. and a height of 3 cm. The paste was carefully packed into the tube tip to avoid possible air gaps, which often enhance the electrode resistance. A copper wire was inserted into the opposite end of the CPE to establish electrical contact. External surface of the carbon paste was smoothed with soft paper. The electrode was finally conditioned for about 48 h by soaking it in a 1.0×10^{-3} M of Cd(II) solution [25-33].

3. RESULTS AND DISCUSSION

3.1. Carbon paste composition

In this work, two kinds of carbon paste were made; modified and unmodified CPEs with a variety of compositions. The results for these CPEs are given in Table 1. The unmodified CPE with optimized composition (electrode no. 3) shows a sub-Nernstian slope of 23.7 mV per decade. Using room temperature ionic liquid instead of paraffin oil leaded to the better electrode response (electrode No. 5). Addition of 5% MWCNTs to the composition of carbon paste electrode also causes improvement of response (electrode No. 9). Finally, the electrode composed of 20% IL, 20% IIP, 54%

graphite powder 1% nano-silica and 5% MWCNTs (no. 11) was found to be optimal for cadmium carbon paste electrode. This composition was selected for further examination. From Table 1, it was obvious that in the absence of IIP and presence of other components (no. 13), the response of the CPE was very low (slope of 6.3±0.5 mV per decade). Using MWCNTs in the carbon paste improves the conductivity of the electrode and, therefore, conversion of the chemical signal to an electrical signal is better occurred. Carbon nano-tubes especially multi-walled ones have many properties that make them ideal as components in electrical circuits, including their unique dimensions and their unusual current conduction mechanism. Using nano-silica in the composition of the carbon paste can also improve the response of the electrode. Nano-silica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the CPE. Also, it enhances the mechanical properties of the electrode. Using room temperature ionic liquid in the composition of the carbon paste electrode, instead of paraffin oil, causes more efficient extraction of ions with high charge density into the carbon paste surface. This is due to the much higher dielectric constant of the ionic liquids as binder compared to paraffin oil [31-33]. As it can be seen from Table 1, using [bmim]BF_4 instead of paraffin oil in the carbon paste composition yields more efficient extraction of Cd^{2+} ion (which is a rather high charge density cation) from the solution into the surface of CPE.

Table 1. The optimization of the Cd(II) carbon paste bio-mimetic sensor

No.	Graphite	IIP	Paraffin	RTIL	MWCNT	NS	Slope (mV decade^{-1})	Linear Range (M)
1	75	10	15	-	-	-	19.7±0.5	$1.0\times10^{-2}-1.0\times10^{-4}$
2	70	15	15	-	-	-	22.7±0.4	$1.0\times10^{-2}-1.0\times10^{-5}$
3	65	20	15	-	-	-	23.7±0.3	$1.0\times10^{-2}-1.0\times10^{-5}$
4	60	25	15	-	-	-	23.3±0.4	$1.0\times10^{-2}-1.0\times10^{-5}$
5	65	20	-	15	-	-	26.6±0.4	$1.0\times10^{-2}-5.0\times10^{-6}$
6	60	20	-	20	-	-	27.2±0.3	$1.0\times10^{-2}-2.0\times10^{-6}$
7	55	20	-	25	-	-	26.9±0.5	$1.0\times10^{-2}-5.0\times10^{-6}$
8	57	20	-	20	3	-	27.9±0.3	$1.0\times10^{-2}-1.0\times10^{-6}$
9	55	20	-	20	5	-	28.3±0.3	$1.0\times10^{-2}-5.0\times10^{-7}$
10	53	20	-	20	7	-	28.1±0.5	$1.0\times10^{-2}-5.0\times10^{-7}$
11	54	20	-	20	5	1	29.2±0.3	$1.0\times10^{-2}-1.0\times10^{-7}$
12	52	20	-	20	5	3	28.3±0.4	$1.0\times10^{-2}-5.0\times10^{-7}$
13	74	-	-	20	5	1	6.3±0.5	$7.0\times10^{-3}-5.0\times10^{-4}$

3.2. Measuring range and detection limit

The measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits. The response of the optimal modified Cd^{2+} carbon paste electrode (no. 11) was tested across Cd^{2+} ion concentration in the range of $1.0\times10^{-8}-1.0\times10^{-1}$ mol L^{-1}. The applicable range of the proposed sensor extends from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} as seen in Fig. 1.

By extrapolating based on the linear portion of the electrode's calibration curve, the detection limit of an ion selective electrode can be calculated. In this work, the detection limit of the proposed membrane sensor was 1.0×10^{-7} mol L^{-1}.

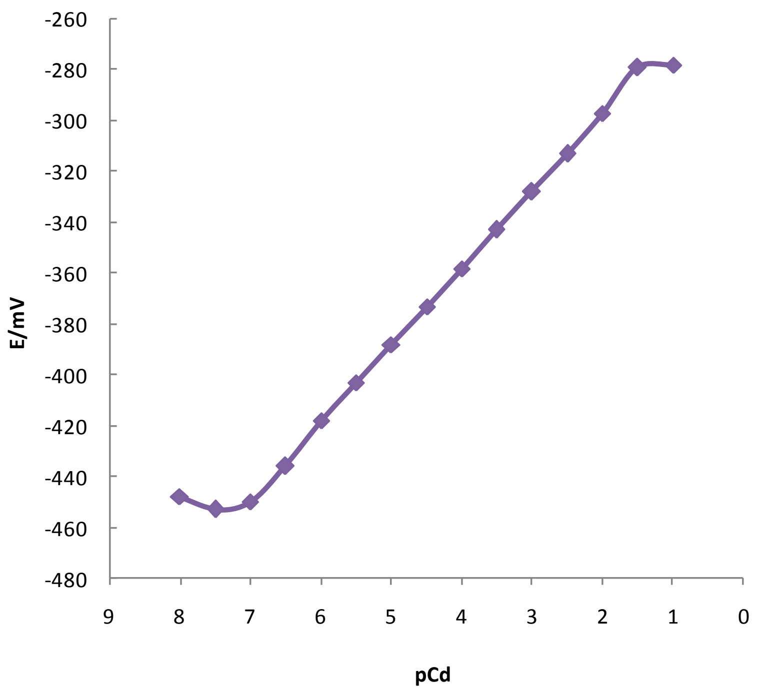

Figure 1. The calibration curve of the Cd(II) nano-composite carbon paste electrode based on IIP/MWCNT/NS/RTIL/Graphite

3.3. pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified Cd(II) sensor (no. 10), the potential was measured for a fixed concentration of Cd(II) ion solutions (10^{-3} mol L^{-1}) at different pH values. The pH was varied from (1-10) by addition of concentrated HNO_3 or NaOH. The changes in potential as a function of pH show that the response of the sensor is independent of pH in the range from 3.5-8.0. In addition, there is no visible interference from H^+ or OH^- in this pH range. Fluctuations at pH greater than 8.0 might be due to the formation of Cd(II) hydroxy complexes and the fluctuations at pH values lower than 3.5 were attributed to the protonation of IIP active sites in the carbon paste.

3.4. Response time

Response time is an important factor for any sensor. For electrochemical sensors, this parameter 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.

Experimental conditions such as stirring or the 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 performing the experiment measurement, any previous usage or preconditioning of the electrode, and the testing temperature can all affect the experimental response time of a sensor [34-40]. For the proposed modified cadmium sensor, the response time was less than 10 s in the concentrated solution (10^{-3}-10^{-2} M) and about 20 s in diluted solutions (10^{-7}-10^{-4} M).

3.5. Selectivity

Selectivity is the most important characteristic of any sensor, and describes an ion selective electrode's specificity toward the target ion in the presence of interfering ions, the potentiometric selectivity coefficients of the proposed nano-composite carbon paste electrode were evaluated by matched potential method (MPM) [41-46], and the results are depicted in Table 2. Concentration of the reference solution of Cd(II) ion was 1.0×10^{-7} mol L^{-1} and the concentration of interfering ions was between 1×10^{-6} to 1.0×10^{-1} mol L^{-1}.

Table 2. The selectivity coefficients of various interfering cations for electrode

Cation	Selectivity Coefficients
Na^+	$<10^{-4}$
K^+	$<10^{-4}$
Mg^{2+}	$<10^{-4}$
Ca^{2+}	$<10^{-4}$
Cu^{2+}	1.3×10^{-4}
Zn^{2+}	1.5×10^{-4}
Co^{2+}	2.1×10^{-4}
Hg^{2+}	3.2×10^{-4}
Pb^{2+}	2.3×10^{-4}
Ag^+	1.7×10^{-4}

3.6. Lifetime

The average lifetime for most ion selective sensors ranges from 4–10 weeks. After this time the slope of the sensor decreases, and the detection limit increases. The lifetime of the proposed nano-composite Cd(II) sensor was evaluated for a period of 12 weeks, during which the sensor was used two hours per day.

The obtained results showed that the proposed sensors can be used for at least 8 weeks. After this time, a slight gradual decrease in the slope from 29.2 to 19.4 mV per decade is observed, as an increase in the detection limit from 1.0×10^{-7} mol L^{-1} to 6.7×10^{-5} mol L^{-1} (Table 3). It is well understood that the loss of sensing material is the primary reason for limited lifetimes of carbon paste electrode.

Table 3. Lifetime of cadmium nano-composite carbon paste electrode

Week	Slope (mV decade^{-1})	Detection Limit (mol L^{-1})
1	29.2±0.3	1.0×10^{-7}
2	29.0±0.4	1.0×10^{-7}
3	28.8±0.3	2.5×10^{-7}
4	28.2±0.4	3.2×10^{-7}
5	28.2±0.3	4.0×10^{-7}
6	28.2±0.2	4.7×10^{-7}
7	27.7±0.3	5.9×10^{-7}
8	27.5±0.4	8.3×10^{-7}
9	26.2±0.3	1.0×10^{-6}
10	26.2±0.4	4.4×10^{-6}
11	24.6±0.3	1.0×10^{-7}
12	19.4±0.5	6.7×10^{-5}

3.7. Analytical application

The proposed nano-composite based sensor worked well under laboratory conditions. To assess the applicability of the proposed sensor to real samples, Cd(II) amounts of some industrial wastewater samples were analyzed. The samples were collected and acidify with HNO_3. Each sample was analyzed three times using the proposed cadmium sensor by calibration method. The samples also analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) as a reference method. The results are given in Table 4, which shows that the amount of cadmium recovered with the help of the sensor are in good agreement with reference method.

Table 4. Results of cadmium analysis in waste water samples

Sample	Nano-composite Sensor	ICP-AES
1	11.5±1.0 mg mL^{-1}	11.3±0.4 mg mL^{-1}
2	11.3±0.8 mg mL^{-1}	11.0±0.3 mg mL^{-1}
3	11.7±1.2 mg mL^{-1}	11.4±0.3 mg mL^{-1}

4. CONCLUSION

A cadmium selective carbon paste electrode based on a novel bio-mimetic recognition element is constructed. Ion imprinted polymer (IIP) as a sensing element, multi-walled carbon nanotube (MWCNT), nanosilica (NS), graphite powder, and room temperature ionic liquid (RTIL) were formed the carbon paste. The best results were obtained from the nano-composite sensor with the electrode composition of 5% MWCNT, 1% NS, 20% IIP, 20% RTIL, and 54% graphite powder. The nano-composite sensor shows a Nernstian response (29.2±0.3 mV decade^{-1}) in the range of 1.0×10^{-7}-1.0×10^{-2} M with detection limit of 1.0×10^{-7} M. The response of the sensor is independent of pH in the range of 3.5-8.0. The nano-composite based Cd(II) sensor displayed very good selectivity, response time, and specially, lifetime.

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