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A Biomimetic Potentiometric Membrane Sensor using Molecularly Imprinted Nano-Polymer for Furosemide Drug Analysis

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Abstract- A potentiometric sensor was made using a non-covalent imprinted nano-polymer for analysis of furosemide pharmaceutical compound. Furosemide is a diuretic drug which is also categorized among the doping agent. The nano-molecularly imprinted polymer (nano-MIP) was prepared through precipitation polymerization, where furosemide was used as a template molecule, acryl amid (AA) as a functional monomer and ethylene glycol dimethacrylat (EGDMA) as a cross-linking agent. The sensor showed a selective and sensitive response to the analyte (the template molecule) in aqueous solutions. The MIP-based sensor responded Nernstian (51.8±0.3 mV decade^{-1}) in a concentration range of 7.5×10^{-6} to 1.0×10^{-1} mol L^{-1} with a lower detection limit of 5.0×10^{-6} mol L^{-1}. The response time of the sensor was ~20 s, a high performance and a satisfactory long-term stability (more than 2 months). The proposed sensor has acceptable accuracy, sensitivity and precision to be used for furosemide assay in some pharmaceutical preparations.

Keywords- Furosemide; Molecularly imprinted polymer; Potentiometry; Sensor

1. INTRODUCTION

Potentiometric PVC membrane sensors have been widely used in determination of many cations, anions and drug molecules [1-10]. In case of a pharmaceutical molecules, they works based on an ion-exchange mechanism. An ion-pair complex placed in the PVC membrane are responsible for such ion exchanging. Ionic forms of a drug molecule is exchanged with its similar species in the membrane. A hydrophobicity of the molecules govern the selectivity of the sensor. Although such electrodes work well in analysis of active ingredients of an electrode, they suffer from lack of selectivity for applications in complex-matrix samples.

Molecularly imprinted polymer (MIP) technology is a powerful technique for preparing artificial molecular recognition sites with specific selectivity for variety of target molecules. Covalent, semi-covalent and non-covalent bonding are used in synthesis of MIPs. However, non-covalent approach is the most flexible method used due to the ability to select the functional monomers and the wide choice of the template molecules [11-16]. Thus, MIPs can be a good candidate for designing more selective potentiometric drug sensors abled to work in complex matrixes .

However, one of the disadvantages of traditional bulky MIP materials is perhaps their slow binding kinetics to target species and suffering from low rebinding capacity especially in case of inner sites [17]. Using nanomaterials synthesis strategies in the preparation of the imprinting polymers solved the disadvantages someway [18-23]. Molecular imprinting nanotechnology greatly enhanced molecular affinity of the MIPs. Nanostructured imprinted materials possess small dimensions with extremely high surface-to-volume ratio, which cause most of imprinted sites are available by placing at the surface or near the surface. Consequently, in spite of the bulky MIP, nano-MIPs can greatly improve binding capacity and kinetics and site accessibility of imprinted materials which is very important in potential response of a potentiometric electrode.

Furthermore, MIPs behave as antibody-like materials and for high selectivity and sensitivity, long-term stability, and insolubility in water and most organic solvents can be stable in PVC membrane [24,25].

The properties of the nano-MIP make them more suitable as selectophore in the chemical sensors especially electrochemical ones. MIP and nano-MIP have been used widely in voltammetric sensors [26-28]. However, despite the relatively simple transduction of a potentiometric signal, there are limited number of reports on designing potentiometric sensors using MIPs [29-31]. These sensors are made by dispersion of MIP particles in a plasticizer and embedment in a polyvinylchloride (PVC) matrix .

In this paper, we present a polyvinyl chloride (PVC) membrane electrode for the potentiometric detection of furosemide based on nano-MIP. The method is applied to the determination of furosemide in some pharmaceutical formulations (tablet and ampule) and some more complex matrix such as urine and plasma.

Medical Commission of the International Olympic Committee has classified diuretic drugs as doping agents in sports. Therefore, their usages are forbidden in competitions [32]. Furosemide is one of the effective diuretic drug which is prescribed for treatment of congestive heart failure, chronic renal failure and cirrhosis of the liver. It inhibits adsorption of salt in the kidney tubules and causes they increase in urine [33]. Such increasing of water and electrolyte depletion reasons for an acute loss of body weight before competition and masks the ingestion of other doping agents by reducing their concentration in urine. Adsorption of furosemide is rather fast. The peak levels are after 60–90 min after a dose consumption and are metabolized through liver and kidney.

Usually furosemide is determined by complex, costly, and time consuming instrumental methods such as HPLC [34-36]. Design and making a sensor that is a suitable substitution for fast determination of drug with high precision and sensitivity could be concerned [37].

2. EXPERIMENTAL

2.1. Chemicals

Acyl amid (AA) from Merck (Darmstadt, Germany) was distilled in vacuum former to be used in order to remove the stabilizers. Hexadecyl trimethyl ammonium bromide (HTAB), 2,2′-azobisisobutyronitrile (AIBN) and Ethylene glycol dimethacrylate (EGDMA) are all from Merck (Darmstadt, Germany). The other chemicals were of analytical grade. The solutions were prepared with distillated water. Furosemide (Fig. 1) active ingredient was obtained from a local company (Mehr Daru, Tehran, Iran) as gift samples and its pharmaceutical formulations were purchased form a local pharmacy (Tehran, Iran). The human plasma sample was obtained from the Iranian Blood Transfusion Service (Tehran, Iran). Human urine was taken from some healthy volunteers.

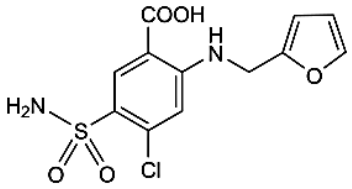


Fig. 1. Chemical structure of Furosemide ((5-(aminosulfonyl)-4-chloro-2-[(2- furanylmethyl) amino]benzoic acid))

2.2. Instruments

A PVC membrane sensor as an indicator electrode was placed in a glass cell, consisted of two Ag/AgCl double junction reference electrodes (Azar-Elelectrode Co., Iran) as external and internal reference electrodes. Two reference and indicator electrodes were connected to an ion

analyzer with a 250 pH/mV meter with ±0.1 mV precision. UV–Vis spectra and absorbance measurements were recorded in 1cm length quartz cell of a PerkinElmer Lambda 2 UV–Vis spectrophotometer. The size and morphology of the products were characterized by scanning electron microscopy (SEM) on a Zeiss SIGMA VP after gold coating.

2.3. nano-MIP and NIP Preparation through Precipitation Polymerization

MIP nanoparticles (nano-MIP) for furosemide were synthesized through precipitation polymerization method in large volume of solvent while stirring or sonication. Here, they were prepared from a reagent mixture obtained by mixing (0.1066mg, 1.5 mmol) of acryl amid, (1.697 mL, 9 mmol) of ethylene glycol dimethacrylate, (0.1653 mg, 0.5 mmol) of furosemide and (60mg, 0.364 mmol) of AIBN in 70 mL acetone. The mixture was homogenously dispersed by sonication (sonic bath model Ultrasonic UTD35-Falc, Via Piemonte, Italy). Next, it was purged with N_2 for 10 min and the glass tube was sealed under this atmosphere. It was, then, stirred in an oil bath maintained at 50°C for 14 h. The template molecule was extracted from the polymers with 90 mL acetonitrile in a Soxhlet extraction system during 24 h. Template extraction from the synthesized polymer created cavities, leading to the specific sorption of the template molecules. Furthermore, removal of other materials from the polymer were also done (materials such as residual monomers or oligomers and initiator fragments). Non-imprinted polymer (NIP) was also made as a control material exactly the same procedure used in synthesis of the MIP used for NIP too but the template molecule, Furosemide, was excluded.

2.4. Fabrication of the Furosemide sensor

MIP-based PVC membrane sensors were made by the following general procedure as mentioned below [38-40]. Different Furosemide imprinted nanoparticles with proper amounts of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF), and then solution was mixed well into a glass dish of 2 cm diameter. Next, THF was evaporated slowly until an oily concentrated mixture was obtained. A plastic tube (about 3 mm o.d.) was dipped into the mixture for about 10 s till a transparent membrane of about 0.3 mm in thickness was formed at the end of tube. The tube was then kept at room temperature for about 10 h. After that, the tube was filled with an internal filling solution of 1.0×10^{-3} mol L^{-1} of furosemide solution. The electrode was finally conditioned for 18 h by soaking in the same solution. For preparation of the NIP-based PVC membrane sensor, the same procedure were applied but instead of MIP, NIP was used as a control tests.

2.5. Standard solution of Furosemide

To prepare the stock solution of Furosemide, the drug molecule was dissolved in 1 mol L^{-1} sodium hydroxide. The standard series solution was prepared by appropriate dilution

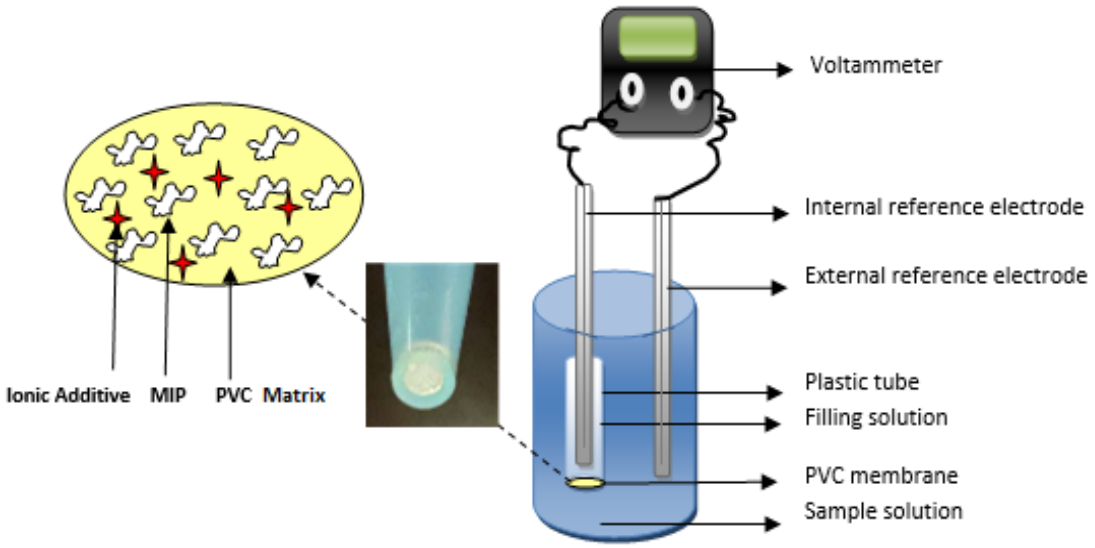
of the stock solution and adjusting the pH. By this way, the anion of the Furosemide is formed which is suitable for potentiometric measurements.

2.6. Sample preparations

The furosemide pharmaceutical formulations in our local market were tablets and injections. Stated content of tablet was 40 mg and in case of injection was 20 mg/2 mL. For analysis of tablets, 10 tablets were weighted carefully and then powdered completely. Then amount equal to the weight of 1 tablet was transferred to a 100-mL volumetric flask added 5 mL NaOH 1 mol L^{-1} and diluted to the mark, stirred for 10 min and filtered. The resulted solution was used for the measurements. For injection sample (Ampoule), just a dilution 1:10 was done. Because real urine and plasma samples having furosemide were not available, synthetic samples prepared by spiked method were used. 10 mL of urine sample was just diluted 1:5 with deionized water and centrifuged at 5000 rpm for 10 min to avoid adsorption of the probable impurities on the surface of the electrode. Then, 10 ml of this solution were encountered the spiked amount of furosemide drug, adjusted the pH and used for the measurements. To precipitate the plasma proteins, 1 mL of the plasma samples was treated with 20 µl nitric acid 1 mol L^{-1}. Next, the mixture was vortexed for 1 min and then centrifuged at 6000 rpm for 10 min. Finally, 100 µl aliquot of the obtained supernatant was diluted 10 times and encountered the spiked amount of furosemide drug, adjusted the pH and used for the measurements.

2.7. Potential measurements

The response of the sensor was examined by measuring the potential of the following electrochemical cell (Scheme 1):



Scheme 1. Schematic of electrode preparation

Ag-AgCl| internal solution (1.0×10^{-3} mol L^{-1} Furosemide) | nano-MIP based PVC membrane | sample solution | Ag-AgCl, KCl (sat.)

The potential response of the sample solution containing varying amounts of Furosemide was measured. The potential was plotted as a function of –log Furosemide concentration.

3. RESULTS AND DISCUSSION

3.1. Characterization of the synthesis nano-MIP

Morphology of the synthesized nano-MIP and NIP as control were both characterized by scanning electron microscopy (SEM). The SEM images were shown in Fig. 2.

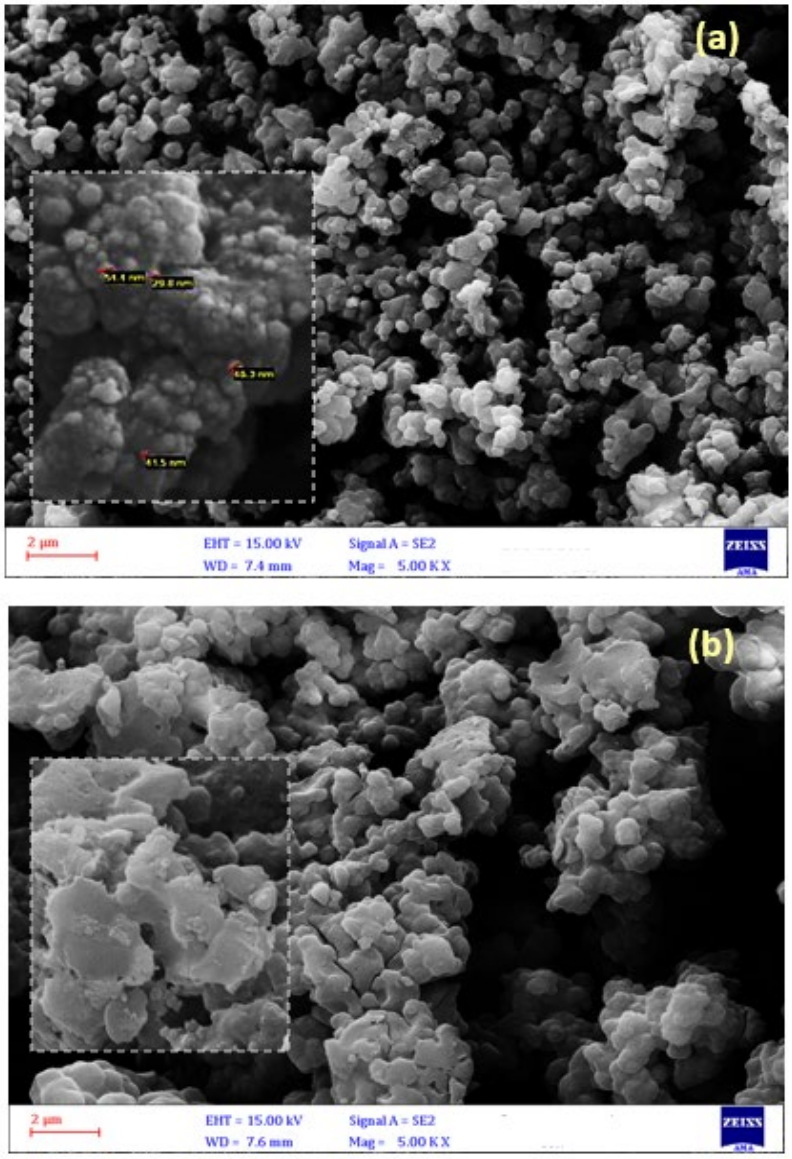


Fig. 2. SEM images of (a) prepared nano-MIP and (b) NIP

As it can be seen, the nano-MIP particles has a homogeneity in the size and the average size of each particle about 58 nm. While in case of NIP molecules such morphology is not seen. Non-uniformity and various sizes is seen. Furthermore, the morphology of the MIP is seen more porous than the NIP, which may be due to the lack of template molecule in synthesis of NIP. Thus, by the extraction process done on the MIP and removing the template more porous structure forms.

To obtain the adsorption capacity of the target molecule by the nano-MIP, UV-Vis spectroscopy was used. For this purpose, 0.05 g nano-MIP and NIP were separately added to 10 mL of 5×10^{-5} mol L^{-1} of Furosemide solutions and well stirred for about 15 min. Then, the solution was centrifuged and filtered and its absorption was studied by spectrophotometer. The results are presented in Fig. 3. As it can be seen, for NIP as a control material the drug molecules have not been separated from the solution.

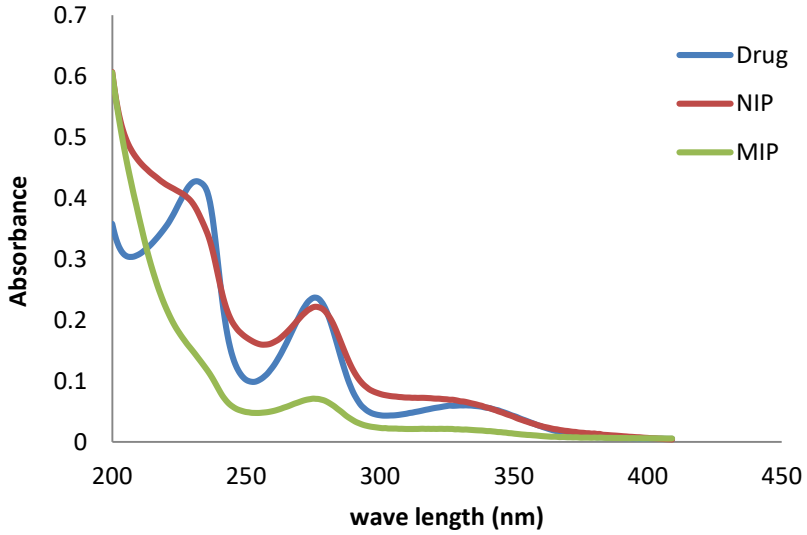


Fig. 3. UV-Vis spectra of Furosemide (5×10^{-5} mol L^{-1}), and the recovery solutions after encountering nano-MIP and NIP

The concentrations of the recovery solutions were calculated through calibration methods. Various mole ratio of the imprinting ingredients were synthesized and the adsorption capacities were investigated as recovery test by UV-Vis spectrophotometry. Table 1 lists the examined mole ratio of the ingredients and the obtained results. According to the initial results, the nano-MIP-3 which has the mole ratio of 1:3 (template: functional monomer) was selected for next studies.

Table 1. Optimization of the ingredients of Furosemide imprinting polymer

No.	Template (mmol)	Functional monomer (mmol)	Cross linker monomer (mmol)	Initiator (g)	Synthesis solvent	Washing Solvent	Recovery (%)
MIP1	1	3	15	0.06	Acetonitrile	Methanol	42.9
NIP1	-	3	15	0.06	Acetonitrile	Methanol	8.1
MIP2	1	4	20	0.07	Acetonitrile	Methanol	15.0
NIP2	-	4	20	0.07	Acetonitrile	Methanol	7.3
MIP3	1	3	15	0.06	Acetone	Acetonitrile	68.0
NIP3	-	3	15	0.06	Acetone	Acetonitrile	6.5

The static adsorption of the synthesized nano-MIP was studied and it was compared to those of NIP. For static adsorption, 0.05 g nano-MIP and NIP was added separately to the solution of 5, 25, 50, 100 mg/L of Furosemide and stirred for 15 min. Then, the absorption of the filtered solutions were recorded at 279 nm. Using equation (1), Q or static adsorption (adsorption capacity at adsorption equilibrium) was calculated. c_i and c_f are the initial and equilibrium adsorptive concentrations, v is the adsorptive volume (volume of initial sample solution) and M is the weight of adsorbent. The related Q values for nano-MIP and NIP were shown in Fig. 4.

$$Q=\frac{(ci-cf)v}{M(MIP)} \quad (1)$$

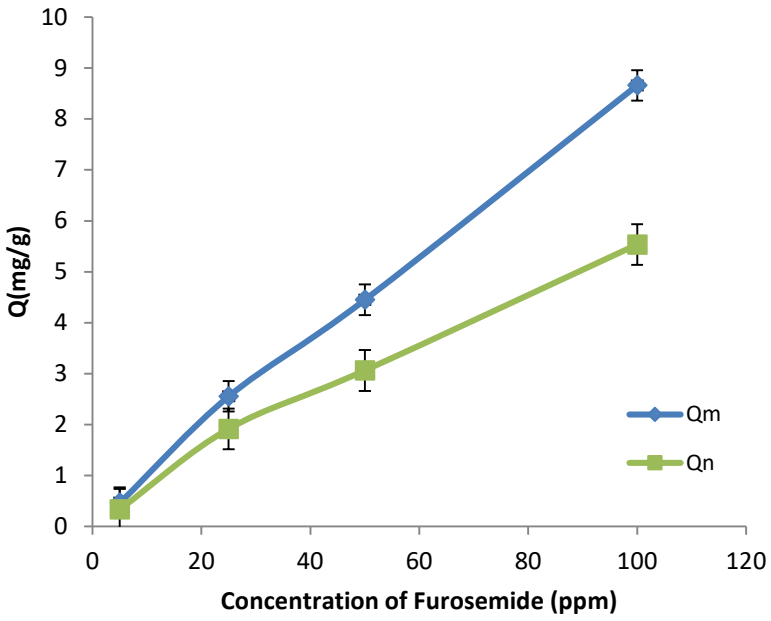


Fig. 4. Static adsorption of nano-MIP and NIP for Furosemide

To test the optimized time for the drug adsorption by nano-MIP, 0.05g nano-MIP was added to 10 mL of 1×10^{-5} mol L^{-1} solution of Furosemide. Then, the Q after 5, 10, 15, 20, and 25 min was calculated. As can be seen in Fig. 5, the optimum time for the maximum adsorption was about 20 min.

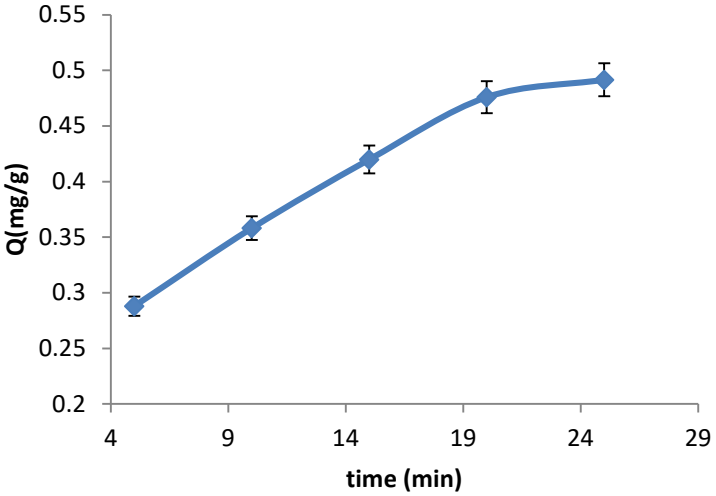


Fig. 5. Optimization of adsorption time for nano-MIP

3.2. PVC membrane composition

In potentiometric sensor, the main factor which can strongly affect the potential response is type and amounts of the membrane ingredients. Here, nano-MIP-3 was applied as a sensing material in the membrane. To find better the effect of the biomimetic selectophore on the potential response of the membrane, some membrane having NIP instead of MIP were also prepared. As can be seen 6 mg MIP in the membrane number 2, showed the best Nernstian response. The role of an ionic additive in the preparation of the potentiometric PVC membrane drug sensor based on MIP is more essential to decrease the Ohmic resistance.

Table 2. Membrane composition optimization

No.	Imprinted Polymer (%)	PVC (%)	Ionic additive (%)	Plasticizer (%)	Linear range (mol L^{-1})	Slope (mV/decade)	R^2
1	MIP 5 NIP 5	30	3	62 DBP	1.0×10^{-5}-1×10^{-1}	41.2 (±0.6) 0.7 (±29.6)	0.982 0.990
2	MIP 6 NIP 6	30	3	61 DBP	7.5×10^{-6}-1×10^{-1}	51.8±(0.3) 27.0±(0.5)	0.995 0.985
3	MIP 7 NIP 7	30	3	60 DBP	5×10^{-6}-1×10^{-1}	0.5 (±45.3) 0.4 (±28.8)	0.991 0.981
4	MIP 6 NIP 6	30	2	62 DBP	1×10^{-5}-1×10^{-1}	0.8 (±37.5) 0.6 (±27.6)	0.981 0.978
5	MIP 6	30	3	61 BA	1×10^{-4}-1×10^{-1}	0.4 (±15.3)	0.983
6	MIP 6	30	3	61 NB	-	-	-

Here, HTAB and NaTPB both which are an anionic and cationic additive were used for this purpose. Since, we wants the potential response of the sensor to an anionic drug was just because of adsorption by MIP sites and not ion-exchanging, NaTPB was used. DBP which is a rather hydrophobic solvent mediator was also selected as the best plasticizer of the membrane. Finally, the composition of 6% MIP, 3% NaTPB, 30% PVC and 61% DBP was selected as the best membrane composition.

3.3. Characterization of the Furosemide biomimetic sensor

Fig. 6 shows the calibration curve of the Furosemide biomimetic sensor and the related control ones. Dynamic response time is an important factor, for the evaluation any sensor. In this study, the practical response time was obtained by changing the furosemide concentrations from the lower (1.0×10^{-2} mol L^{-1}) to the higher (1.0×10^{-3} mol L^{-1}) concentrations. The electrode shows its equilibrium response in a short time of about 20 s.

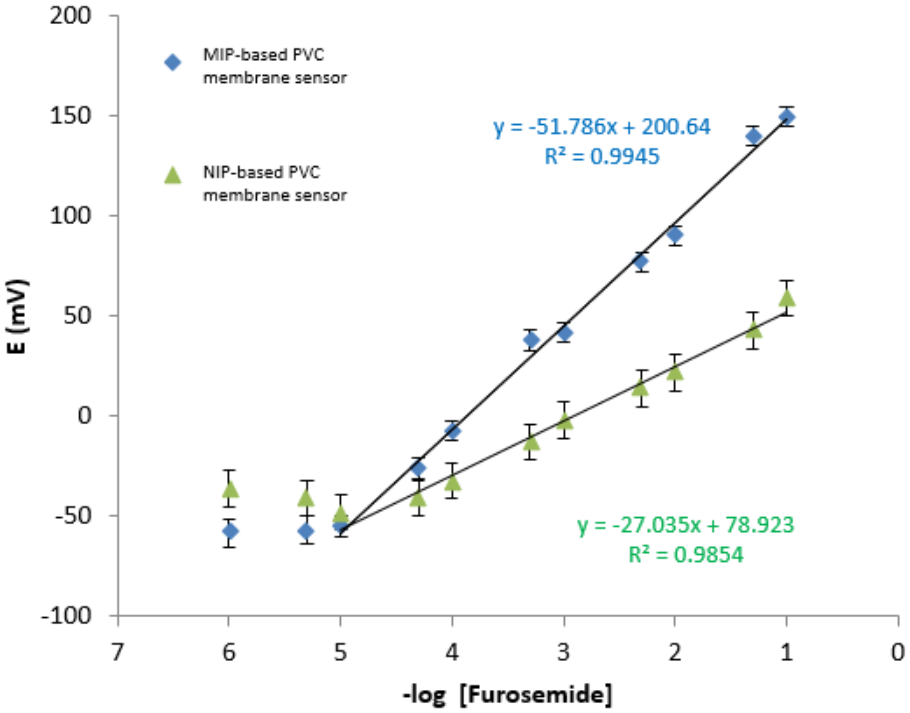


Fig. 6. Calibration curve of the potentiometric sensor based on nano-MIP and NIP

To examine the effect of pH on this electrode responses, the potential was measured at a specific concentrations of the furosemide solution (1.0×10^{-4} mol L^{-1}) from the pH value of 4 up to 12.5 (concentrated NaOH or HCl solutions were employed for the pH adjustment. The results indicated that the potential remained constant in the pH range of 6.5 to 9.5, which indicates the applicability of this electrode in the specified pH range.

Selectivity is the most important characteristic of any sensor, and describes affinity of the indicator electrode toward target species in the presence of interfering species. The selectivity coefficients of the proposed biomimetic potentiometric sensor were calculated through matched potential method (MPM) [41-43], and the results are shown in Table 3. Concentration of the reference solution of furosemide was 1.0×10^{-5} mol L^{-1} and the concentration of interfering ions was between 1×10^{-5} mol L^{-1} to 1.0×10^{-2} mol L^{-1}.

Table 3. Potentiometric selectivity coefficient values, $K_{furosemide}^{MPM}$ (PVC membrane electrode)

Interference	**Log K_{MPM}**
Nitrate	-2.27
Carbonate	-2.21
Thiosulfate	-2.37
Pyrophosphate	-2.19
Sulfate	-2.59
Acetate	-2.23
Chloride	-2.23
Magnesium	-2.31
Calcium	-2.51
Potassium	-2.75
Phosphate	no interference

As can be seen from the results in Table 3, most of the tested interference species has no effect on the potential response of the Furosemide, which is confirmed the high selectivity of the proposed sensor.

Lifetime of a sensor can be tested by calibration curve of a standard solution and its Nernstian slope periodically. For this purpose, three electrodes were used for 1 hour per day during 10 weeks. The average lifetime for the reported potentiometric sensors is in the range of 4–10 weeks [38-45]. Here, after 8 weeks of utilization, a slight gradual decrease in the Nernstian slope and an increase in the detection limit were observed. Losing plasticizer, sensing element, or ionic site from the polymeric film due to leaching into the sample solution after several times of usage, can be a reason for such limited lifetimes of the sensors besides their low mechanical stabilities.

The accuracy of the analysis was also tested by calculating the recovery% of a known concentration of a Furosemide solution. The mean percentage recovery, obtained by applying the calibration curve method, was 98.5% (n=5).

3.4. Analysis of Furosemide in pharmaceutical formulations and biological matrixes

The proposed membrane based nano-MIP sensor was applied for the Furosemide determination in some pharmaceutical formulations. The resulting data, using the calibration curve procedure, were statistically compared with the stated content. Table 4 shows the results of real sample analysis. According to the obtained data, the proposed sensor can be successfully used in determination of Furosemide active ingredients of the tablets and ampules.

Table 4. Furosemide assay in tablets formulations by means of the described potentiometric procedure

Sample	Company	Labeled amount	Found by sensor*	RSD%
Tablet	Mehr Daru	40.0 (mg/tab)	42.5±0.7	6.2
Ampule	Caspian Tamin	20.0 (mg/2 mL)	21.1±0.3	5.5

*The results are based on 5 replicate measurements.

Also, the proposed sensor was used in analysis of Furosemide in some spiked human plasma and urine samples (Table 5).

Table 5. Performance of the proposed sensor in plasma and urine matrixes

Sample	Added (mol L^{-1})	Found (mol L^{-1})	RSD% n=3	Recovery%
Urine	0	Not detected	-	-
	1×10^{-3}	9.8×10^{-4}	2.3	98
	5×10^{-4}	4.80×10^{-4}	3.1	96
	1×10^{-4}	9.5×10^{-5}	2.7	95
	5×10^{-5}	4.8×10^{-5}	3.3	96
Plasma	0	Not detected	-	-
	1×10^{-3}	9.5×10^{-4}	2.6	95
	5×10^{-4}	4.7×10^{-4}	3.3	94
	1×10^{-4}	9.6×10^{-5}	3.4	96
	5×10^{-5}	4.6×10^{-5}	3.5	92

The proposed sensor was successfully applied for the determination of Furosemide in pure solution, pharmaceutical formulation and biological matrixes. Linearity, limit of detection, recovery test, selectivity, precision, accuracy, lifetime and ruggedness/robustness were the parameters used for the method validation.

Life time of the sensor as explained above was about 8 weeks. For repeatability experiment, 3 standard Furosemide samples were measured for 3 times. The RSD values by PVC membrane based nano-MIP were 2.71, 3.12 and 3.44%. For reproducibility study, 3 sensors were made

by a same procedure and in the same conditions. Then a standard solution of Furosemide was measured by them (each sensors three times). The RSD% in the responses of the three replicate sensors was not more than 4.72%. For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for Furosemide obtained by two analysts. The RSD% values for the intra- and inter-day assays in the cited formulations performed in the same laboratory by two analysts did not exceed 4.6%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Furosemide %recoveries were acceptable under optimized conditions, and not showing any significant change when critical parameters such as temperature or pH were changed slightly.

4. CONCLUSION

Molecular imprinting polymers are interesting molecules which are increasingly used as a sensing materials in electrochemical sensors. MIPs offer an opportunity to design suites of materials/recognition elements for the same target analyte with unique binding characteristics. According to this study, a potentiometric method using MIP doped in a PVC membrane based electrode was introduced for furosemide assessment. The proposed MIP-based sensor exhibited a Nernstian response (51.8±0.3 mV decade^{-1}) in a wide concentration range of 7.5×10^{-6} to 1.0×10^{-1} mol L^{-1} with a lower detection limit of 5.0×10^{-6} mol L^{-1}. The response time of the sensor was ~20 s. Its accuracy, reproducibility, simplicity and selectivity suggest its application in the quality control analysis and clinical laboratories. The life time of the nano-MIP based sensor was about 8 weeks. The method shows a new strategy to make a biomimetic potentiometric sensor for a specific, rapid and simple furosemide detection in pharmaceutical formulations and even complex matrixes such as urine and plasma.

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REFERENCES

[1] H.A. Zamani, F. Malekzadegan, and M.R. Ganjali, Anal. Chim. Acta 555 (2006) 336.
[2] F. Faridbod, M.R. Ganjali, L. Safaraliee, S. Riahi, M. Hosseini, and P. Norouzi, Int. J Electrochem. Sci. 4 (2009) 1419.
[3] M. Shamsipur, S. Rouhani, M.R. Ganjali, H. Eshghi, and H. Sharghi, Microchem. J. 63 (1999) 202.
[4] H.A. Zamani, M.R. Ganjali, and M. Adib, Sens. Actuators B 120 (2007) 545.

[5] M. Javanbakht, A. Shabani-Kia, M.R. Darvich, M.R. Ganjali, and M. Shamsipur, Anal. Chim. Acta 408 (2000) 75.
[6] H.A. Zamani, M.R. Ganjali, P. Norouzi, and S. Meghdadi, J. Appl. Electrochem. 37 (2007) 853.
[7] M.R. Ganjali, T. Poursaberi, M. Hosseini, M. Salavati-Niasari, M. Yousefi, and M. Shamsipur, Anal. Sci. 18 (2002) 289.
[8] H.A. Zamani, G. Rajabzadeh, and M.R. Ganjali, J. Brazil. Chem. Soc. 17 (2006) 1297.
[9] M.R. Ganjali, L. Naji, T. Poursaberi, M. Shamsipur, and S. Haghgoo, Anal. Chim. Acta 475 (2003) 59.
[10] M.R. Ganjali, R. Kiani-Anbouhi, M. Shamsipur, T. Poursaberi, M. Salavati-Niasari, Z. Talebpour, and M. Emami, Electroanalysis 16 (2004) 1002.
[11] P.A.G. Cormack, and A.Z. Elorza, J. Chromatogr. B 804 (2004) 173.
[12] T. Alizadeh, M.R. Ganjali, and M. Zare, Anal. Chim. Acta 689 (2011) 52.
[13] M. Akhoundian, T. Alizadeh, M.R. Ganjali, and P. Norouzi, Talanta 200 (2019) 115.
[14] T. Alizadeh, N. Hamidi, M.R. Ganjali, and F. Rafiei, Microchim. Acta 185 (1) (2018).
[15] M. Khadem, F. Faridbod, P. Norouzi, A. Rahimi Foroushani, M.R. Ganjali, S.J. Shahtaheri, and R. Yarahmadi, Electroanalysis 29 (2017) 708.
[16] M. Akhoundian, T. Alizadeh, M.R. Ganjali, and F. Rafiei, Biosens. Bioelectron. 111 (2018) 27.
[17] G. Guan, B. Liu, and Z. W. Z. Zhang, Sensors 8 (2008) 8291.
[18] C. Xie, Z. Zhang, D. Wang, G. Guan, D. Gao, and J. Liu, Anal. Chem.78 (2006) 8339.
[19] C. Xie, B. Liu, Z. Wang, D. Gao, G. Guan, and Z. Zhang, Anal. Chem. 80 (2008) 437.
[20] T. Alizadeh, M. R. Ganjali, M. Akhoundian, and P. Norouzi, Microchim. Acta, 183 (2016) 1123.
[21] D. Gao, Z. Zhang, M. Wu, C. Xie, G. Guan, and D. Wang, J. Am. Chem. Soc. 129 (2007) 7859.
[22] C. Lu, W. Zhou, B. Han, H. Yang, X. Chen, and X. Wang, Anal. Chem. 79 (2007) 5457-5461.
[23] F. Vandevelde, A.S. Belmont, J. Pantigny, and K.H. Haupt, Adv. Mater. 19 (2007) 3717.
[24] C. Jantarat, Application of Molecularly Imprinted Polymer for Drug Delivery and Membrane Separation of Chiral Drugs, A Thesis Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Pharmaceutical Sciences Prince of Songk, (2009).
[25] S.A. Piletsky, and A.P.F. Turner, Electroanalysis 14 (2002) 317.
[26] T. Alizadeh, M. Zare, M. Reza, P. Norouzi, and B. Tavana, Biosens. Bioelectron. A 25 (2010) 1166.

[27] T. Alizadeh, M. Reza, P. Norouzi, M. Zare, and A. Zeraatkar, Talanta 79 (2009) 1197.
[28] M.R. Ganjali, A.R. Rahmani, R. Shokoohi, A. Farmany, and M. Khazaei, Int. J. Electrochem. Sci. 14 (2019) 6420.
[29] M.R. Ganjali, T. Alizade, and P. Norouzi, Int. J. Electrochem. Sci. 7 (2012) 4800.
[30] S. Mahmoudi, H. Rashedi, and F. Faridbod, Anal. Bioanal. Electrochem. 10 (2018) 1654.
[31] M.R. Ganjali, T. Alizade, B. Larijani, F. Faridbod, and P. Norouzi, Int. J. Electrochem. Sci. 7 (2012) 4756.
[32] V. Hugo, M. Luiz, L. Pezza, and H.R. Pezza, Microchem. J. 109 (2013) 68.
[33] K.M. Ho, and B.M. Power, Anaesthesia 65 (2010) 283.
[34] A. Amtssygehus, F. Andreasen, C. K. Christensen, F. K. Jakobsen, and C. E. Mogensen, Acta Pharmacol. Toxicol. (Copenh) (1981) 223.
[35] M. B. Barroso, R. M. Alonso, and M. Rosa, J. Liquid Chromatogr. Related Technol. 19 (1996) 231.
[36] L. J. Lovett, G. Nygard, P. Dura, P. Drug, and N. D. State, J. Liquid Chromatogr. 8 (1985) 1611.
[37] V. Suryanarayanan, C. Wu, K. Ho, Electroanal. 22 (2010) 1795.
[38] H. A. Zamani, A. Imani, A. Arvinfar, F. Rahimi, M. R. Ganjali, F. Faridbod, and S. Meghdadi, Mater. Sci. Eng. C 31 (2011) 588.
[39] M.R. Ganjali, P. Norouzi, A. Atrian, F. Faridbod, S. Meghdadi, and M. Giahi, Mater. Sci. Eng. C 29 (2009) 205.
[40] M.R. Ganjali, B. Larijani, and E. Pourbasheer, Int. J. Electrochem. Sci. 11 (2016) 2119.
[41] F. Mizani, S. Salmanzadeh Ardabili, M.R. Ganjaliab, F. Faridbod, M. Payehghadr, and M. Azmoodeh, Mater. Sci. Eng. C 49 (2015) 861.
[42] F. Faridbod, N. Davarkhah, M. Beikzadeh, M. Yekefallah, and M. Rezapour, Int. J. Electrochem. Sci. 12 (2017) 876.
[43] F. Faridbod, N. Davarkhah, and S. Karamdoust, Int. J. Electrochem. Sci. 10 (2015) 8308.
[44] F. Faridbod, and A. Shafaat, Curr. Anal. Chem. 13 (2017) 52.
[45] F. Faridbod, and T. Jamshidpour, Anal. Bioanal. Electrochem. 8 (2016) 397.