

Chloramphenicol Biomimetic Molecular Imprinted Polymer Used as a Sensing Element in Nano-Composite Carbon Paste Potentiometric Sensor

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A Chloramphenicol selective nano-composite carbon paste sensor based on a molecular imprinted polymer (MIP) as a sensing element is made. The artificial host for chloramphenicol (CAP) was imprinted based cross-linked polymer. Methacrylic acid (MAA) was used as a functional monomer and chloroform was used as polymerization solvent. Then, nano-composite paste were made of MIP as a sensing element, multi-walled carbon nanotube (MWCNT), nanosilica (NS), graphite powder, and room temperature ionic liquid (RTIL) as binder. The best results were obtained by the nano-composite sensor having composition of 5% MWCNT, 1% NS, 20% CAP-MIP, 20% RTIL, and 54% graphite powder. The proposed sensor shows a Nernstian response (59.1 ± 0.4 mV decade⁻¹) in the range of 1.0×10^{-6} - 1.0×10^{-2} mol L⁻¹. The nano-composite carbon paste electrode showed very good selectivity, fast response time, and long lifetime. It was successfully applied in analysis of Chloramphenicol in pharmaceutical formulation.

Keywords: Molecular Imprinted Polymer (MIP), Chloramphenicol, Sensor, Potentiometry, Nanosilica (NS), Multi-walled carbon nanotube (MWCNT), Room Temperature Ionic Liquid

1. INTRODUCTION

Chloramphenicol (CAP), Fig. 1, is an efficient antibiotic with broad spectrum activity which is used in both human, veterinary medicine and now produced by chemical synthesis. Also its use was extended for the treatment of typhoid fever, meningitis, cholera and ricketts diseases. However, side effects of CAP, such as aplastic anemia (a rare but fatal blood disorder), had been demonstrated in humans [1]. In view of the toxic effects, the use of CAP was banned in food-producing animals. A

minimum required performance limit (MRPL) for CAP determination was recently set by the EU at $0.3 \mu\text{g kg}^{-1}$ in all food of animal origin [2]. For these reasons, sensitive detection techniques are required for a strict control of this compound.

Currently used methods for the determination of CAP include microbiological methods [3], immunoassays [4], gas chromatography–mass spectrometry (MS) [5], sensors [6], and liquid chromatography (LC)–MS/MS [7].

These methods are very accurate and precise for analysis. However, fast, simple and inexpensive measurement of this compound is of great importance in the therapeutic applications, toxicological studies and especially in pharmaceutical factories or food industries.

Various electrochemical method have been recently used for drug monitoring [8-10], but potentiometric detection based on selective electrodes, 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 [11-18]. These electrodes are widely used in different applications now days [19-31]. The most important part of this kind of electrodes is finding a suitable sensing element. Among the existing techniques, molecularly imprinted polymers (MIPs) appear as excellent candidates to get done such requirements, because of the possibility of synthesizing polymers with a predetermined selectivity for a particular analyte. Biological recognition materials such as antibodies, enzymes and aptamers have been used as specific receptors for detection of a target molecule in a wide variety of sensors or biosensors. However, they have many difficulties for their practical uses such as lack of stability, reusability, cost and not easy to obtain. Besides, MIPs can behave specifically, and mimic bio-receptors; thus, they are called “biomimetic recognition elements”.

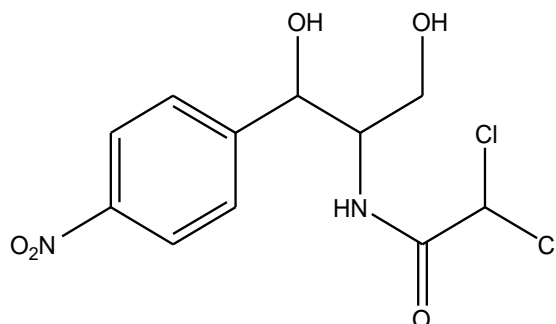


Figure 1. Chemical structure of Chloramphenicol

Molecular imprinting polymer (MIP) is gained by arranging functional monomers around a template compound and then fixing the monomers in this spatial arrangement with a cross-linker [32]. In the last years, MIPs were extensively used for the selective enhancement and pretreatment of target compounds existing in a complex matrix due to they are reusable and exhibit high stability. A technique for producing specific recognition sites in synthetic polymers is called molecular imprinting that has achieved wide acceptance [33]. The template molecule (target or print molecule) is then

removed to produce a polymer with molecular recognition sites, which are able to selectively rebind the template and analyte with similar structures [34]. They are low-cost to produce, reusable, appropriate to a number of different operating conditions, and display high mechanical and chemical stability [35].

Potentiometric sensors based on carbon paste are the best choice when the recognition element is a MIP. Carbon paste electrodes provide a renewable surface, stable response and low ohmic resistance and also can be easily modified by nano-materials [36-41]. Here, a molecular imprinted polymer (MIP) for CAP was synthesized and used as a selective sensing element in construction of CAP nano-composite carbon paste electrode.

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell in which the potentiometry was carried out into contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode and nano-composite carbon paste electrode as an indicator electrode. Both electrodes were connected to a mili-voltmeter (± 0.1).

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



2.2. Reagents

The multi-walled 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 ($[\text{bmim}]\text{BF}_4$) and chloride and nitrate salts of the cations were all purchased from Merck Co. Nanosilica is Wacker HDK® H20. Chloramphenicol Molecular imprinted polymer was synthesized according to the previously reported procedure [9]. CAP as the template and methacrylic acid (MAA) as a functional monomer was used. The polymerization solvent was chloroform. To synthesis a molecular imprinted polymer, 1 mmol of template molecule (CAP), 5 mmol methacrylic acid and 50 mL of dry chloroform were placed into a 100 mL round-bottomed flask and the mixture was left in contact for 10 min. Then, 30 mmol EDMA and 0.2 mmol AIBN were added. The flask was sealed and the mixture was purged with nitrogen gas for 15 min. The polymerization of the mixture was carried out in a water bath at 60 $^\circ\text{C}$ for 24 h. The final polymer was powdered and then the template was removed by soxhlet extraction with methanol for 48 h. In order to obtain the finer and smaller MIP particles, the obtained powder was sequentially immersed three times in acetonitrile and the supernatant portions were collected for final use.

2.3. Preparation of nanocomposite-CPE

The procedure for nanocomposite-CPE preparation was as follows: various amounts of CAP-MIP 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 [36-41]. The electrode was finally conditioned for about 40 h by soaking it in a 1.0×10^{-3} M of CAP solution.

3. RESULTS AND DISCUSSION

3.1. Carbon paste composition

Paste composition effect on potential responses of the electrodes was tested. The operating characteristics of a carbon paste sensor can be significantly modified by changing the relative proportions of the paste components. Thus, modified and unmodified carbon pastes were prepared with a variety of compositions. The results are given in Table 1. The unmodified CPE with optimized composition (electrode no. 3) shows a sub-Nernstian slope of 40.7 mV per decade.

From Table 1, it was obvious that in the absence of CAP-MIP and presence of other components (no. 12), the response of the CPE was very low (slope of 6.5 ± 0.7 mV per decade).

Table 1. Optimization of the carbon paste ingredients

No.	Graphite	CAP - MIP	Paraffin	RTIL	MWCNT	NS	Slope (mV decade ⁻¹)	Linear Range (mol L ⁻¹)	Response Time
1	75	10	15	-	-	-	22.6±0.6	5.0×10^{-4} - 5.0×10^{-3}	2.4 min
2	70	15	15	-	-	-	29.8±0.5	1.0×10^{-4} - 5.0×10^{-3}	1.2 min
3	65	20	15	-	-	-	40.7±0.4	5.0×10^{-5} - 7.0×10^{-3}	50 s
3	60	25	15	-	-	-	38.9±0.5	6.0×10^{-5} - 8.0×10^{-3}	57 s
4	65	20	-	15	-	-	49.7±0.4	7.0×10^{-6} - 1.0×10^{-2}	42 s
5	60	20	-	20	-	-	51.2±0.3	5.0×10^{-6} - 1.0×10^{-2}	37 s
6	55	20	-	25	-	-	50.4±0.5	5.0×10^{-6} - 1.0×10^{-2}	39 s
7	57	20	-	20	3	-	54.7±0.4	3.0×10^{-6} - 1.0×10^{-2}	29 s
8	55	20	-	20	5	-	58.2±0.3	2.0×10^{-6} - 1.0×10^{-2}	24 s
9	53	20	-	20	7	-	53.5±0.5	3.0×10^{-6} - 8.0×10^{-3}	32 s
10	54	20	-	20	5	1	59.1±0.4	1.0×10^{-6} - 1.0×10^{-2}	18 s
11	52	20	-	20	5	3	55.4±0.7	5.0×10^{-6} - 5.0×10^{-3}	42 s
12	74	-	-	20	5	1	6.5±0.7	5.0×10^{-4} - 5.0×10^{-3}	3 min

MWCNTs in the carbon paste improve 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. 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 [38]. As it can be seen from Table 1, using [bmim]BF₄ instead of paraffin oil in the carbon paste composition yields more efficient extraction of CAP from the solution into the surface of CPE.

Finally, the electrode composed of 20% IL, 20% CAP-MIP, 54% graphite powder, 1% nano-silica and 5% MWCNTs (no. 10) was found to be optimal for CAP carbon paste electrode. This composition was selected for further examination.

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.

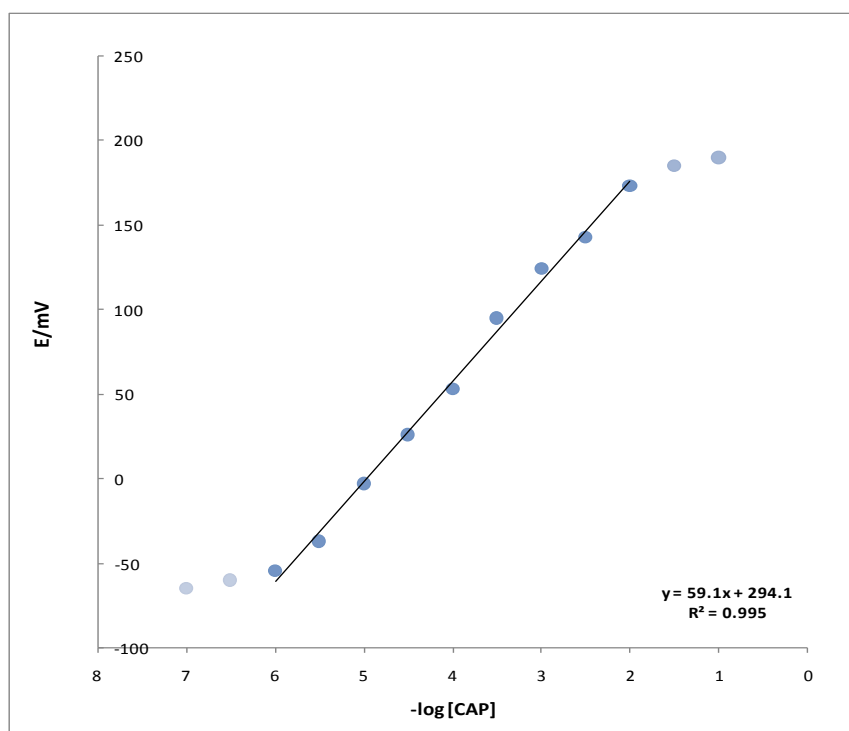


Figure 2. The calibration curve of the modified CPE (no. 10)

The response of the optimal modified CAP carbon paste electrode (no. 10) was tested across CAP concentration in the range of 1.0×10^{-7} - 1.0×10^{-1} mol L⁻¹. The applicable range of the proposed sensor extends from 1.0×10^{-6} to 1.0×10^{-2} mol L⁻¹ as seen in Fig. 2.

By extrapolating of the linear portion of the calibration curve, the detection limit of an ion selective electrode can be calculated [43-52]. In this work, the detection limit of the proposed membrane sensor was 1.0×10^{-6} mol L⁻¹.

3.3. pH effect on the electrode response

In order to study the effect of pH on the response of the nano-composition CPE (no. 10), the potential was measured for a fixed concentration of CAP solutions (10^{-3} mol L⁻¹) at different pH values. The pH was varied from (2-10) by addition of concentrated HNO₃ 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 3.5-5.0. In addition, there is no visible interference from H⁺ or OH⁻ in this pH range. Fluctuations at pH greater than 5.0 might be due to the remove of the charges on CAP compound and the fluctuations at pH values lower than 3.5 were attributed to the protonation of MIP 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 [50-57].

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. For the proposed modified mercury sensor, the response time was about 18 s in the whole concentrated solution.

3.5. Selectivity

Selectivity is the most important characteristic of any sensor, and describes an ion selective electrode's specificity toward the target species in the presence of interfering species, the potentiometric selectivity coefficients of the proposed nano-composite carbon paste electrode were evaluated by matched potential method (MPM) [58-62], and the results are depicted in Table 2. Concentration of the reference solution of CAP was 1.0×10^{-6} mol L⁻¹ and the concentration of interfering ions was between 1×10^{-6} to 1.0×10^{-2} mol L⁻¹.

Table 2. The selectivity coefficients of various interfering cations for nano-composite CPE

Species	Selectivity Coefficients	Species	Selectivity Coefficients
Na ⁺	<10 ⁻⁴	Cl ⁻	<10 ⁻⁴
K ⁺	<10 ⁻⁴	CO ₃ ⁻	<10 ⁻⁴
Mg ²⁺	1.2×10 ⁻⁴	Co ²⁺	1.6×10 ⁻⁴
Ca ²⁺	<10 ⁻⁴	Glucose	1.5×10 ⁻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 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 gradual decrease in the slope from 59.1 to 44.3 mV per decade is observed, as an increase in the detection limit from 1.0×10⁻⁶ mol L⁻¹ to 4.7×10⁻⁵ 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 mercury nano-composite carbon paste electrode

Week	Slope mV per decade	Detection Limit (mol L ⁻¹)
1	59.1±0.4	1.0×10 ⁻⁶
2	58.7±0.4	2.0×10 ⁻⁶
3	58.3±0.4	3.5×10 ⁻⁶
4	58.1±0.3	4.3×10 ⁻⁶
5	57.8±0.4	4.8×10 ⁻⁶
6	57.4±0.3	5.1×10 ⁻⁶
7	57.3±0.3	5.3×10 ⁻⁶
8	57.0±0.5	5.5×10 ⁻⁶
9	56.8±0.3	6.2×10 ⁻⁶
10	44.3±0.6	4.7×10 ⁻⁵
11	34.9±0.5	2.0×10 ⁻⁴
12	25.3±0.4	5.7×10 ⁻⁴

3.7. Analytical application

Linearity, limit of detection, recovery test, selectivity, precision, accuracy, and

ruggedness/robustness were the parameters used for the method validation.

As mentioned before, the sensors were measured between 1×10^{-6} and 1×10^{-2} mol L⁻¹. The calculated detection limit of the sensors was 1.0×10^{-6} mol L⁻¹ (0.4 µg/mL).

3.7.1. Recovery Test from Tablet

The proposed sensor was evaluated by measuring the drug concentration in some pharmaceutical formulations (Table 4).

Table 4. Potentiometric determination of CAP in pharmaceutical formulations

Sample	Labeled amount (mg/tab.)	Found by proposed sensor* (mg/tab.)
Tablet 1	250	254.8±1.3
Tablet 2	250	244.9±1.2
Tablet 3	250	258.5±1.4

* The results are based on five replicate measurements

The drug concentration was determined with the calibration method. The results are in good agreement with the labeled amounts. The corresponding recovery percentage value varied from 97.9-103.4%.

3.7.3. Precision and accuracy

For repeatability monitoring, 3 replicate standard samples of 4, 40, 400 µg/mL were measured. The mean concentrations were 4.3±0.3, 46.3±2.1, 412.6±6.2 µg/mL with respective RSD values of 5.4, 3.9, and 1.4%.

3.7.4. Ruggedness/Robustness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for CAP obtained by two analysts.

The RSD values for the intra- and inter-day assays in the cited formulations performed in the same laboratory by the two analysts did not exceed 4.3%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. CAP recovery percentages were good under most conditions, and not showing any significant change when the critical parameters were modified.

4. CONCLUSION

A CAP selective nano-composite carbon paste electrode based on a novel biomimetic recognition element is constructed. Molecular imprinted polymer (MIP) 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% CAP-MIP, 20% RTIL, and 54% graphite powder. The nano-composite sensor shows a Nernstian response (59.1 ± 0.4 mV decade⁻¹) in the range of 1.0×10^{-6} - 1.0×10^{-2} mol L⁻¹ with detection limit of 1.0×10^{-6} mol L⁻¹. The response of the sensor is independent of pH in the range of 3.5-5.0. The nano-composite sensor displayed very good selectivity, response time, and specially, lifetime.

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