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A Molecularly Imprinted Polymer (MIP)-based Biomimetic Potentiometric sensing device for the analysis of Clarithromycin

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Abstract- A molecular imprinted polymer (MIP)-based biomimetic sensing device was constructed for the analysis of clarithromycin (CM). The novel MIP was prepared using a methacrylic acid (MAA) (functional monomer) and Ethylene glycol dimethylacrylate (EGDMA) (cross-linker) and the target species (i.e.CM) as the template molecule. The resulting MIP had considerable adsorption capacity and excellent selectivity toward CM compound. After some experiments, optimum 1:6 mole ratio of template to MAA was selected for the synthesis of CM MIP. The non-covalent CM-MIP was used for the construction of a potentiometric sensor for CM. The proposed had selective and sensitive response to CM concentration in aqueous media. The electrode response had a Nernstian response of 50.8±1.0 mV decade−1from 1.0×10-6 to 5.0×10-3 M and had a detection limit as low as 8.0×10^{-7} M. The response time of the electrode was about 15 s, and it had a long-term stability of over 45 days. The sensor also proved applicable to the analysis of CM concentration in tablets with good sensitivity and accuracy.

Keywords- Clarithromycin, Sensor, Potentiometry, Molecularly imprinted polymer

1. INTRODUCTION

Ionic or molecular imprinting is a tool for preparing material for building recognition elements of sensing devices. The MIPs introduce high selectivity and sensitivity to the resulting sensors over rather wide concentration ranges [1-7]. A most applicable imprinting technology is molecularly imprinted polymers (MIP) using organic monomers. The imprinting procedure involves polymerizing a so-called functional monomer using a cross-linker in a mixture containing template species, and then removing the template to obtain the imprinted polymer. The empty sites of the imprinted polymers, have high affinities for the template species both due to the steric favorability and the arrangement of the functional groups present inside their structure .

As the name indicates, non-covalent MIPs are based on non-covalent interactions among the template and the monomer species in the course of synthesis. These materials have received a wide range of attention [8,9], especially in the development of the chemical sensors. Given that imprinted polymers function similar to antibodies they are also referred to as biomimetic molecules, in the area of designing selective and sensitive sensors. Some examples of electrochemical sensors based on imprinted polymers including impedance measurement [10], field effect transistor [11], capacitance [12], conductometric [13], amperometric [14,15] and voltammetric [16-21] methods .

Although the transduction of potentiometric signals are rather simple, there exist only few reports on the construction and application of MIP-based potentiometric sensors [22-28]. The existing reports are mostly based on dispersing MIP particles through a plasticized poly(vinyl chloride) (PVC) matrix.

On the other hand, clarithromycin (CM) (Fig. 1) is a very effective semi-synthetic macrolide antibiotic prescribed for a variety of gram-positive and -negative organisms. It also has the advantage of treating gastric ulcer in combination with other drugs [29].

The reports on the analysis of CM in biological samples range from using microbiological bioassays [30] HPLC with electrochemical detection and UV [31], mass-spectrometric analysis [32], fluorescence analysis after pre-column derivatization [33].

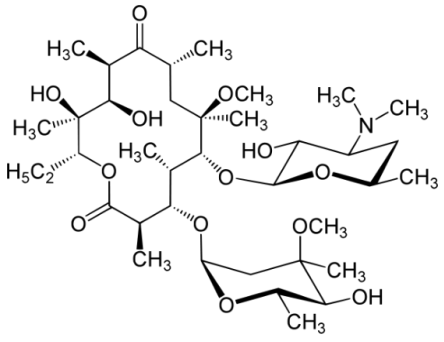

Fig. 1. Chemical structure of clarithromycin (CM)

In this study, a CM-MIP was prepared based on methacrylic acid (MAA) functional monomers. The polymer was then evaluated in terms of its physical and chemical characteristics, adsorption capability and selectivity, and then used to prepare potentiometric membrane sensors.

2. EXPERIMENTAL SECTION

2.1. Apparatus

A PerkinElmer Lambda 2 UV–Vis spectrophotometer was used for recording the quantitative and qualitative UV–Vis data. pH readings were run on a Metrohm pH-meter using a double junction glass electrode .

A potentiometric cell was build using the MIP-PVC sensors as the indicator electrode, and a double junction Ag/AgCl external reference electrode (Azar-Elelectrode Co., Iran). The indicator and reference electrodes were linked to a 250±0.1 mV pH/mV meter. The analytical cell assembly can be illustrated as below :

Ag-AgCl || 1.0×10^{-3} M CM | MIP-PVC membrane | sample ||Ag-AgCl, KC1 (satd.)

2.2. Chemicals

Reagent grade methacrylic acid (MAA), ethylene glycol dimethylacrylate (EGDMA), and 2,2-azobisisobutyronitrile (AIBN), dibutyl phthalate (DBP) and tetrahydrofuran (THF) were obtained from Merck . MAA was vacuum distilled prior to use. High-molecular weight PVC (Fluka) Except for MAA all reagents were used as received. Bulk CM and its tablets were the curtsey of a local pharmaceutical manufacturer (Tehran, Iran).

2.3. MIP synthesis

To prepare the MIP 1 mmol of CM, 6 mmol of methacrylic acid and 50 mL of dry chloroform were transferred to a 100 mL flask rested for about 1h before adding 30 mmol of EGDMA and 0.07 g of AIBN. Next the flask was then sealed and the reaction mixture was slowly purged with N_2 gas slowly for 1200 seconds. The reaction was performed by keeping the flask in a water bath at 60°C for 1 day, and the final product was separated and powdered. The template CM was eliminated through chloroform through soxhlet for 2 days. A sample of non-imprinted polymer (NIP), was prepared under similar conditions and used as control material.

2.4. Adsorption of CM by MIP

0.07 g of dried powdered polymer was added to 10 mL of a 1.0×10^{-3} M solution of CM. Then, the mixture was centrifuged by magnetic agitator for 40 min at 750 rpm. It was expected that the target molecules of solution would be adsorbed by molecularly imprinted polymer cavities. Afterward, the polymer composition was filtered and the remained solution was analyzed by spectrophotometer for indicating drug absorption. A stable peak at 283 nm was observed at the UV-Vis spectra of the CM solutions. Based on the absorption value and calibration curve, the molar concentration of CM was determined. In addition (adsorption) efficiency can be calculated using equation (1). The procedure described above, was repeated for NIPs as control.

$$\text{Adsorption efficiency} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

2.5. Binding capacity of CM MIP

A known amount of CM were dissolved in 10 mL of a phosphoric acid solution. Next 70 mg of the imprinted or non-imprinted (control) polymer were added to the solution and the mixture was stirred at 750 rpm for 40 min by magnetic agitator. Then the sample was centrifuged at 600 rpm for 600 seconds and the concentration of free substrate in the supernatant was analyzed by UV-Vis spectrophotometry.

Based on the changes in the concentration of CM before and after the adsorption phenomena and using equation (2) the binding capacity (Q) of the MIP was calculated. This equation (M and C (M) are the symbols for the initial and final concentrations of CM , and V (mL) and W (g) are the symbols for the solution volume and mass of the polymers.

$$Q = ((C_0 - C) \times V)/W \quad (2)$$

2.6. Standard Clarithromycin solutions

A 1.0×10^{-2} M CM solution was prepared and the rest of the solutions in the concentration rage of 1.0×10^{-6} to 1.0×10^{-2} M were formed by diluting various volumes thereof.

2.7. The PVC membrane electrodes

The PVC membrane sensors were formed by admixing PVC, plasticizer and MIP (1:6) in proportions of 8, 10 and 12% (w/w) using THF as the solvent. The resulting mixture was transferred to a 2 cm glass dish and the solvent was allowed to evaporate to form an oily mixture. Next the tip of a 3 mm (o.d.) plastic tube was inserted into the mixture for about 10

s, This way a thin (about 0.3 mm thick) transparent membrane was formed on the opening of the tube. The assembly was stored in ambient temperature for about 10 h to allow the membrane to dry, before the tube was filled with a 1.0×10^{-3} M solution of acidic clarithromycin (pH=3)). The final preparation step involved conditioning the electrodes through soaking them in an identical solution for one day [34-42].

2.8. Preparation of the tablet samples

10 tablets were carefully weighed, and powdered in a mortar and pestle. Next a weight equivalent to that of 1 tablet was transferred to a 100 mL A-grade volumetric flasks. To the flasks was then added 70 mL of 0.1 M hydrochloric acid. 5 samples were prepared through the same procedure, and all flasks were sonicated for around 1 hour. Then the flasks were filled with hydrochloric acid to the mark. Desired volumes of the solutions were next filtered using a 0.45µm milli-pore filter (Gelman Sciences, Rossdorf, Germany). Various standard samples were then obtained by further dilution of these sample with hydrochloric acid.

3. RESULTS AND DISCUSSION

3.1. Preparation and evaluation of the MIP

The CM MIP samples were prepared through precipitation polymerization. The mole ratio of CM to MAA in pre-polymerization mixtures is optimized and the related results has been shown in Table 1.

Table 1. Composition of the polymerization mixtures and absorption efficiency for MIPs and NIPs

Polymers	Ratio	Template (mmol)	MAA (mmol)	EGDMA (mmol)	AIBN (g)	Efficiency (%)
MIP1 NIP1	1:4	1 1	4 4	20 20	0.06 0.06	18.00 4.02
MIP2 NIP2	1:5	1 1	5 5	25 25	0.06 0.06	31.00 7.00
MIP3 NIP3	1:6	1 1	6 6	30 30	0.06 0.06	72.00 15.00
MIP4 NIP4	1:7	1 1	7 7	35 35	0.06 0.06	80.80 64.00

Based on the obtained results, MIP in comparison with NIP shows better adsorption of the target molecule. The optimized mole ratio of CM to MAA for the synthesis was selected 1:6. When the ratios of CM to MAA are 1:4 and 1:5, the absorption capacity is low due to low amount of the functional monomers and hence the binding sites. At a CM/MAA ratio of 1:7, excess of functional monomers lowers the selectivity by increasing the interactions among CM and MAA through more than one site leads to forming more than one type of complex and several sites in MIP so adsorption efficiency decreases.

3.2. Measurement of CM

Fig. 2a shows the spectra of CM in acidic solutions. A stable peak at 283 nm appears for CM solutions. This wavelength can be used to measure CM concentration. Fig. 2b illustrates the standard curve based on equation (3).

$$y = 580.97x + 0.0626 \quad (3)$$

In this equation y expresses the absorbance, x is the CM concentration in M, and the correlation coefficient is 0.993.

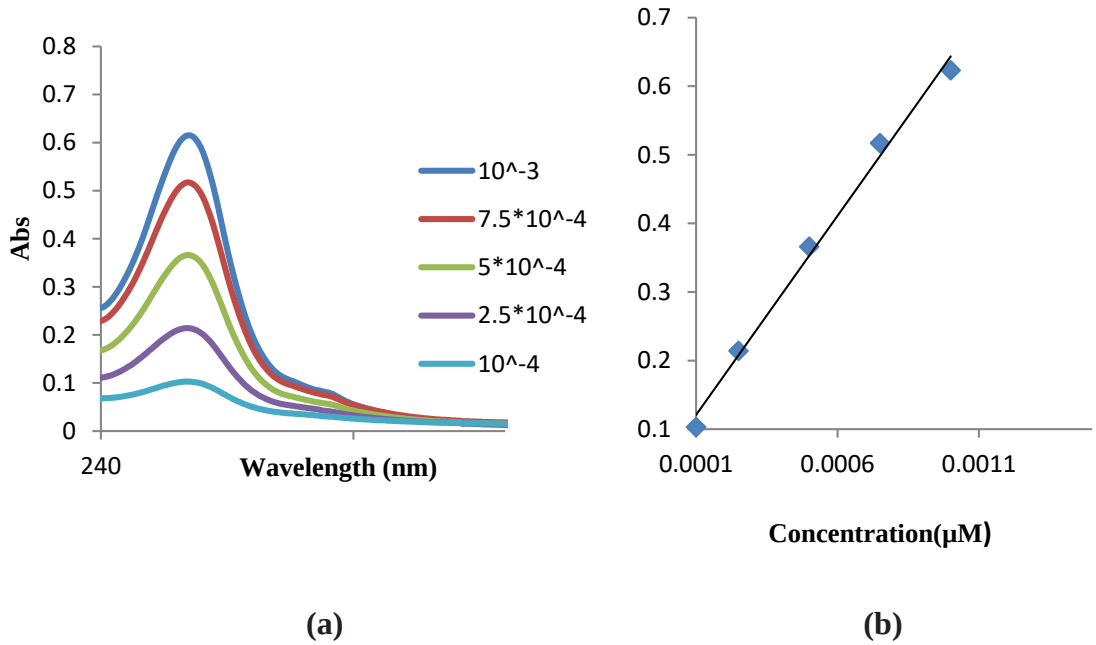

Fig. 2. (a**)** Absorption spectra of various CM concentrations (b) Calibration curve corresponded to the CM standard solutions absorptions at λ_{max} 283 nm

3.3. Kinetics evaluations

The kinetics of the adsorption phenomena occurring among the MIP and CM was studied through altering the contact time from 30 to 60 min. The CM concentration was kept at

1.0×10^{-3} M in the acidic solution. Next 70 mg of MIP was added to 10 mL of the solution, and the mixture was stirred at 30 rpm for half an hour under ambient conditions. Then the sample was centrifuged and 2 mL of the supernatant was studied through UV-Vis spectrophotometry. Fig. 3 shows the plots of adsorption dynamics of both the MIPs and control samples (NIPs), clearly indicating that CM binding is much higher with MIPs as opposed to the NIPs. Besides, adsorption of CM by MIP is much faster than NIP. The amount of binding capacity increases in the first 40 min rapidly. After this time, the amount of released CM is too low. This rather low value may be because of the CM adsorption on the polymer through weak interactions.

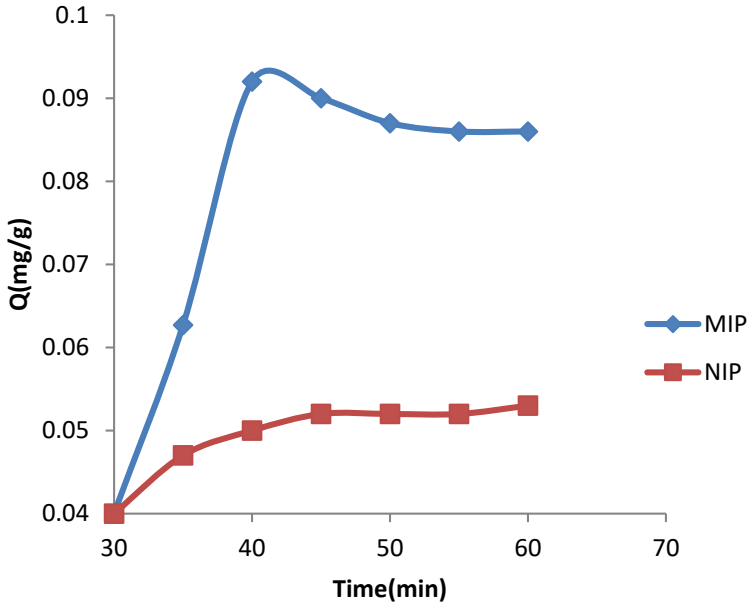

Fig. 3. Adsorption dynamic curves of the MIPs and NIPs

3.4. Adsorption isotherm of the imprinted polymer

The adsorption isotherm studies were used to evaluate the thermodynamics of adsorption phenomena. Plots were obtained at various CM concentrations (from 1.0×10^{-3} to 7.5×10^{-4} M) in 10 mL of acidic solutions using 70 mg of the MIP and NIP (in Table 1) for 40 min.

3.5. Sensor response characteristics

The application of MIP in the determination of pharmaceuticals has been subject of various research studies in recent years, yet this is, to the best of our knowledge, the first attempt to use an MIP-based PVC membrane electrode the analysis of CM. Initially, it was

discovered that the conditioned MIP-PVC membrane electrodes establish stable potentials in CM ion solutions and had remarkable selectivity as opposed to electrodes based on non-imprinted PVC membrane (Fig. 5).

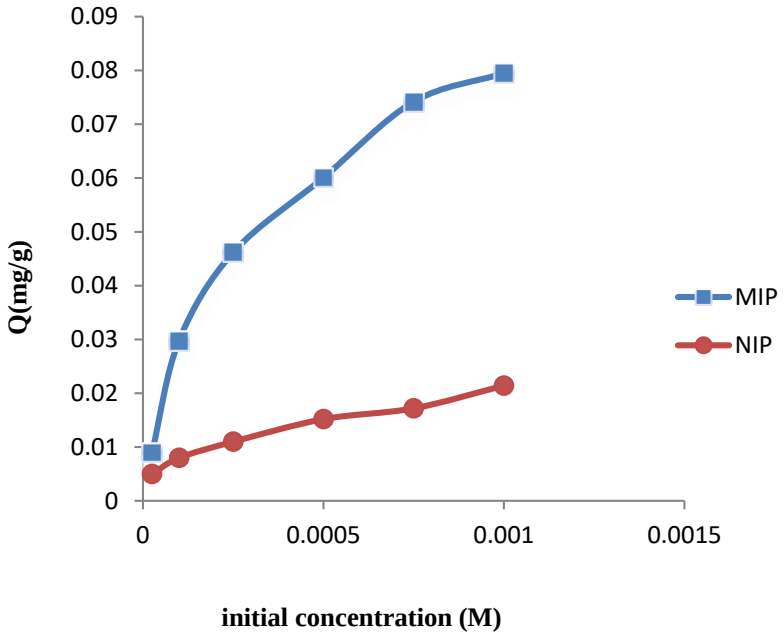

Fig. 4. Static equilibrium adsorption isotherm of MIPs and NIPs microspheres

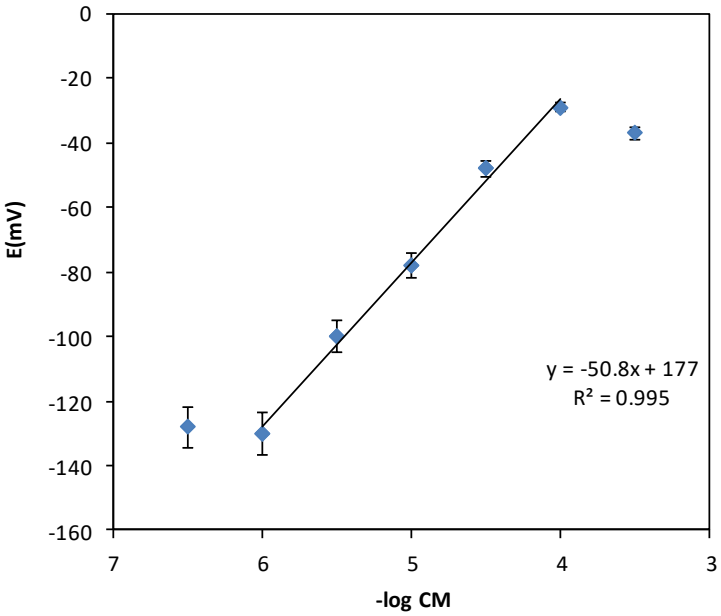

Fig. 5. Potentiometric response properties of PVC membrane electrodes, based on the MIP as modifier

This was attributed to the high selectivity of the MIP and the fast exchange kinetics of the CM-MIP complex. Consequently, changes in the membrane potential were concluded as being the result of host–guest complexation at the MIP membrane.

Table 2 shows the values of the slope, response linearity range and limit f detection of the developed sensor obtained from the potentiometric calibration curves recorded for an acidic solutions (pH=3.5). The data shows that an electrode with DBP /PVC/ Ion liquid/ MIP contents of 60%/30%/2%/10% produced the optimal response (a Nernstian slope of 50.8 mV over a CM concentration range of 1.0×10^{-6} M and 5.0×10^{-3} M).

Using room 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), which is a temperature ionic liquids (RTILs), as one of the ingredients of the liquid membrane sensor, its performance was improved due to the lowered Ohmic resistance of the polymeric membrane [34].

In the light of the results the composition of membrane no. 2 was chosen as the optimal value and applied in further studies. The value of LOD in the case of this electrode was 8.0×10^{-7} M. This value was obtained by extrapolating the linear sections of the calibration graph.

Table 2. Composition of the PVC membrane electrodes and their potentiometric response characteristics

No.	PVC	Plasticizer DBP	MIP/NIP	Ionic liquid	Slop MIP (mV /decade)	Slop NIP (mV /decade)	Linear rang (M)	LOD (M)
1	30	58	8	4	24.5±0.5	7.9±0.7	5.0×10^{-6}-5.0×10^{-3}	4.5×10^{-6}
2	30	55	10	5	50.8±0.3	14.5±0.6	1.0×10^{-6}-5.0×10^{-3}	8.0×10^{-7}
3	30	52	12	6	21.0±0.4	16.0±0.5	1.0×10^{-6}-5.0×10^{-3}	7.5×10^{-7}

3.5.1. Response time

Defined as the time required for an electrode to reach a potential of ±1 mV of the equilibrium value upon a 10 fold concentration change, the response time of the electrode was found to be ~15 s. The electrode reaction was found to be reversible, but the time required for the electrode to reach equilibrium potentials in high-to-low experiments was longer than that of the low-to-high sample concentration. This was attributed to the filling of the cavities of the imprinted polymer ingredient and the slow reversal of the phenomenon.

3.5.2. Effect of pH

The specific binding of CM to the active sites of the MIP is the results of the shape of the sites and the favorable orientation of the functional monomer (i.e. MAA which includes carboxyl functional groups). The carboxylic groups can lead to the formation of hydrogen bonds, as well as electrostatic force. Consequently solution pH has a key role on the response of the sensor and hence the pH values were adjusted for each and every study. Yet during the conditioning process the response was negligibly influenced changes of the pH in the range of 2.5 up to 4.5. Above this range, however, the binding interactions dropped.

3.5.3. Reusability and Life time

To study capability of the sensor to be reused , three electrodes, prepared exactly the same, were used for analysis of two standard samples having the concentrations of 1.0×10^{-5} M and 1.0×10^{-4} M [40-48]. All measurements were performed three times using each electrode. The measurements were repeated inter-day (five times in a day) and intra-day (within 7 days). RSD% for inter-day assay was less than 4.23% and in case of intra-day assay. After each use, the electrodes were washed with acidic solution of hydrochloric acid (0.01 M), then rinsed with distilled water and stored in ambient temperature. Before the next use, the electrode was placed in 0.001 M of CM solution for about 30 min. In such way, the proposed senor by calibration can be used frequently without any significant potential drift .

The lifetime of the sensor was also evaluated through frequently calibrating runs using three electrodes over a 10 week period. The electrodes was used 1 hour per day and then rinsed, dried and keep for the next usage. After conditioning, the sensors were calibrated once a week and the results showed no considerable performance changes for 42 days, indicating that the electrode lifetime extends this period. It is worthy to note that the data were recorded using electrodes without any surface renewal or treatments.

3.5.4. Method validation and Analysis of CM tablets

The procedure was applied to the determination of CM in tablets. The concentration of CM was analyzed through the standard addition technique. The corresponding relative standard error percentage value was less than 3.6%. The resulting data were checked with the labeled values on the tablet packages (Table 3). Linearity, detection limit, recovery, selectivity, precision, accuracy, and ruggedness/robustness of the electrodes were considered for validation. The information of the detection limit, and linearity ranges have already been discussed. For repeatability measurement, 5 replicate standard samples of CM (1.0×10^{-4} M) were analyzed. The RSD values by the proposed sensor was less than 3.7% .

Table 3. Potentiometric determination of CM in pharmaceutical formulation

Sample	**Labeled amount**	**Found by the electrode (n=3)**	**Relative Error%**
1	500 mg/tab	512.5±0.5 mg/tab	2.2%
2	250 mg/tab	259.0±0.1 mg/tab	3.6%

Table 4. Selectivity coefficients of various interfering compounds for CM sensors

Interfering ions	**Log K_{MPM}**
Na^+	-3.8
K^+	-3.6
Ca^{2+}	-3.7
Mg^{2+}	-3.6
NH_4^+	-3.5
CO_3^{2-}	-3.9
HPO_4^{2-}	-4.0
$H_2PO_4^-$	-4.1
Erythromycin	-2.7
Glucose	-4.4

In terms of ruggedness of the method intra- and inter-day assay results were compared. In both cases the RSD values obtained by two users during inter- and intra-day experiments in the same laboratory were not more than 4.6%. Further, the robustness of the sensor was evaluated through slightly changing parameters such as pH and laboratory temperature. The values obtained for CM recovery percentages were acceptable (RSD less than 3.3%) in most cases, and did not undergo considerable changes even when the critical parameters were altered. The selectivity, which is one of the most important parameter for characterization and validation of a sensor, describes as an ion-selectivity of the working electrode for the target species ion when interfering species are present. The potentiometric selectivity coefficients were calculated through the matched potential method (MPM) [49-52] and the results are presented in Table 4. It is evident that all selectivity coefficients are below than 10^{-4}, confirming the negligible effect of interferences in the readings performed using the electrode.

4. CONCLUSION

A novel clarithromycin imprinted polymer was prepared through polymerizing the monomers (MAA) and cross-linker (EGDMA) in the presence of CM as the template. The composition of CM to MAA was optimized, and the optimum molar ratio was 1:6. In the following, a potentiometric sensor for CM detection was made using the optimal MIP. Employing CM-MIP as the active material in a liquid membrane potentiometric sensor provides an efficient way for the CM assessment. The investigated potentiometric method was found to be simple, rapid, low cost and more selective than the complex instrumental methods.

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