# Bio-Mimetic Ion Imprinted Polymer Based Potentiometric Mercury Sensor Composed of Nano-Materials

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A mercury selective sensor based on a novel biomimetic recognition element and nano-composite carbon paste electrode is introduced. The artificial host was imprinted in vinyl pyridine based cross-linked polymer. The nano-composite paste were made of ion imprinted polymer (IIP) as a sensing element, multi-walled carbon nanotube (MWCNT), nanosilica (NS), graphite powder, and room temperature ionic liquid (RTIL). The best results were obtained from the nano-composite sensor with the electrode composition of 5% MWCNT, 1% NS, 15% IIP, 10% RTIL, and 69% graphite powder. The proposed sensor shows a Nernstian response ($31.1 \pm 0.2$ mV decade$^{-1}$) in the range of $1.0 \times 10^{-7}$-$1.0 \times 10^{-2}$ M with detection limit of $1.0 \times 10^{-7}$ M. The response of the sensor is independent of pH in the range of 3.5-9.0. The nano-composite based Hg(II) sensor displayed very good selectivity, response time, and specially, lifetime.

## 1. INTRODUCTION

Mercury is a toxic element that affects the biological system. Mercury and its derivatives tend to bio-accumulate in the body which causes symptoms such as weakness, sleeplessness, paranoia, excessive salivation, skin itching and swelling, fever, memory loss, elevated blood pressure, tremors, gingivitis, excitability etc. Mercury poisoning can result from inhaling its vapor, its ingestion, injection or absorption through the skin and does most of the damage to the neurologic, gastrointestinal, and renal systems [1-3]. Mercury and its derivatives are found as industrial waste because of its growing area in production of some batteries, thermometers, cameras, cathode tubes, medical laboratory

chemicals, and have been used as a catalyst in production of urethane polymers for plastics, a cathode in electronic production of chlorine, mercury vapor lamps and barometers. Hence, monitoring mercury levels in our environments is important.

Common instrumental methods for mercury analysis are complexometry, spectrophotometry, flameless or cold-vapour atomic absorption spectrometry, inductively coupled plasma (ICP), fluorimetry, and X-ray fluorescence [4-7]. These methods involve expensive instrumentation and sample pretreatment, which is time consuming and inconvenient. Potentiometric detection based on ion-selective electrodes (ISEs), offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost [8-18].

Thus, the development of a selective sensor for mercury(II) has been a subject of investigation to analytical chemists. Several organic and inorganic compounds have been tested as an ionophore in producing ISEs. Most of the previously reported potentiometric method for determination of Hg(II) were based on using an organic compound as an ion carrier [19-22].

Those ISEs have a short lifetime, and interfered by a number of metal ions such as silver, iron, and cadmium ions. However, here, a new synthesized ion imprinted polymer (IIP) is introduced as a very selective carrier for Hg(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) [23-27].

## 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 $Hg^{2+}$ 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 $Hg^{2+}$ ion solution | Ag/AgCl–KCl (satd.)
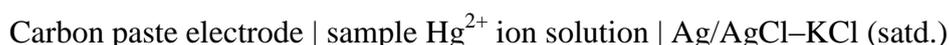
## 2.2. Reagents and materials

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 Hg(II) imprinted polymer, 1 mmol Hg(NO$_3$)$_2$ were dissolved in the 20 mL of dimethyl sulfoxide (DMSO) and then 4 mmol 4-vinyl pyridine was added to the solution. The solution was stirred for 3 min in order to complete the complexation process. Finally 0.15 g initiator (2,2′-(2-methyl propionitrile) ) and cross-linker of divinyl benzene (DVB) ,dissolved in 3 mL DMSO, was mixed with the previous solution and followed by purging with N$_2$ gas for 10 min. The polymerization was performed in the water bath in 70 °C for 24 h. The resulted polymer was grounded well in a mechanical mortar. The particles were firstly washed with ethanol and then washed with 0.5 mol L$^{-1}$ HCl solution, serially. Finally, the particles were washed with distilled water and dried at 60 °C. The non-imprinted polymer (NIP) that did not contain Hg(II) was prepared simultaneously using the same protocol [28].

## 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 mercury(II) solution [29-35].

## 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.  2) shows a sub-Nernstian slope of 23.7 mV per decade. However, the electrode composed of 10% paraffin oil, 15% IIP, 69% graphite powder 1% nano-silica and 5% MWCNTs (no. 10) was found to be optimal for erythromycin 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. 6), the response of the CPE was very low (slope of 5.5±0.6

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 [36,37]. 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 $Hg^{2+}$ ion (which is a rather high charge density cation) from the solution into the surface of CPE.

**Table 1.** The optimization of the Hg(II) carbon paste sensor

| No. | Graphite | IIP | Paraffin | RTIL | MWCNT | NS | Slope (mV decade$^{-1}$) | Linear Range (M) |
|-----|----------|-----|----------|------|-------|----|--------------------------|------------------|
| 1 | 80 | 10 | 10 | - | - | - | 21.2±0.6 | $1.0\times10^{-2}$-$1.0\times10^{-4}$ |
| 2 | 75 | 15 | 10 | - | - | - | 23.7±0.5 | $1.0\times10^{-2}$-$1.0\times10^{-5}$ |
| 3 | 70 | 20 | 10 | - | - | - | 23.2±0.5 | $1.0\times10^{-2}$-$1.0\times10^{-5}$ |
| 4 | 75 | 15 | - | 10 | - | - | 27.5±0.3 | $1.0\times10^{-2}$-$1.0\times10^{-6}$ |
| 5 | 70 | 15 | - | 15 | - | - | 27.1±0.5 | $1.0\times10^{-2}$-$3.0\times10^{-6}$ |
| 6 | 90 | - | - | 10 | - | - | 5.5±0.6 | $5.0\times10^{-3}$-$5.0\times10^{-4}$ |
| 7 | 72 | 15 | - | 10 | 3 | - | 28.7±0.4 | $5.0\times10^{-3}$-$8.0\times10^{-7}$ |
| 8 | 70 | 15 | - | 10 | 5 | - | 30.1±0.4 | $1.0\times10^{-2}$-$5.0\times10^{-7}$ |
| 9 | 68 | 15 | - | 10 | 7 | - | 29.1±0.4 | $5.0\times10^{-3}$-$5.0\times10^{-7}$ |
| 10 | 69 | 15 | - | 10 | 5 | 1 | 31.2±0.3 | $1.0\times10^{-2}$-$1.0\times10^{-7}$ |
| 11 | 67 | 15 | - | 10 | 5 | 3 | 29.8±0.5 | $1.0\times10^{-2}$-$5.0\times10^{-7}$ |

*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 $Hg^{2+}$ carbon paste electrode (no. 10) was tested across $Hg^{2+}$ 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 $1.0\times10^{-7}$ to $1.0\times10^{-2}$ 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 $1.0\times10^{-7}$ mol L$^{-1}$.
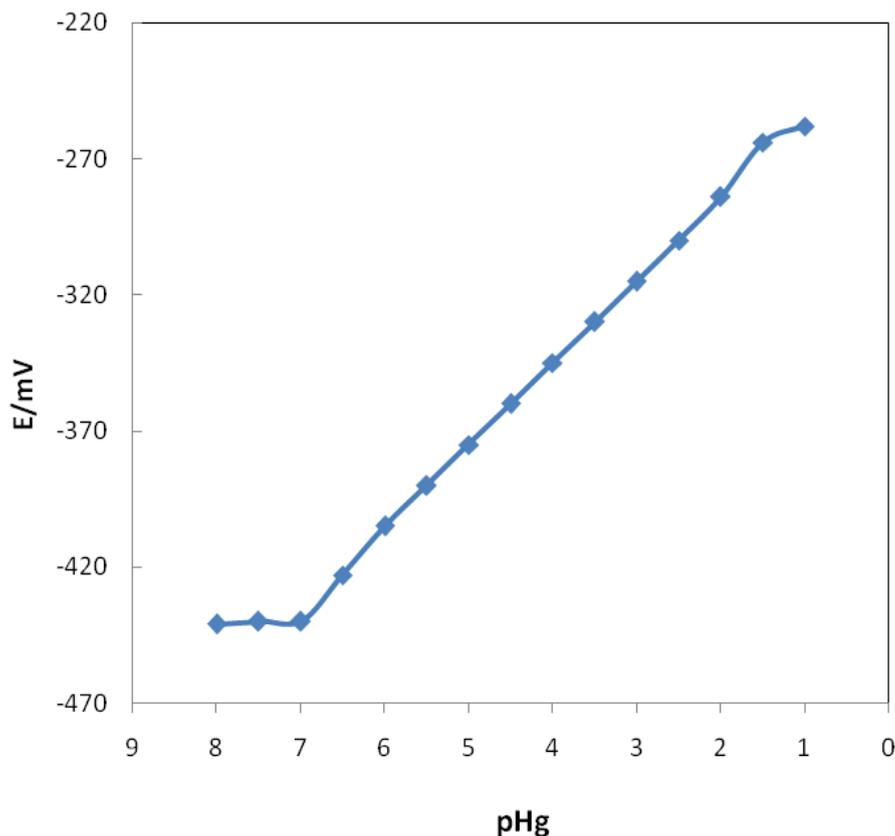
**Figure 1.** The calibration curve of the $Hg^{2+}$ nano-composite carbon paste electrode based on IIP/MWCNT/NS/RTIL/Graphite

*3.3. pH effect on the electrode response*

In order to study the effect of pH on the response of the optimal modified $Hg^{2+}$ sensor (no. 10), the potential was measured for a fixed concentration of $Hg^{2+}$ 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 2.0-4.0. In addition, there is no visible interference from $H^+$ or $OH^-$ in this pH range. Fluctuations at pH greater than 4.0 might be due to the formation of $Hg^{2+}$ hydroxy complexes and the fluctuations at pH values lower than 2.0 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 [38-43]. For the proposed modified mercury sensor, the response time was less than 15 s in the concentrated solution ($10^{-3}$-$10^{-2}$ M) and about 25 s in diluted solutions ($10^{-7}$-$10^{-4}$ M).

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

| Cation | Selectivity Coefficients |
|--------|--------------------------|
| $Na^+$ | $<10^{-4}$ |
| $K^+$ | $<10^{-4}$ |
| $Mg^{2+}$ | $<10^{-4}$ |
| $Ca^{2+}$ | $<10^{-4}$ |
| $Cu^{2+}$ | $2.5\times10^{-4}$ |
| $Zn^{2+}$ | $3.7\times10^{-4}$ |
| $Co^{2+}$ | $1.2\times10^{-4}$ |
| $Cd^{2+}$ | $5.7\times10^{-4}$ |
| $Pb^{2+}$ | $3.5\times10^{-4}$ |
| $Ag^+$ | $1.5\times10^{-4}$ |

*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) [44-46], and the results are depicted in Table 2. Concentration of the reference solution of $Hg^{2+}$ ion was $1.0\times10^{-7}$ mol $L^{-1}$ and the concentration of interfering ions was between $1\times10^{-6}$ to $1.0\times10^{-1}$ mol $L^{-1}$.

*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 $Hg^{2+}$ 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 9 weeks. After this time, a slight gradual decrease in the slope from 31.2 to 19.3 mV per decade is observed, as an increase in the detection limit from $1.0\times10^{-7}$ mol $L^{-1}$ to $6.3\times10^{-5}$ 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 mercury nano-composite carbon paste electrode

| Week | Slope mV per decade | Detection Limit (mol L$^{-1}$) |
|------|---------------------|-------------------------------|
| 1 | 31.2±0.3 | $1.0\times10^{-7}$ |
| 2 | 31.0±0.4 | $1.0\times10^{-7}$ |
| 3 | 30.8±0.3 | $2.5\times10^{-7}$ |
| 4 | 30.2±0.4 | $3.2\times10^{-7}$ |
| 5 | 31.2±0.3 | $4.0\times10^{-7}$ |
| 6 | 31.2±0.2 | $4.7\times10^{-7}$ |
| 7 | 29.9±0.3 | $5.9\times10^{-7}$ |
| 8 | 29.6±0.4 | $8.3\times10^{-7}$ |
| 9 | 29.1±0.3 | $1.0\times10^{-6}$ |
| 10 | 27.2±0.4 | $4.4\times10^{-6}$ |
| 11 | 24.6±0.3 | $1.0\times10^{-7}$ |
| 12 | 19.3±0.5 | $6.3\times10^{-5}$ |

*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, $Hg^{2+}$ 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 mercury 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 mercury recovered with the help of the sensor are in good agreement with reference method.

**Table 4.** Results of mercury analysis in waste water samples

| Sample | Nano-composite Sensor | ICP-AES |
|--------|-----------------------|---------|
| 1 | 5.6±1.2×10$^{-6}$ mol L$^{-1}$ | 5.3±0.3×10$^{-6}$ mol L$^{-1}$ |
| 2 | 7.3±0.8×10$^{-6}$ mol L$^{-1}$ | 7.0±0.4×10$^{-6}$ mol L$^{-1}$ |
| 3 | 6.1±1.3×10$^{-6}$ mol L$^{-1}$ | 5.8±0.5×10$^{-6}$ mol L$^{-1}$ |

# 4. CONCLUSION

A mercury selective carbon paste electrode based on a novel biomimetic 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, 15% IIP, 10% RTIL, and 69% graphite powder. The nano-

composite sensor shows a Nernstian response ($31.1\pm0.2$ mV decade$^{-1}$) in the range of $1.0\times10^{-7}$-$1.0\times10^{-2}$ M with detection limit of $1.0\times10^{-7}$ M. The response of the sensor is independent of pH in the range of 3.5-9.0. The nano-composite based Hg(II) sensor displayed very good selectivity, response time, and specially, lifetime.

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