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Using Potentiometry and Electrochemical Impedance Spectroscopy Techniques for Studying Effect of Nanomaterials on Salicylate Ion-selective Electrode Response

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Abstract- A novel anion-selective electrode for salicylate ion with new ionophore was designed based on modified carbon paste electrode with multi walled carbon nanotubes (MWCNTs). Electrode made was evaluated for electrochemical studies using potentiometric and impedance techniques and results compared with together. The results of the potentiometric method using modified carbon paste electrode showed that the prepared electrode has a Nernstian slope 60.1±0.1 mV in concentrations measurement range 1.0×10^{-7}-1.0×10^{-1} M, the detection limit 5.4×10^{-8}, with pH range of 3.5-9.3, while using the impedance technique, the concentration measurement range increased to 1.0×10^{-9}-1.0×10^{-1} M, pH range increased to 3.8-10.7 and the detection limit decreased to 4.3×10^{-10} M.

Keywords- Multi-walled carbon nanotube, Potentiometry, Electrochemical impedance spectroscopy, Nanomaterials, Chemometrics

1. INTRODUCTION

Salicylic acid is one of the common metabolites of acetylsalicylic acid (aspirin), which is widely used as an analgesic and inflammatory agent and, recently, also as a preventive of

heart attacks [1]. The free acid is widely used as an antiseptic and a preservative for food. Salicylic acid is also employed in analytical practice and in synthesis of dyes [2,3]. The levels of salicylic acid higher than 2.2 $mmolL^{-1}$ level are regarded as toxic for patients [4]. Thus, finding a simple method for specifying salicylate is considered. A couple of methods such as liquid chromatography (HPLC) [5,6], voltammetry [7], atomic absorption [8], and etc. are reported recently. However, as most of these methods are difficult and need expensive equipment, the ion-selective electrodes method was applied in order to measure salicylate ion, because this method is simpler in the light of preparing sample and its apparatus compared with previous methods.

ISEs are detector electrodes being able to selectively measure an activity of a special type of ion. Ion-selective electrodes application is recognized as a common method in most laboratories in recent years as they have a lot of advantages such as simplicity, quick respond, high sensitivity and low cost [9-12]. In order to measure anions, potentiometric method is often used by applying ion-selective electrodes.

Another method that is used in order to investigate the accomplished interactions in the length of membrane, obtain the information about reaction speeds, electric doubled layer capacitor capacity and also the resistant of charge transfer is electrochemical impedance spectroscopy (EIS). In this method, the periodic signals with a very low amplitude is utilized unlike most of electrochemical methods which leads to very small turbulence in a studied system and make the system stabilize and presents high quality outputs [13,14].

Today, the application of carbon nanotubes (CNTs) is more frequent in constructing ion-selective electrodes. In comparison with membrane electrodes, carbon paste electrode has attracted a lot of attention as ion-selective electrodes, that its main reasons are renewability, stable respond, low ohmic resistance, lack of internal solution and cheapness [15,16].

System performance improvement and augmentation of processes efficiency without increasing cost is an important issue. The application that is used for this purpose is called optimization. The optimization term in analytical chemistry is usually used as a tool for finding the conditions in which processes create the best respond [17]. Today, due to expansive increase of ion-selective electrodes and also with the help of chemical poll (chemometrics) a couple of ions can be simultaneously measured with accuracy, high speed and selectivity.

According to the importance of measuring salicylate anion in biologic and pharmaceutical samples, our objective is to build simple ion-selective electrode for measuring salicylate ions based on applied techniques and by applying cheap and accessible materials CNT in order to increase the respond domain of electrode in lower density areas. This electrode has lower detection limit, the more applicable pH domain area, quicker responsiveness time, higher linear range of concentration compared with previous attempts over 2010-2016. Following results show that increasing nanomaterial, due to their high conductivity leads to the

augmentation of selectivity, the reduction of detection limit, improvement in linear range of concentration, increasing of lifetime and intensification of applicable pH range of carbon nanotubes electrodes compared with polymer membrane electrodes. Also, another attempt that is done in this research is the application of chemometrics method in presence of nanomaterial for optimization of membrane elements.

2. EXPERIMENTAL

2.1. Materials and Reagents

Methyl trioctyl ammonium chloride (MTOAC) was purchased from Sigma. Dioctyl phthalate (DOP), pure graphite powder (particle size <50 μm), high viscose paraffin oil (density=0.88 kg L^{-1}), potassium or sodium salts of all the anions, and all other chemicals were purchased from Merck except multiwall carbon nanotube (10–40 nm diameters and 1–25 μm length) which was purchased from Fluka. The Schiff base complex of dichloro(N-(2-pyridinylmethylene)benzoylhydrazone) copper(II), $Cu(HL)Cl_2$ as ionophore was used for the preparation of the carbon paste electrode (CPE). All the solutions were prepared using double distilled water. The pH adjustments were made with dilute nitric acid and sodium hydroxide solutions as required [14].

2.2. Synthesis of ionophore

Copper complexes (II) providence; benzyl hydrazide (1.213 g, 8.9 mmol) and acetyl pyridine (1 mL, 8.9 mmol) were added to 30 mL solvent acetic acid. The mentioned solution was set for 2 hours in ambient temperature of reflux conditions. After that, the Schiff base crystals was appeared and deposited. The obtained sediments were filtered and then they were rinsed by methanol and finally were dried.

2.3. Construction of carbon paste electrode

First, ionophore, graphite powder and carbon nanotube were combined in a crystal. Then, paraffin oil, DOP and ion additive were added in a small mortar to the mentioned mixture. Finally, it was grinded for approximately one hour in order to obtain a completely uniform mixture. The resulted paste was compressed well at the end of a glassy tube and also a thin copper wire was incorporated for establishing electricity connection and one side of wire was set inside paste. In required situation, the surface of electrode was polished gently on a weighing paper in order to remove pollution from its surface and obtain new and mirror-like surface. After it was prepared the electrode was placed in the 1.0×10^{-2} M sodium salicylate solution for 2 hours in order to make it stabilized.

2.4. The optimization of carbon paste electrode components by applying RSM method

In order to optimize the components of carbon paste electrode and obtaining their optimized amounts, central composite chemometrics design (CCD) was applied. The impressive variables on the performance and responsiveness of electrode are consisted of ionophore (F1), carbon nanotubes (F2) and additive (F3). Each variable was investigated at 3 levels of (-1, 0, 1). The number of experiments or in other words the number of electrodes that should be constructed can be obtained by the formula of: $N=2^F+2F+m$.

Therefore, the number of needed experiments for three variables and three repetitions in central points equals 17. The computation of this optimization was performed by software Minitab V.16 [18].

For describing the relation among variables and the respond of electrode, a quadratic equation was presented by applying RSM method.

$$Response=\beta_0+\beta_1F_1+\beta_2F_2+\beta_3F_3+\beta_{11}F_1^2+\beta_{22}F_2^2+\beta_{33}F_3^2+\beta_{12}F_1F_2+\beta_{13}F_1F_3+\beta_{23}F_2F_3 \quad (1)$$

2.5. Potentiometric Measurements

Potentials were measured with a digital pH-ion meter (Zag Chimi, Iran, model 162) [14]. An electrochemical cell consisting of two electrodes a saturated calomel electrode (SCE) as the reference electrode and a carbon paste electrodes as the indicator electrode. During these experiments which were done in concentration range 1.0×10^{-7}-1.0×10^{-1} M, sample solution was riled by magnetic stirrer and finally the potential curve was drawn based on the negative concentration logarithm of sodium salicylate.

2.6. Impedance measurements

Impedance measurement was done by 3-electrode system in which SCE electrode was applied as reference electrode; carbon paste electrode was incorporated as working electrode and platinum electrode was deployed as counter electrode. The modified carbon paste electrode measurement was done in a concentration range of 1.0×10^{-9}-1.0×10^{-1} M and it was done by potentiostat/galvanostat device (Autolab PGSTAT 302). The sample solution was completely static and the measurement impedance was done in a range of 60000 to 100 Hz frequency for modified carbon paste electrodes and the frequency points were considered as 40. Finally, the resistance chart of charge transfer (R_{ct}) was drawn proportional to negative concentration logarithm.

3. RESULTS AND DISCUSSION

In order to investigate the selectivity of ionophore compared with salicylate ion, the potentiometric experiments were done on various anions.

3.1. Investigating the ionophore impact on potentiometer method

In order to figure out the selectivity of ionophore compared with salicylate ion, the potentiometric experiments were done on various anions. As it can be seen in Figure 1 the interactions between ionophore and salicylate ion leads to the creation of an electrode with better Nernst slope and higher concentration range [2].

3.2. Optimization of carbon paste electrode components by applying RSM method

The optimization of membrane components is done by RSM method. CCD design experiment was investigated for three variables in this method. The coefficients of each variable are obtained by least squares method in Minitab V.16. The obtained quadratic equation is as follows:

$$Slope=56.6577+0.2900\ F1-3.2200\ F3-6.8261\ F11+5.3239\ F33+1.2250\ F1F3 \quad (2)$$

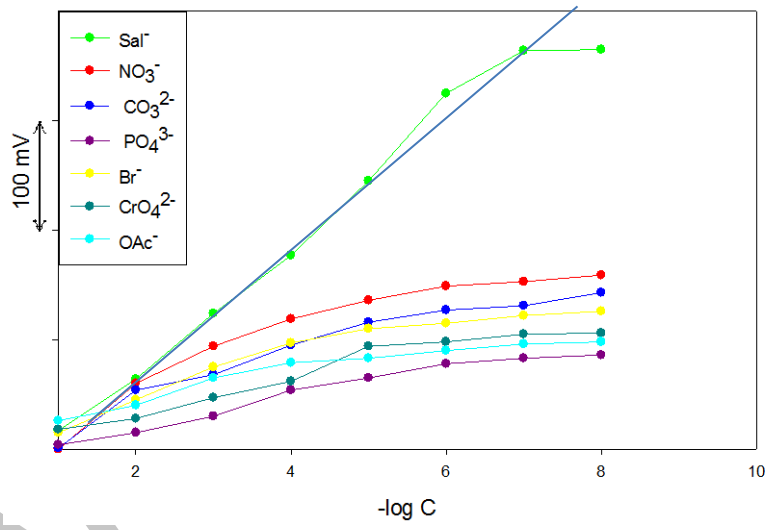

Fig. 1. Comparison of the potentiometric response of different anions with ionophore

The importance of each variable can be obtained by applying each variable P values [18,19]. Results show that variables F_1, F_3, F_1^2, F_3^2 and F_1F_3 have an important effect on respond.

The amounts of R^2, adjusted R^2 and predicted R^2 for suggested model are respectively 96.75%, 92.58% and 81.79%. In this situation the closeness of R^2 amounts to 1, shows the appropriateness of suggested model. R^2=96.75% for the equation of model 2 shows that just 3.25% total variances aren't defined satisfyingly by model. The forecasted slope chart with equation 2 against empirical slope in Figure 2 show the low amounts of residual.

In order to examine the effects of the interaction between the two variables on the response we have drawn three-dimensional and two-dimensional graphs and the results we

collected were in accordance with the prior findings. The optimized amounts for each variable are:

MTOAC (0.003 g), MWCNT (0.004 g) and ionophore (0.002 g). By applying the obtained amounts, carbon paste electrode was constructed. This electrode had a Nernst slope of 60.1±0.1 mV.decade^{-1} in the concentration scope of 1.0×10^{-7}-1.0×10^{-1} M.

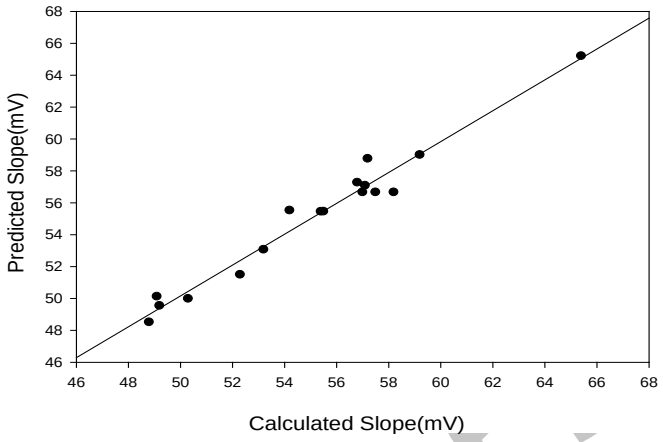

Fig. 2. The chart of forecasted tangent against empirical tangent for modified carbon paste electrode with multi-layer carbon nanotubes

3.3. Investigating the salicylate ion-selective electrode by applying the two technique of potentiometric and impedance

3.3.1. EIS studies

The impedance spectrum of carbon paste membrane was investigated in presence and absence of carbon nanotubes.

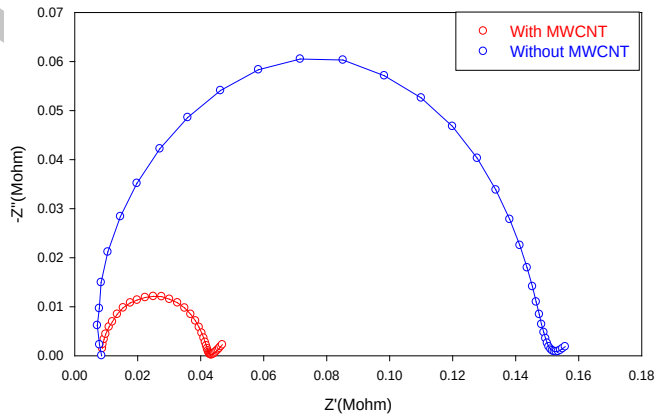

Fig. 3. The impedance results of carbon paste electrode with or without CNT. The concentration of external solution: 1.0×10^{-2} M

The results presents in Figure 3. The amount of the electrode charge transfer resistance that doesn't have nanotube is (0.151 Mohm) higher compared with the membrane that has nanotube (0.043 Mohm). These results show that the presence of nanotube in membrane decreases charge transfer resistance significantly. That means its presence increases electrical conductivity [18].

3.4. Electrode response investigation

After carbon paste electrode construction, respond curve was drawn proportional to optimized components.

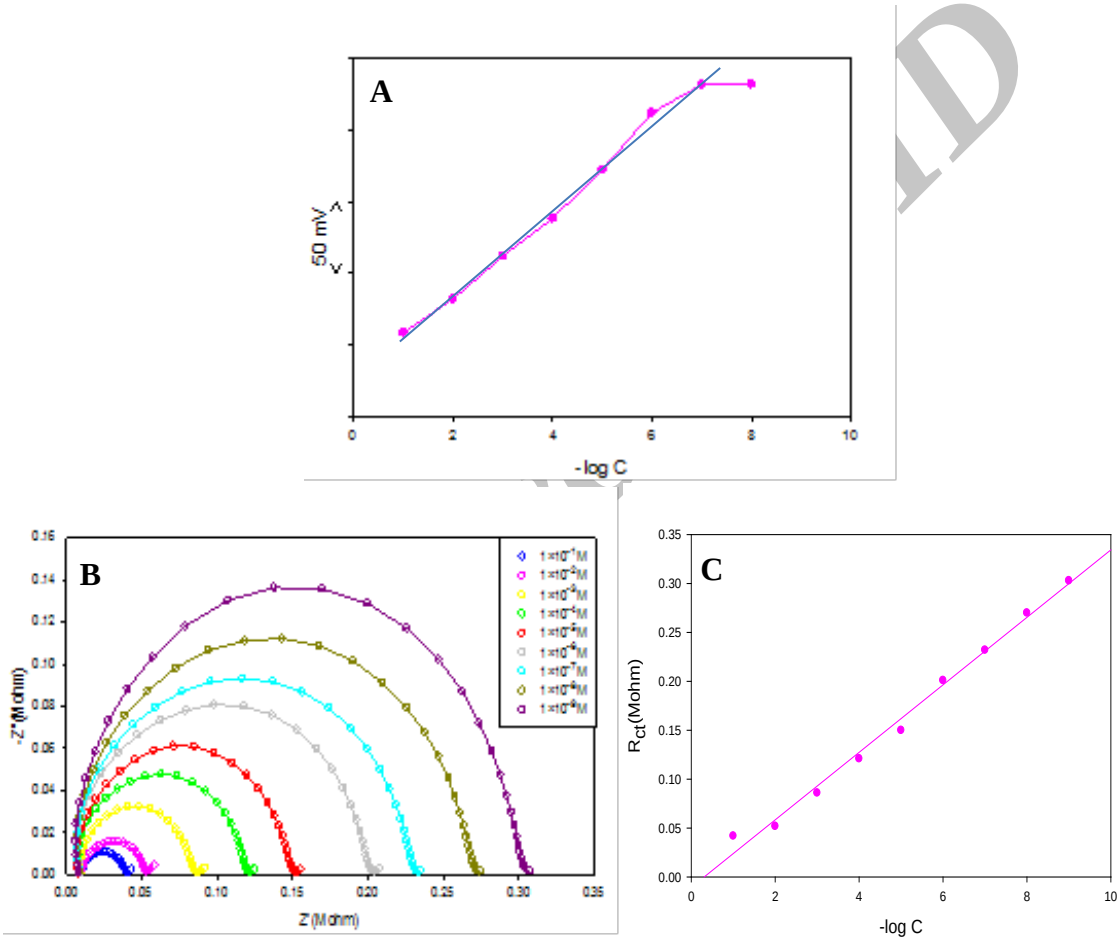

Fig. 4. (A) electrode respond curve of salicylate carbon paste. The concentration of external solution: 1.0×10^{-8}-1.0×10^{-1} M sodium salicylate; **(B)** Nyquist diagram of carbon paste electrode response for salicylate specification. The concentration of external solution: 1.0×10^{-9}-1.0×10^{-1} M sodium salicylate; **(C)** The charge transfer resistance diagram of modified carbon paste electrode with multi-layer carbon nanotubes

After setting an optimized electrode in the 1.0×10^{-2} M solution and in presence of salicylate ion about 2 hours, the potentiometric measurement was done. As it is shown in

Figure 4A this electrode responds well to the salicylate ion and has a good Nernst slope of 60.1±0.1 mV at linear concentration range of 1.0×10^{-7}-1.0×10^{-1} M and detection limit of 5.4×10^{-8} M.

In other section, sodium salicylate solutions with the concentration of 1.0×10^{-9}-1.0×10^{-1} M was applied in order to investigate carbon paste electrode response by the method of electrochemical impedance spectroscopy. Nyquist diagram of electrode response presents in Figure 4B. As this figure shows carbon paste electrode responds in a more expansive range of concentration to salicylate ion compared with potentiometric method. Also, in order to better understanding of carbon paste electrode behavior, the charge transfer resistance chart is shown in Figure 4C. It can be understood from charge transfer resistance figure that the constructed electrode shows a linear respond to salicylate ion to the concentration of 1.0×10^{-9}-1.0×10^{-1} M and detection limit of 4.3×10^{-10} M.

That this is because of carbon nanotubes presence that decreases charge transfer resistance and consequently increases conductivity and leads to the intensification of linear range [18].

3.5. Investigating pH effect

Due to the importance of pH on electrode response, after the optimization of the electrode's components the effect of measured pH solution on the response of the modified carbon paste electrodes was investigated on salicylate with the concentration of 1.0×10^{-4} M that its result presents in figure 5A. By investigating the obtained chart it is resulted that the potential is steady in the range of 3.5-9.3 and it is applied as an applicable pH range of sensor. The reason of increasing electrode potential in acidic pH is maybe as a result of hydronium ion interference in the performance of ionophore that it makes ionophore to respond concurrently to H^+ ion and Sal^- anion [20,21] and also the reason of severe potential reduction in high pH is the presence of hydroxide obtrusive type [22].

In the other section the effect of pH changes was investigated in the modified carbon paste electrode with carbon nanotubes by impedance technique. Nyquist diagram in Figure 5B shows the results of investigations. For observing more details of changes, the chart of charge transfer resistance compared with pH changes is shown in Figure 5C. The chart of R_{ct} changes compared with pH states that there is a possibility of salicylate ion measurement in pH range of 3.8-10.7. The impedance studies show that the effect of multi-layer carbon nanotubes presence in carbon paste electrode structure can lead to the reduction of these electrodes charge transfer resistance and as Autolab device can measure low amount of resistance therefore the applicable pH range for carbon paste electrode increases compared with potentiometric method.

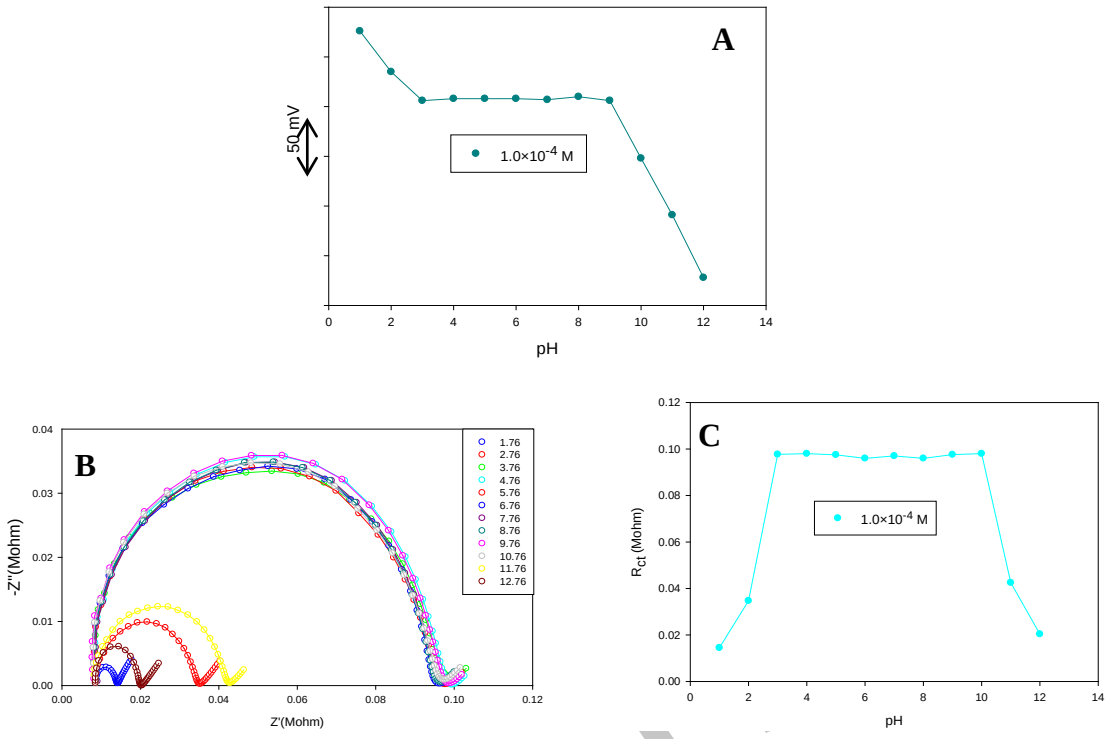

Fig. 5. (A) The pH effect on carbon paste electrode response curve. The concentration of external solution: 1.0×10^{-4} M; **(B)** Nyquist diagram of carbon paste electrode that in different pH. The concentration of external solution: 1.0×10^{-4} M; **(C)** The impact of pH solution variation on charge transfer resistance of carbon paste electrode

3.6. Response time and life time

An electrode response time is an important factor in analytical applications and it relates to concentration variations [5]. The response time was investigated for modified carbon paste electrode with carbon nanotubes in the concentration range of 1.0×10^{-7}-1.0×10^{-1} M sodium salicylate. The results present that the response time of ion-selective electrode is around 8 seconds in the 1.0×10^{-7} M solution and as it was expected the response time lessens in solutions with higher concentrations in a way that the response time decreases to 3 seconds in the 1.0×10^{-1} M solution.

In order to investigate the lifetime of carbon paste electrode over a time period of 60 days it was recognized that the constructed electrode has a good Nernst slope for 45 days, however after that their slope and linear range decreases. The reason of this behavior can be regarded to the destruction of electrode surface as a result of long term exposure to salicylate solution.

3.7. Interferences investigation

One of the most important features of ion-selective membrane is their selective behavior in investigating the level of reliable measurement capability for sample [20]. In examining

the interfering ions in measuring potentiometric and selectivity coefficients using prepared carbon paste electrodes the matched potential method (MPM) was used. The results of these investigations have been shown in Table 1.

Table 1. Selectivity coefficients of interference ions

Interference ion	**K^{pot} (MPM)**	**Interference ion**	**K^{pot} (MPM)**
ClO_4^-	1.0×10^{-2}	CrO_4^{2-}	1.0×10^{-3}
IO_3^-	1.0×10^{-3}	CO_3^{2-}	1.0×10^{-2}
MnO_4^-	1.0×10^{-3}	NO_2^-	1.0×10^{-2}
SCN^-	1.0×10^{-3}	NO_3^-	1.0×10^{-3}
ClO_3^-	1.0×10^{-2}	Cl^-	1.0×10^{-4}
PO_4^{3-}	1.0×10^{-2}	Citrate	1.0×10^{-3}
Br^-	1.0×10^{-3}	$Cr_2O_7^{2-}$	1.0×10^{-3}
OAC^-	1.0×10^{-2}	SO_4^{2-}	1.0×10^{-4}
BrO_3^-	1.0×10^{-4}	F^-	1.0×10^{-2}
$C_2O_4^{2-}$	1.0×10^{-2}	I^-	1.0×10^{-2}

The results show that the constructed carbon paste electrode has a very good selectivity compared with salicylate ion and as a result of carbon nanotubes presence. The selectivity coefficients of different anions show that there isn't any disturbance for salicylate ion. As a result of low selectivity coefficients of different anions, the suggested electrode can be applied well for salicylate measurement in biologic samples.

4. CONCLUSION

In this work, a novel modified carbon paste electrode was prepared using new Schiff base copper complex. Electrode made was evaluated for electrochemical studies using potentiometric and impedance techniques and results compared with together. The results of the potentiometric method using modified carbon paste electrode showed, the prepared electrode, have a Nernstian slope 60.1±0.1 mV in concentrations measurement range 1.0×10^{-7}-1.0×10^{-1} M, the detection limit 5.4×10^{-8} M, applied 3.5-9.3 pH range. While using the impedance technique, the concentration measurement range increased to 1.0×10^{-9}-1.0×10^{-1} M pH range increased to 3.8-10.7 and the detection limit decreased to 4.3×10^{-10} M.

Also, one of the other processes conducted in the research was the optimization of the components of the carbon paste electrodes via chemometrics technique that the most

important advantages of this method are the number of experiments reduction, saving time and costs.

The results presented in Table 2 show, the advantages of these new constructed electrodes compared with the ones that are built over 2010–2016 are the improvement of concentration linear range, the augmentation of pH range, the reduction of detection limit and lower response time.

Table 2. Comparing the results of constructed electrode with previous electrodes over 2010-2016

Articles	**Year**	**Slope (mV.decade^{-1})**	**Linear range (M)**	**Detection limit (M)**	**pH range**	**Respond time (s)**	**Ref.**
1)	2010	56±1.0	3.0×10^{-6}-1.0	1.0×10^{-6}	5.0-12.0	5	[1]
2)	2011	-59.5±1.0	1.0×10^{-7}-1.0×10^{-1}	5.0×10^{-7}	6.0-9.5	20	[23]
3)	2012	57.8	5.0×10^{-7}-5.0×10^{-1}	8.0×10^{-8}	5.0-7.0	20	[24]
4)	2013	58.8±1.0	1.0×10^{-5}-1.0×10^{-1}	3.9×10^{-6}	4.0-12.0	11-35	[25]
5)	2016	-60.5	1.0×10^{-6}-1.0×10^{-1}	4.0×10^{-7}	4.5-8.5	5	[3]
6)	-	60.1±0.1	1.0×10^{-7}-1.0×10^{-1}	5.4×10^{-8}	3.5-9.3	3-8	This work

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REFERENCES

[1] M. Mazloum-Ardakani, M. A. Sheikh-Mohseni, and A. Benvidi, Anal. Bioanal. Electrochem. 2 (2010) 155.

[2] M. Mazloum-Ardakani, M. S. Jalayer, J. Safari, Z. Sadeghi, and H. R. Zare, Anal. Biochem. 341 (2005) 259.

[3] O. R. Shehab, and A. M. Mansour, Electroanalysis 28 (2016) 1100.

[4] M. Nur Ayanoğlu, K. Ertürün, H. Elif, A. Demirel Özel, Ö. Şahin, M. Yılmaz, and E. Kılıç, Electroanalysis 27 (2015)1676.

[5] S. Erden, A. Demirel, S. Memon, M. Yılmaz, E. Canel, and E. Kılıç, Sens. Actuators B 113 (2006) 290.

[6] M. K. A. El-Rahman, M. R. Rezk, A. M. Mahmoud, and M. R. Elghobashy, Sens. Actuators, B 208 (2015) 14.
[7] L. Lu, X. Zhu, X. Qiu, H. He, J. Xu, and X. Wang, Int. J. Electrochem. Sci. 9 (2014) 8057.
[8] S. Chandra, A. Malik, P. K. Tomar, A. Kumar, and S. Sadwal, Anal. Bioanal. Electrochem. 3 (2011) 379.
[9] T. A. Ali, M. H. Soliman, and G. G. Mohamed, Int. J. Electrochem. Sci. 11 (2016) 1055.
[10] F. M. Abdel-Haleem, and O. R. Shehab, Electroanalysis 28 (2016) 800.
[11] J. Hu, A. Stein, and P. Bühlmann, TrAC, Trends Anal. Chem. 76 (2016) 102.
[12] A. Nezamzadeh-Ejhieh, and M. Shahanshahi, J. Ind. Eng. Chem. 19 (2013) 2026.
[13] A. J. Bard, and L. R. Faulkner, Electrochemical Methods, Fundamental and Applications, 2nd Ed, John Wiley & Sons, New York (2001).
[14] M. Mazloum-Ardakani, A. D. Manshadi, M. Bagherzadeh, and H. Kargar, Anal. Chem. 84 (2012) 2614.
[15] H. Bagheri, A. Shirzadmehr, and M. Rezaei, Ionics 22 (2016) 1241.
[16] M. R. Ganjali, H. Khoshsafar, A. Shirzadmehr, M. Javanbakht, and F. Faridbod, Int. J. Electrochem. Sci. 4 (2009) 435.
[17] K. Farhadi, M. Bahram, D. Shokatynia, and F. Salehiyan, Talanta 76 (2008) 320.
[18] M. Mazloum-Ardakani, A. A. Mandegari, S. Masoum, and H. Naeimi, JNS 2 (2012) 333.
[19] H. Kalavathy, I. Regupathi, M. G. Pillai, and L. R. Miranda, Colloids Surf. B 70 (2009) 35.
[20] B. Rezaei, S. Meghdadi, and R. F. Zarandi, J. Hazard. Mater. 153 (2008) 179.
[21] V. K. Gupta, A. K. Jain, and P. Kumar, Electrochim. Acta 52 (2006) 736.
[22] A. Soleymanpour, E. Hamidi Asl, and M. A. Nasseri, Electroanalysis 18 (2006) 1598.
[23] M. Mazloum-Ardakani, P. Pourhakkak, M. Salavati-Niasari, M. A. Karimi, and M. H. Mashhadizadeh, J. Braz. Chem. Soc. 22 (2011) 30.
[24] T. Poursaberi, and M. Hassanisadi, J. Porphyrins Phthalocyanines 16 (2012) 1140.
[25] I. M. Isa, N. M. Sohaimi, N. Hashim, A. Kamari, A. Mohamed, M. Ahmad, and S. A. Ghani, Int. J. Electrochem. Sci. 8 (2013) 2112.