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Employment of Optimal Mixture Design to Optimize Selective and Sensitive Manganese (II) Potentiometric Sensor in Environmental and Biological Samples

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Abstract- A potentiometric sensor as a selective, straightforward, and sensitive device was prepared based on a carbon paste electrode (CPE) as an indicator electrode for determining manganese (II) ions in environmental water and biological samples. A novel and synthetic ligand, 5,5'-((2E,2'E)-2,2'-(1,2-diphenylethane-1,2-divlidene)bis(hydrazin-1-yl-2-ylidene))bis (4-amino-4H-1,2,4-triazole-3-thiol) (called BBP), which has a selective interaction with Mn^{2+} ion, was chosen as an ionophore in the CPE composite. An optimal mixture design was generated to optimize the CPE components' percentages, including BBP, MWCNTs, an ionic liquid, and graphite powder, and to investigate binary interactions between the component amounts. Effects of several modifier agents, such as MWCNTs, NH2-MWCNTs, and COOH-MWCNTs, were evaluated in the CPE composite. The ability of two binders (Paraffin oil and an ionic liquid ([Bmim][BF₄])) in the CPE composite was compared, indicating that ionic liquid has a better response than paraffin oil due to an increase in electrical conductivity and flexibility of CPE. Under the CPE components optimization, the sensor displayed a wide pH range from 2.8 to 8.2, a short response time (5 s), and a long lifetime (11 weeks) for the Mn^{2+} ion determination. The sensor also has a wide linear range from 1.0×10^{-7} - 1.0×10^{-1} M with a LOD of 3.1×10⁻⁸ M and an R-squared of 0.998 without significant interfering effects of other ions for the Mn²⁺ ion measurement. The sensor performance was studied by analyzing river water, well water, and human urine samples, and the results were compared with flame atomic absorption spectrometry.

Keywords- Potentiometric sensor; Manganese (II) ion; Optimal mixture design; Ionic liquid; Multi-walled carbon nanotubes

1. INTRODUCTION

Manganese (Mn) is an essential element with various physiological functions in the human body that inadequate intake of this element may cause symptoms, including impaired growth, skeletal deficiency, impaired glucose tolerance, and decreased fertility in humans[1,2]. Manganese is present in many foods, and its deficiency in the human body is usually eliminated by using dietary supplements[3,4]. Exposure to large amounts of magnesium, especially in the industrial process, can lead to its accumulation in the nervous system and cause adverse effects in humans, such as Parkinson's disease, sperm damage, and decreased libido [5,6]. Therefore, the Mn determination in food samples using a new procedure with suitable selectivity, reasonable sensitivity, low cost, and high speed to investigate its effects on the human body is very valuable in analytical laboratories.

Potentiometric sensors were widely applied as straightforward, selective, and sensitive devices for determining the activity of various metal ions in real samples. The most advantages of these sensors for the metal ion measurement include high speed, simple operation and preparation, long lifetime, non-destructiveness of the sample solution, small size, simple and straightforward automation, and reusability [7-9]. In the potentiometric sensors, an indicator electrode's potential versus a reference electrode is determined to measure metal ion activity in a sample solution. Carbon paste electrodes (CPEs) are desirable indicator electrodes for preparing potentiometric sensors with unique properties such as straightforward preparation, easy application, wide potential window, high chemical stability, good reproducibility and repeatability, low chemical consumption, short response time, and low ohmic resistance [10-12]. The CPE performance for an analyte determination is usually enhanced by selecting appropriate components in the CPE composite, including the type of binder, ionophore, and nanomaterials [13-16].

Due to the special physicochemical properties of Nanomaterial, such as ordered structure with high surface-to-volume ratio, ultra-light weight, excellent mechanical strength, high electrical conductivity, high thermal conductivity and chemical performance, this structure developed for utilized as a modifier agent in CPEs The using of nanomaterials can enhance the CPE ability through generating high potential stability, resistance to various external factors, and straightforward sensor miniaturizes [17-20].

Ionophore has the highest effect on CPE to interact with an analyte. The selectivity, lifetime, and sensitivity of CPE are dependent on its chemical structure and interaction type with the analyte [21,22]. Therefore, the synthesis of an appropriate ionophore is essential for CPE's success in determining the analyte. The ionophore acts as a complexing agent to interact with the analyte through electrostatic attraction, hydrogen bonding, cation- π -stacking interaction, etc. [23,24]. Obviously, the functional groups on the ionophore play a crucial role in interacting the ionophore with an analyte selectively. Nanomaterial was also utilized as a modifier agent in CPE for enhancing the CPE ability through generating high potential

stability, resistance to various external factors, and straightforward sensor miniaturizes [25]. Another development in CPE is the use of ionic liquids as a binder that modifies the CPE properties by increasing its electrical conductivity and flexibility compared to traditional binders such as paraffin oil [26].

The slope and linear range obtained for the analyte determination using a CPE is affected the percentage of the CPE components [12]. Thus, the amount of CPE components has been optimized with one factor at a time or experimental design procedure [27,28].

The performance of electrochemical sensors and electrodes is highly dependent on the materials and components used in their design. Therefore, it is important to optimize electrode components to achieve the desired performance characteristics, such as sensitivity, selectivity, and stability. Experimental design is a powerful tool for optimizing electrode components because it allows for the systematic variation of multiple factors simultaneously while minimizing the number of experiments required. By using experimental design, researchers can identify the most important factors affecting electrode performance and determine the optimal levels of these factors to achieve the desired performance characteristics. Experimental design can also be used to study the interactions between different factors affecting electrode performance. Furthermore, experimental design can help to reduce the time and cost required for optimizing electrode components. By using a systematic approach, researchers can minimize the number of experiments required and reduce the amount of trial and error typically associated with traditional optimization methods. Overall, the use of experimental design is essential for optimizing electrode components and achieving the desired performance characteristics in electrochemical sensors and electrodes. Experimental design can reduce the number of tests, cost, and study time [29,30]. The CPE Components with a meaningful effect on the CPE's slope for the analyte measurement and the impacts of interactions between components can also be investigated in this method [31].

A potentiometric sensor as a sensitive and straightforward device was introduced for Mn²⁺ ion determination in environmental water and biological samples. Four components, including graphite powder, ionic liquid, ionophore, and multi-walled carbon nanotube, were utilized to prepare CPE as an indicator electrode. The percentage of the CPE components was optimized by an experimental design based on an optimal mixture design. Effects of the component percentage and their binary interactions were also evaluated in the design. Several critical parameters on the CPE performance for the Mn²⁺ ion determination, such as response time, pH, lifetime, and sensor selectivity, were studied. The sensor was utilized to analyze real water and urine samples, and the results were compared with the flame atomic absorption spectrometry.

2. EXPERIMENTAL SECTION

2.1. Chemical and instrument

Graphite powder, Manganese (II) nitrate hydrate, Paraffin oil, and all nitrate salts (using for the CPE selectivity study) were obtained from Merck >98% (Germany). 1-butyl-3-methyl imidazolium tetrafluoroborate ([Bmim][BF₄]) was purchased from Sigma Aldrich >98% (USA). Multi-walled carbon nanotubes, amino-functionalized multi-walled carbon nanotube, and carboxyl-functionalized multi-walled carbon nanotube were obtained from US Research Nanomaterials, >90% Inc. (USA). A pH meter (model 691, Metrohum, Switzerland) was applied to adjust the pH of the sample solution and measure the sensor potential. A saturated calomel electrode (Azar Electric Co., Iran) and the prepared carbon paste electrode were used as a reference electrode and indicator electrode for the Mn^{2+} ion determination, respectively. The atomic absorption measurements were performed using AA990F model (PG Instruments, Britain) and hallow cathode lamps (PG Instruments, Britain) was used with emitting wavelength of Mn (257.61 nm).

2.2. Carbon paste electrode preparation

A mixture of four components under optimization percentages, including graphite powder (1.0898 g), multi-walled carbon nanotubes (0.3000 g), ionic liquid (0.2074 g), and ionophore 5,5'-((2E,2'E)-2,2'-(1,2-diphenylethane-1,2-diylidene)bis(hydrazin-1-yl-2-ylidene))bis (4-amino-4H-1,2,4-triazole-3-thiol) (BBP, 0.4008 g), Figure 1, was poured into a porcelain mortar and mixed for 30 min using a pestle. A metal rod (5 mm of ID and 3.0 cm of length) was thoroughly and carefully filled with the obtained uniform paste to prepare CPE. The prepared paste was completely compressed inside the rod to prevent the formation of air bubbles inside the metal rod and increase the CPE electrical resistance. A Pt wire was applied for an electrical connection between the carbon paste inside the rod and the pH meter. The provided CPE was immersed into the Mn²⁺ ion solution $(1.0 \times 10^{-2} \text{ M})$ under stirring at 300 rpm for 24 h before its application.

The potentiometric study for the Mn^{2+} ion determination was performed using the following cell:

Hg|Hg₂Cl₂; KCl (saturated) || Mn²⁺ ion sample solution | Carbon paste electrode



Figure 1. Chemical structure of BBP

3. RESULTS AND DISCUSSION

3.1. The CPE composite optimization

3.1.1. Carbon nanotube and its derivatives

Multi-walled carbon nanotubes (MWCNTs) and two derivatives were selected as modifier agents in the CPE composite. For this purpose, three CPEs were prepared using graphite powder (65.0%), BBP (15.0%), paraffin oil (10.0%), and MWCNTs or each its derivatives (COOH-MWCNTs or NH₂-MWCNTs) (10.0%). A CPE was also prepared without increasing MWCNT and its derivatives with graphite powder (75.0%), constant BBP, and paraffin oil percentages to compare with three designed CPEs (Table 1). The best response was obtained in the presence of MWCNTs as a modifier agent. Obviously, MWCNT and its derivatives can enhance the CPE conductivity and modify the CPE ability to determine Mn^{2+} ion by increasing the CPE linear range. The MWCNT also showed a better response than its derivatives in the CPE composite for measuring Mn^{2+} ion due to reducing the conductivity properties of these derivatives, including carboxyl and amine function groups. Therefore, MWCNT was selected as the best modifier agent for further investigation.

СРЕ	Modifier agent	Linear range (M)	Slope (mVdecade ⁻¹)	R ²
1		1.0× 10 ⁻⁴ - 1.0× 10 ⁻²	19.63±0.87	0.765
2	MWCNT	1.0×10^{-5} - 1.0×10^{-2}	26.71±0.59	0.935
3	COOH- MWVNT	1.0×10^{-5} - 1.0×10^{-2}	23.11±0.67	0.891
4	NH ₂ -MWCNT	1.0×10^{-5} - 1.0×10^{-2}	24.31±0.73	0.895

Table 1. Effects of MWCNT and its derivatives on the CPE response

3.1.2. Binder type

Ionic liquids (ILs) and paraffin oils are two types of non-volatile solvents that are commonly used in the fabrication of ion-selective electrodes (ISEs) and electrochemical sensors. However, ILs have several advantages over paraffin oils, which make them more efficient in sensor fabrication. One of the main advantages of ILs is their high ionic conductivity. ILs are salts that are liquid at room temperature, and they typically have a much higher ionic conductivity than paraffin oils. This high conductivity allows for faster ion transport between the electrode and the solution being measured, resulting in faster response times and improved sensor performance. Another advantage of ILs is their wide electrochemical window. The electrochemical window is the range of voltages that can be applied to the electrode without causing unwanted chemical reactions or breakdown of the electrode or solution. ILs have a wider electrochemical window than paraffin oils, which allows for the use of higher voltages and a wider range of measurement conditions. ILs also have a

lower viscosity than paraffin oils, which allows for easier electrode fabrication and better contact between the electrode and the solution being measured. Additionally, ILs have a higher thermal stability than paraffin oils, which makes them more suitable for use in high-temperature applications. Overall, the higher ionic conductivity, wider electrochemical window, lower viscosity, and higher thermal stability of ILs make them more efficient than paraffin oils in sensor fabrication. These advantages allow for improved sensor performance, faster response times, and wider measurement conditions [32,33].

Component		Name	Units	Туре	Minimum	Maximum
А	Graphite powder		%	Mixture	50	65
В	Ν	IWCNTs	%	Mixture	5	15
С	Io	nic liquid	%	Mixture	10	15
D		BBP	%	Mixture	20	30
Run	Α	В	С	D	Slope(n	nVdecade ⁻¹)
1	61.3	8.5	10	20.2	2	28.48
2	50	6.8	15	28.2	3	32.81
3	50	12.9	12.4	24.7	3	31.41
4	56.8	8.8	10	24.4	3	30.61
5	57.3	10.1	12.6	20		28.8
6	56.8	8.8	10	24.4	3	80.61
7	55	15	10	20	29.03	
8	55.1	5	11.7	28.2		32.3
9	54.3	6.2	15	24.5		30.9
10	52.7	9.1	11.7	26.5	3	31.86
11	50	10	10	30	3	33.53
12	52.8	10.7	15	21.5	2	29.85
13	50	12.9	12.7	24.7	3	31.47
14	50	12.9	12.4	24.7	3	31.41
15	55.1	5	11.7	28.2		32.3
16	57.3	10.1	12.6	20		28.8
17	50	15	15	20	2	29.53
18	65	5	10	20	2	28.03
19	60.7	5	10	24.3	3	30.18
20	58.4	5	15	21.6	2	29.33

Table 2. The optimal mixture design for the optimization of CPE composite

Two CPEs were prepared using an ionic liquid ([Bmim] [BF₄]) or paraffin oil as a binder. The composites of both CPEs included graphite powder (65.0%), BBP (15.0%), MWCNT (10.0%) and [Bmim][BF₄], paraffin oil (10.0%). The CPE based on [Bmim][BF₄] or paraffin oil showed linear ranges of $5.0 \times 10^{-5} - 1.0 \times 10^{-2}$ and $1.0 \times 10^{-5} - 1.0 \times 10^{-2}$ M, and slopes of 26.93 ± 0.51 and 26.71 ± 0.59 , with R² of 0.939 and 0.935, respectively. Thus, the use of ionic

liquid ($[Bmim][BF_4]$) improved the CPE quality to determine Mn^{2+} ions by increasing the sensor conductivity, faster repose time and wonder dynamic range.

3.1.3. Optimal mixture design

The percentage of the CPE components was evaluated and optimized using an experimental design based on an optimal mixture design. The percentage range of each CPE component, experimental runs, and the obtained slope (response) were presented in Table 2. The slope of each CPE was determined by plotting the calibration curve for the standard solution of Mn^{2+} ions in the concentration range of 1.0×10^{-5} - 1.0×10^{-2} M. The results were investigated by analysis of variance (ANOVA) at a 95 % confidence limit (Table 3). The p-value is a suitable and straightforward parameter in the ANOVA table to evaluate and determine the significance of components or their interactions in Mn^{2+} ion measurement. Factors with smaller p-values (<0.05) were considered more significant than those with larger p-values. This allows researchers to prioritize the factors that have the greatest impact on the outcome of interest.

Each CPE component or binary interaction with a p-value lower than 0.05 at a 95% confidence limit was considered a significant variable in measuring Mn^{2+} ions. A linear mixture of CPE components was a critical variable, indicating that all components in the CPE composite have a considerable effect on Mn^{2+} ion determination. Two binary interactions, including the interaction between the amount of graphite powder and BBP (AD) and the interaction between the amount of MWCNTs and BBP (BD), have a p-value lower than 0.05, and so are significant variables. The results indicated that ionophore (BBP) is a critical component in the CPE composite with highly significant effects due to its meaningful impacts on the linear mixture of CPE components and binary interactions. The provided model based on the slope analysis is a considerable parameter because its p-value is lower than 0.05 and the lack of fit is also nonsignificant (p-value of 0.7351).

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significant
Model	56.20	9	6.24	199.16	< 0.0001	+
Linear Mixture	55.54	3	18.51	590.42	< 0.0001	+
AB	0.0324	1	0.0324	1.03	0.3333	-
AC	0.1046	1	0.1046	3.34	0.0977	-
AD	0.3244	1	0.3244	10.35	0.0092	+
BC	0.0472	1	0.0472	1.50	0.2481	-
BD	0.1600	1	0.1600	5.10	0.0475	+
CD	0.0732	1	0.0732	2.33	0.1575	-
Residual	0.3136	10	0.0314			
Lack of Fit	0.1115	5	0.0223	0.5517	0.7351	-
Pure Error	0.2021	5	0.0404			
Cor Total	56.52	19				

Table 3. The ANOVA results for investigating the obtained slopes



Figure 2. Three-dimensional surface plots for the Mn^{2+} ion determination

The obtained model can describe using a quadratic equation in the design to determine the relationship between the CPE component percentage and its slope as follow:

Slope=+31.59770A+7.62397B+200.50021C+145.63651D+46.68625AB-263.43123AC-148.77290AD-190.40886 BC-133.23559 BD-240.10069CD Eq.1

R squared and adjusted R squared are two simple parameters to evaluate the model fit with the obtained slope. The R squared and adjusted R squared for the obtained equation for Mn^{2+} ion determination is 0.994 and 0.989, respectively, indicating that the model fitted with the obtained slope well. The equation showed that two CPE components, including the amount of ionic liquid and ionophore, have the highest effect on the sensor slope because of their high and positive coefficients in the equation. All binary interactions have a negative impact on the

CPE slope because their coefficients are negative in the equation except the interaction between the amount of graphite powder and MWCNTs (AB). Three-dimensional surface plots of the CPE are shown in Figure 2. In each graph, the effects of simultaneous changes of three components on the CPE slope are shown, while the fourth component is fixed at a specific value. The optimum percentage of the CPE components was predicted using the obtained model and equation. The slope was considered in the range of 28.5-29.5 to determine their optimum percentage. The optimum amount of graphite powder, MWCNTs, ionic liquid, and BBP were 54.59, 15.00, 10.37, and 20.04%, respectively, with a predicted slope of 29.05 mVdecade⁻¹ at a 95% confidence limit.

3.2. Figure of merit

The calibration curve for the Mn^{2+} ion determination was drawn using the prepared sensor with the optimum percentage of the CPE components. The standard aqueous solutions of Mn^{2+} in the range of 1.0×10^{-9} - 1.0×10^{-1} M were utilized to draw the calibration curve. The linear range was in the concentration range of 1.0×10^{-7} - 1.0×10^{-1} M with an R-squared of 0.986. The obtained slope for the prepared CPE to measure Mn^{2+} ions was 28.54 ± 0.26 mVdecade⁻¹ with a limit of detection of 3.1×10^{-8} M at 23.0 ± 0.8 °C.

3.3. pH effect

The performance of potentiometric sensors can be affected by the pH of the sample solution. The change in pH can affect the interaction between the analyte and the sensor by changing the analyte species in the sample solution and changing the surface charge of the ionophore functional groups.



Figure 3. pH Effects on the CPE response for the Mn²⁺ ion determination

Therefore, the effects of the pH on the CPE response for determining Mn^{2+} ions with a concentration of 1.0×10^{-4} M were studied in the range of 2.0-9.0. The pH of the sample solution was adjusted using nitric acid and sodium hydroxide solution (0.1 M). The results are shown in Figure 3, indicating that the sensor potential remains constant in the range of 2.8-8.2. Therefore, the prepared sensor can be applied in this pH range to measure Mn^{2+} ions without significant error.

3.4. Response time and lifetime

The response time is a crucial parameter to apply the sensor for commercial use. The response time was determined based on the IUPAC definition. For this purpose, the sensor was immersed into a series of Mn^{2+} ion standard solutions with a ten-fold difference in concentration. Then, the time required to reach 95% of the equilibrium potential as response time was determined. The Mn^{2+} concentration was selected in the range of 1.0×10^{-7} - 1.0×10^{-2} M to determine the static response time. According to Figure 4, the response time for the Mn^{2+} ion determination with the prepared sensor was founded to be five s.



Figure 4. Response time of the sensor for the Mn^{2+} ion determination

The sensor stability to determine Mn^{2+} ions was investigated based on the study of the sensor lifetime. The sensor slope and R-squared for the Mn^{2+} ion determination at a concentration range of 4.0×10^{-7} - 1.0×10^{-2} M were determined weekly. After using the sensor, it was rinsed with distilled water and stored in the dark at 24 ± 2 °C for reuse. The prepared sensor was used for 3 months. The sensor slope does not change significantly for up to 11

weeks. However, a decrease in the sensor slope may be due to the degradation of electrode components such as BBP and MWCNTs during electrode maintenance under ambient conditions.

3.5. CPE selectivity

The sensor performance to determine an analyte as a primary ion in the presence of other ions is an essential parameter and is known as the sensor selectivity. Several procedures can be used to study the sensor selectivity. The matched potential method (MPM) is a well-established technique for evaluating the selectivity of ion-selective electrodes (ISEs) in potentiometry [24]. Besides the advantage of providing quantitative measurements of the selectivity coefficient, MPM has several other advantages for ISEs selectivity evaluation. One of the main advantages of the MPM method is its simplicity and ease of implementation. MPM only requires the measurement of the electrode potential in solutions containing the analyte of interest and one interfering species, while the concentration of the interfering species is varied until the electrode potential matches that obtained in a solution containing only the analyte. This makes the MPM method a time-efficient technique for evaluating the selectivity of ISEs. Another advantage of the MPM method is its applicability to a wide range of samples and analytes. MPM can be applied to different types of ISEs, such as glass, polymer, and solid-state electrodes, and can be used to evaluate the selectivity of ISEs for a wide range of analytes, including cations, anions, and neutral species. However, the MPM method also has some limitations and disadvantages. One of the main limitations of the MPM method is that it assumes the activity coefficients of the interfering species and the analyte are identical, which may not always be the case.

Interfering ion (M)	$K^{pot}_{Mn.M}$	Interfering ion (M)	$K^{pot}_{Mn.M}$
Ca ²⁺	3.8×10 ⁻⁴	Cr ³⁺	2.8×10^{-3}
Sr^{2+}	$7.1 imes 10^{-4}$	Cu^{2+}	6.3×10^{-4}
Na^+	5.3×10^{-4}	Fe ³⁺	3.0×10^{-3}
\mathbf{K}^+	$6.9 imes 10^{-4}$	Fe^{2+}	$7.5 imes 10^{-4}$
Al^{3+}	$4.7 imes 10^{-4}$	Co^{2+}	2.7×10^{-4}
Hg^{2+}	1.2×10^{-5}	Co ³⁺	5.8×10^{-4}

Table 4. Selectivity of the sensor for the determination of Mn²⁺ ions

The MPM method also only provides a measurement of the selectivity coefficient for a single interfering species, while in real-world applications, the ISE may be exposed to multiple interfering species, which can affect the selectivity. Overall, the MPM method is a useful and widely used technique for evaluating the selectivity of ISEs in potentiometry due to its

simplicity, applicability, and quantitative measurement of the selectivity coefficient. However, it is important to keep in mind the limitations and assumptions of the MPM method and to consider other selectivity evaluation methods when evaluating ISEs for specific applications. In this study, the matched potential method (MPM) was selected to evaluate the sensor selectivity based on the calculation of the selectivity coefficient ($K_{Mn,M}^{pot}$). The selectivity coefficients for the Mn²⁺ ion determination is presented in Table 4, showing the selected ions have no significant interfering effects on the Mn²⁺ ion measurement. Therefore, the sensor can be applied to determine Mn²⁺ ions in the presence of these ions in real samples without meaningful interfering effects.

3.6. Real sample assay

The prepared sensor was utilized for determining the activity of the Mn^{2+} ions in several real samples, such as well, river water, and human urine samples. Well and river water obtained from the outskirts of Khaf (Iran) and Shast dareh River (Torbat Heydariyeh, Iran). Human urine samples were obtained from male volunteers aged 30-40 in a medical clinic (Mashhad, Iran). The reason for sampling was explained to the volunteers, and sampling was performed with their consent.

Sample	Spike	Prepared se	ensor	Atomic absorption Spectrometry		
	(M)	Found (M)	Recovery%	Found (M)	Recovery%	
Well water	0	$(7.3 \pm 0.23) \times 10^{-7}$		$(7.6 \pm 0.25) \times 10^{-7}$		
	$5.0 imes10$ $^{-6}$	$(5.51 \pm 0.16) \times 10^{-6}$	95.6	$(5.55 \pm 0.17) \times 10^{-6}$	95.8	
	$5.0 imes 10^{-5}$	$(4.96 \pm 0.14) \times 10^{-5}$	97.7	$(4.98 \pm 0.15) \times 10^{-5}$	98.1	
River water	0	$(6.4 \pm 0.21) \times 10^{-7}$		$(6.5 \pm 0.24) \times 10^{-7}$		
	5.0 imes10 -6	$(5.49 \pm 0.16) \times 10^{-6}$	95.2	$(5.53 \pm 0.18) \times 10^{-6}$	97.6	
	$5.0 imes 10^{-5}$	$(4.97 \pm 0.13) \times 10^{-5}$	97.9	$(4.97 \pm 0.14) \times 10^{-5}$	98.1	
Urine sample	0	ND^1		ND		
	5.0 imes10 -6	$(4.71 \pm 0.16) \times 10^{-6}$	94.2	$(4.76 \pm 0.18) \times 10^{-6}$	95.2	
	5.0×10 $^{\text{-5}}$	$(4.83 \pm 0.14) \times 10^{-5}$	96.6	$(4.89 \pm 0.17) \times 10^{-5}$	97.8	

Table 5. Determination of Mn^{2+} ion in well, river water, and human urine samples

¹ Not detect

All samples were analyzed with the prepared sensor without any initial sample preparation procedure and were then spiked at 5.0×10^{-6} and 5.0×10^{-5} M concentrations with standard Mn²⁺ ion solution, and their recovery was calculated. Each analysis was repeated three times. For comparison, the obtained results using the sensor were compared with the results of atomic

absorption spectrometry (Table 5). The recoveries for the Mn^{2+} determination with the sensor were in the range of 94.2-97.9% with a relative standard deviation of 2.6-3.4%. The results show that the sensor measured has a good recovery and are not significantly different from the atomic absorption spectrometry method. In addition, the relative standard deviation using the sensor is slightly better than the atomic absorption spectrometry method.

The sensor was utilized to determine the endpoint of Mn^{2+} ion titration. A standard solution of EDTA (1.0×10^{-2} M) as a titrant was prepared for titration of the Mn^{2+} ion solution (10.0 mL) with a concentration of 1.0×10^{-3} M. The titration curve is presented in Figure 5, indicating a sharp potential change near the endpoint of the titration with a suitable sigmoid shape.



Figure 5. Titration of Mn^{2+} ion solution with standard solution oF EDTA (1.0×10^{-2} M) at pH of 6.0

3.7. Comparison with other sensors

Several ion-selective electrodes were selected to compare with the prepared sensor in the term of linear range, limit of detection, pH range, response time, and lifetime [34-39]. All data are summarized in Table 6. The sensor showed a linear range equal or better than from a linear range of other sensors. LOD for the Mn^{2+} ion determination using the sensor was lower than all sensors except the sensor (No. 5). However, the detection limit obtained from the sensor does not show a significant difference with the sensor (No. 5). The sensor has a wider pH range and lower (or equal) response time to determine Mn^{2+} ions than other sensors. In addition, a suitable lifetime was obtained for the prepared sensor compared with other sensors. The comparison indicated that the ready sensor also has valuable abilities to determine Mn^{2+} ions with reasonable properties, including recoveries and relative standard deviations for real sample analysis.

No.	Linear range (M)	LOD (M)	pH range	Response time	Lifetime	Ref.
				(s)	(weeks)	
1	5.0×10 ⁻⁶ -1×10 ⁻¹		3.0-6.5	10	10	[34]
2	1.1×10 ⁻⁷ -0.8×10 ⁻¹	5.5×10 ⁻⁸			10	[35]
3	1.0×10 ⁻⁵ -1×10 ⁻¹	8.0×10 ⁻⁶	4.0-9.0	15	8	[36]
4	1×10 ⁻⁶ -1×10 ⁻¹	7.8×10 ⁻⁷	4-8	8	12	[37]
5	1×10 ⁻⁷ -1×10 ⁻¹	2.7×10 ⁻⁸	3-9	5	16	[38]
6	1×10 ⁻⁷ -1×10 ⁻¹	1×10 ⁻⁷	3.0-8.0	5	11	[39]
7	1×10 ⁻⁷ -1×10 ⁻¹	3.1×10 ⁻⁸	2.8-8.2	5	11	This work

Table 6. Comparison of the prepared sensor with other electrodes

4. CONCLUSION

A new and sensitive carbon paste electrode as an indicator electrode for the potentiometric determination of Mn^{2+} ion was introduced in the study. The percentages of the CPE components were optimized by an optimal mixture design, including twenty experimental runs. The significance of CPE components and their interactions were also investigated with the method. A synthetic ligand (BBP) was selected as a novel ionophore in the CPE composite. Effects of MWCNT and Its two derivatives, including amino-functionalized MWCNTs and carboxyl-functionalized MWCNTs as a modifier agent in the CPE composite, were evaluated, indicating the best slope was obtained using MWCNTs as a modifier agent. Paraffin oil and an ionic liquid ([Bmim][BF4]) were selected as a binder in the CPE preparation, showing that ionic liquid has a better response than paraffin oil due to an increase in electrical conductivity and flexibility of CPE. The prepared sensor can be used in a wide pH range from 2.8 to 8.2 with a suitable response time (5 s) and a long lifetime (11 weeks) for the Mn^{2+} ion determination. Also, the sensor has an excellent selectivity in the presence of other ions, leading to the proper application of the sensor for the real sample analysis.

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