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Design and Preparation of Magnesium (II) Selective Electrode Based on Novel Synthetic Ligand and Optimization by D-optimal Method

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Abstract

The utility of carbon as the base material for carbon paste electrodes has been considered for many years. In this work, we applied MWCNT as a modifier and Schiff base chitosan and 5-nitro isatin as ionophores along with carbon. Prepared CPE shows a Nernstian response of 29.567 mV per decade in a wide linear dynamic range of 1.0×10^{-5} to 1.0×10^{-1} M for Mg^{2+} ion. The optimization process was performed by Mixture design in the design expert software. This present sensor has a short response time of about 10 s. The applicable pH range was obtained 3.51-9.0 and the Detection limit was calculated 1.4×10^{-5} M. Lastly, the prepared sensor was used in the indirect potentiometry (potentiometric titration) as an indicator or working electrode. The data obtained from the experiments showed that the electrode was usable in analytical applications.

Keywords: Mg^{2+} ion, Potentiometry, Experimental design, Mixture design, Carbon paste electrode (CPE), D-optimal.

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Introduction

Magnesium ion, as an alkaline earth metal ion, plays a fundamental role in activities such as biological [1], industrial [2], foods [3], and many more. Magnesium is a metal used to protect other metals from corrosion. In addition, it has many applications in the aerospace industry due to its good strength, stiffness, and lightweight. In the structure of the dry battery and reverse cell battery are applied to [2] seafood, fish, meat, and mineral water are also magnesium sources [3]. This ion had determined via various methods in the past decades. Some methods include Atomic Absorption spectroscopy methods [4-6], electrochemical methods [7-9], and others [10, 11]. Among these methods, electrochemical methods are simple, cheap, and available. Many ion-selective electrodes [12] for Magnesium have been reported so far [13-17].

Schiff bases are compounds that form good complexes with metals due to the presence of oxygen and nitrogen atoms and have recently been highly synthesized and used [18-20]. Schiff bases are used as ionophores in the manufacture of sensors [20, 21]. The role of Schiffs in the construction of sensors is related to the fact that due to the existence of special functional groups, it forms selective complexes with cantions.

Carbon paste electrodes (CPEs) are one type of ion-selective electrode [22-24] that have many applications [25-33]. CPEs are composed of graphite as a base material for electrodes, paraffin oil, or similar materials as plasticizers and modifiers (e.g., MWCNT or other nanomaterials) [34, 35]. Multivariate optimization was applied by design expert software. One of the optimization methods is mixture design. In the Mixture is the sum of total ingredients 100%. Generally, the mixture design method applies to mixture formulation [36]. In this study, a D-optimal mixture design was applied. The advantage of the D-optimal configuration is the immethodical experimental region, not simplex [37]. This design has a low number of runs compared with other designs and therefore less costly tests [38].

Experimental

Materials and Methods

The high purity graphite, size of 1-2 μm had bought from Merck (Germany). 95% purity MWCNT with 10-40 nm diameter had purchased from Research Institute of the Petroleum Industry (Iran). The pure Paraffin oil and analytical grade of other materials such as salts obtained from Merck (Germany) or Aldrich (US) companies. A new synthetic Schiff base of chitosan and 5-nitro isatin [39] as ionophore was used in this work (Figure 1). All aqueous solutions were prepared with double-distilled water (Padina Company, Iran).

For the potentiometric measurements, we applied Metrohm 691 pH/mV meter along with a saturated calomel electrode (SCE) as an external reference electrode. All statistical calculations were carried out on a computer with 8 GB memory and an Intel Pentium 7 3.07 GHz CPU. The Design Expert 7 software was used for experimental designs, statistical evaluation, and model fitting in this work.

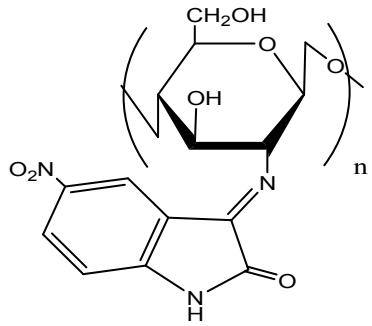


Figure 1. Chemical structure of Schiff base chitosan and 5-nitro isatin.

Preparation of modified CPE

Similar to previous works, the specified amount of paraffin, ionophore and MWCNTs was weighed and mixed. The mixture of these materials was placed in a metal or Teflon tube with a metal end. This tube had a 5 mm inner diameter and 3 cm height. After the full mixture packing, a conductor wire was inserted into the other end of the tube, for establishing an electrical connection. To varnish the electrode's outer surface, it was used on soft sanding to create a new surface by socking the electrode in 1.0×10^{-2} M cation solution for 24 hours**.**

The method of measurements

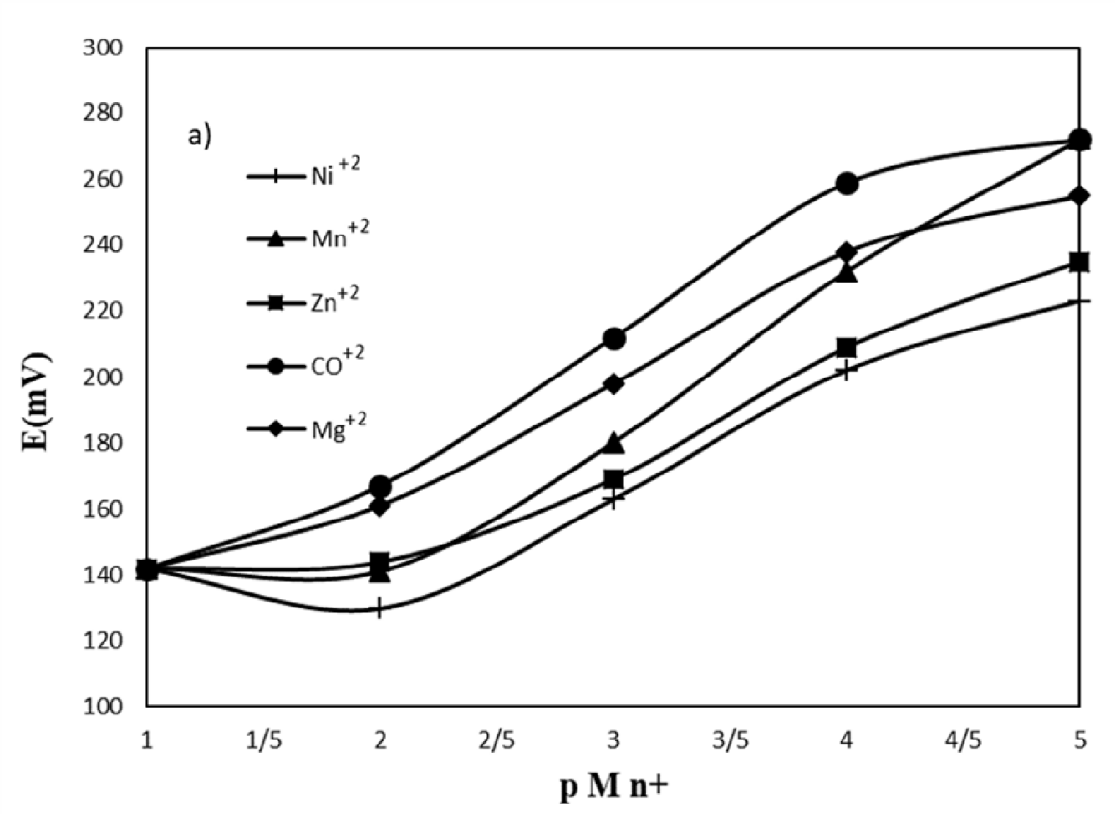
In this work, the whole experiment was implemented at a constant temperature (about 25°C). The following cell is applied:

MCPE/test solution of Mg^{2+}/ SCE

The solutions of cations such as Mg^{2+}, Ni^{2+},pb^{2+},…were prepared and diluted from 1×10^{-2} to 1×10^{-10} M by serial dilution. The performance of MCPE was checked by potential measuring of solutions from diluted to dense next to be constant potential. The experiment started as a continuation of the introduction on the previous page.

Results and discussion

One of the highly effective parameters of selectivity is a type of ionophore [40]. In the primary experiments, to study the selectivity of prepared CPE, some CPEs with specified compositions were prepared and different cations were determined. Results are exhibited in Figure 2 (a, b). Because of the existence of oxygen (O) and Nitrogen (N) atoms in ionophores, this ligand forms a powerful complex with alkali, alkaline earth, or intermediate or heavy metals. This Schiff base is coordinated to metal through its carbonyl oxygen and azomethine nitrogen and acts as a bidentate ligand (Figure 3). This CPE shows an acceptable response matching the Nernst equation. The reason for this behavior can be the reaction between magnesium cation as a soft acid and the CN group in the ligand as the soft base. Those reactions resulting from hard-hard and soft-soft interactions are more desirable than mixed reactions of hard-soft reactants. In addition, the presence of aromatic rings and л electrons causes a stable complex to form.



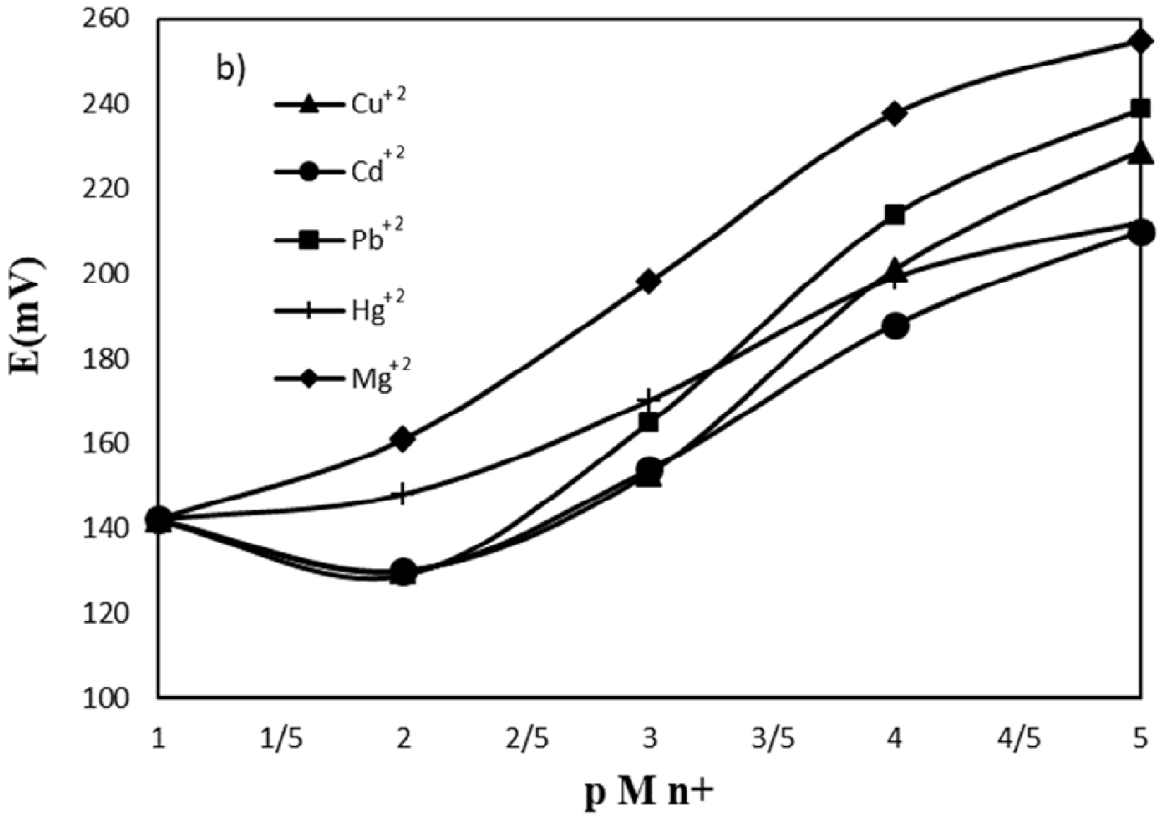
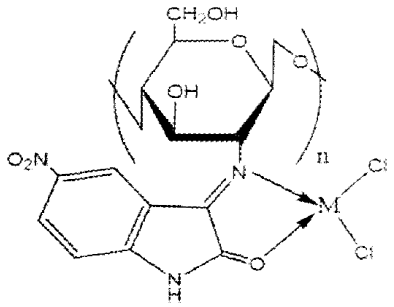


Figure 2. Comparison of the behavior of various cations on the carbon paste electrode.



$[M(L)Cl_2]$

Figure 3. Coordinated style of ligand to metal ion M^{2+}.

Optimization process

Inspired by research on CPE electrodes, in this project all test conditions were considered almost constant, and only the composition of the electrode changed. There are two methods to optimize the composition of the electrode percentage, which also have an excellent effect on the electrode response [41]. In this work, the multivariate optimization method was used instead of the one-variable-at-the-time method (OVAT). One of the advantages of the

experimental design is studying the interaction between the factors. Another advantage is using few tests to optimize many factors. Both advantages can save time and money [42]. The design and model carried out in this work are Mixture and D-optimal, respectively. The amounts and levels of the 4 factors as low (–) and high (+) had represented in Table 1.

The applied four factors in this work were accidentally designed in 20 runs. The table of design and the average of 3 times repetition of response for each run are reported in Table 2. For 5 runs can be seen the Nernstian response, and the other 5 runs can show a near-Nernstian response. The special cubic models expressed an empirical relationship between response and input variables. It can define coded (1) and uncoded (2) values according to the following equations:

The final equation in terms of l_pseudo components:

Slope= -28.14 * A -183.23* B +31.50 * C +30.00* D+558.82* A * B +92.85* A * C +96.27 * A * D +268.71 * B * C +241.64 * B * D -39.00 * C * D -608.91* A * B * C -419.62 * A * B * D +12.52 * A * C * D +130.41 * B * C * D

(1)

The final Equation in Terms of Actual Components:

Slope = -20.45260 * Graphite -74.84619 * Paraffin -95.41216 * Ligand -61.73006 * MWCNT +1.77762 * Graphite * Paraffin +2.13496 * Graphite * Ligand +1.54416 * Graphite * MWCNT +4.4774 * Paraffin * Ligand +3.14520 * Paraffin * MWCNT -0.58325 * Ligand * MWCNT -0.076114 * Graphite * Paraffin * Ligand -0.052452 * Graphite * Paraffin * MWCNT+1.56468E-003 * Graphite * Ligand * MWCNT+0.016301 * Paraffin * Ligand * MWCNT

(2)

Table 1. Presentation of the effective factors on the composition of carbon paste electrode in D-optimal design.

Factors	Sign	Unite	Low(-)	High(+)
Graphite	A	%W/W	50	60
Paraffin	B	%W/W	25	30
Ligand	C	%W/W	5	25
MWCNT	D	%W/W	0	20

Table 2. The mixture matrix for the components of carbon paste with the responses.

std	Run	A: Graphite	B: Paraffin	C: Ligand	D: MWCNT	Slope
7	1	55	30	15	0	24
16	2	50	25	5	20	29.9
2	3	50	30	20	0	28.2
9	4	60	27.5	12.5	0	26
10	5	50	25	5	20	30.1
20	6	50	30	5	15	22
15	7	52.5	27.5	16.875	3.125	30.5
17	8	60	30	5	5	32
18	9	60	27.5	12.5	0	25
6	10	50	25	15	10	21
3	11	50	25	25	0	32
8	12	55	27.5	5	12.5	32
11	13	55	27.5	11.25	6.25	29.5
4	14	60	30	5	5	31
19	15	50	25	25	0	31
5	16	50	30	5	15	22
12	17	55	25	20	0	34
1	18	60	25	5	10	25
13	19	50	30	12.5	7.5	24.2
14	20	60	25	10	5	22.9

For this work, ANOVA (analysis of variance) had obtained in Table 3. This Table indicates the effects of interaction between the factors on the response. As shown in Table 3, the factors with a p-value < 0.05 at 95% confidence level are statistically significant. Accordingly, total binary interactions (AB, AC, AD, BC, BD, CD) are significant. Triple factors such as ABC and BCD are significant, too. The R^2, R^2-(adj) and R^2-(pred) for the models were obtained as 0.9952, 0.9847, and 0.9808, respectively.

The results were fitted with the cubic model. Optimal values for all factors (paraffin, MWCNT and Ligand) were estimated (Table 4). Contour diagram that shows the relationship between three variables (percentage of Graphite, percentage of Paraffin, percentage of Ligand) was exhibited in Figure 4.

Table 3. The obtained ANOVA table for this model.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	313.53	13	24.12	95.2	< 0.0001	significant
Linear Mixture	28.98	3	9.66	38.13	0.0003	
AB	11.95	1	11.95	47.16	0.0005	
AC	18.29	1	18.29	72.18	0.0001	
AD	10.45	1	10.45	41.25	0.0007	
BC	13.29	1	13.29	52.46	0.0004	
BD	10.88	1	10.88	42.96	0.0006	
CD	76.25	1	76.25	300.99	< 0.0001	
ABC	12.32	1	12.32	48.63	0.0004	
ABD	2.12	1	2.12	8.38	0.0275	
ACD	0.11	1	0.11	0.45	0.5271	
BCD	12.01	1	12.01	47.41	0.0005	
Residual	1.52	6	0.25			
Lack of Fit	2.41E-06	1	2.41E-06	7.94E-06	0.9979	not significant
Pure Error	1.52	5	0.3			
Cor Total	315.05	19				

Ta**ble 4.** The optimum amounts obtained by mixture design and the estimated slope by the software.

Factors	Graphite	Paraffin	Ligand	MWCNT	Detection Limit	Predicted Slope	Obtained Slope
Optimum amount	55	27.5	11.25	6.25	1.4×10^{-5}	29.499	29.567

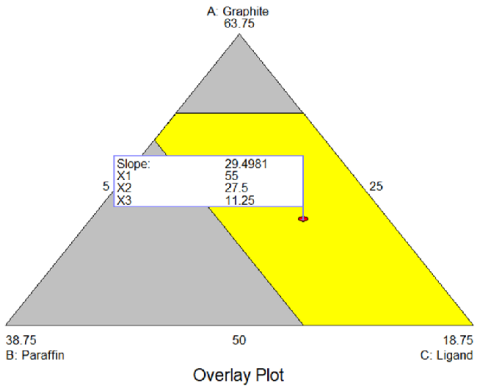


Figure 4. Contour diagram of relationship between three variable, (A)percentage of Graphite (B) percentage of Paraffin (C) percentage of Ligand.

Calibration graph

Based on the linear dynamic range, CPE response was drawn at a range of 1×10^{-8} - 1×10^{-1} M. Some of CPEs were prepared based on Table 4 and investigated in this range. The linear range was obtained from 1.0×10^{-5} to 1.0×10^{-1} M. Nernstian response was 29.5mV/decade in this range, too. The detection limit was gained as 1.4×10^{-5} M (Figure 5).

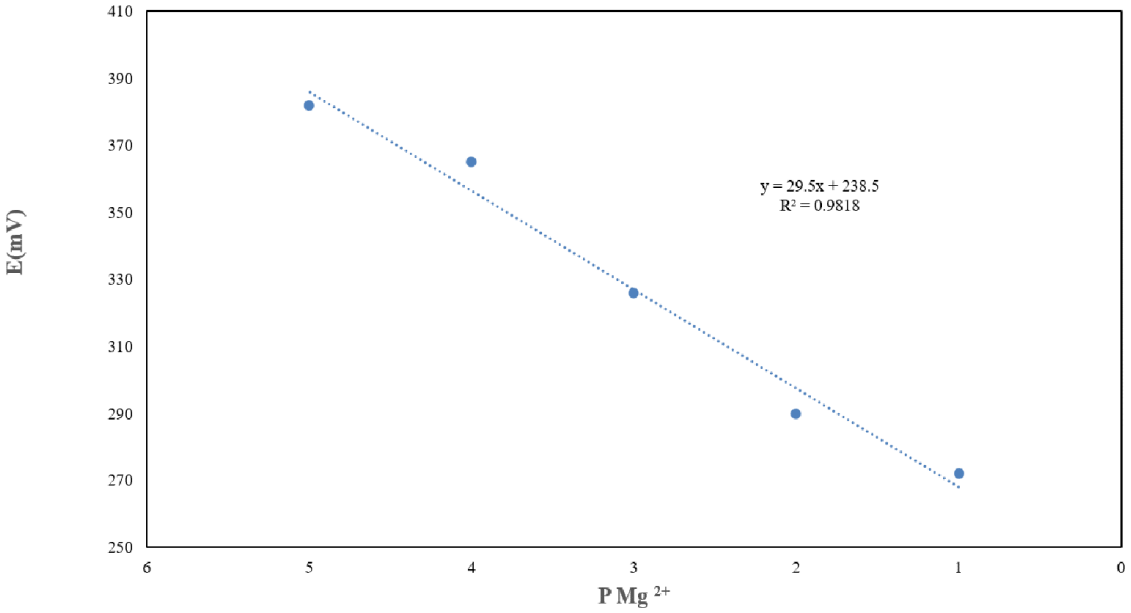


Figure 5. Calibration graph for prepared Mg/CPE.

pH effect

One of the most important parameters in the behavior of CPE is pH. Therefore, the pH of Mg^{2+} cation solution was adjusted by NaOH or HNO_3 1.0 M. pH was studied in the range of 1 to 12 for solutions of Mg^{2+}. As viewed in Figure 6, pH was constant and independent of potential in the range of 3.51-9.0. Potential changes in high pH values may be due to the formation of Magnesium hydroxide precipitates. In low pH or acidic medium, ionophores can protonate and respond to H^+ ions. In other words, the electrode selectivity decreased to magnesium (Figure 6).

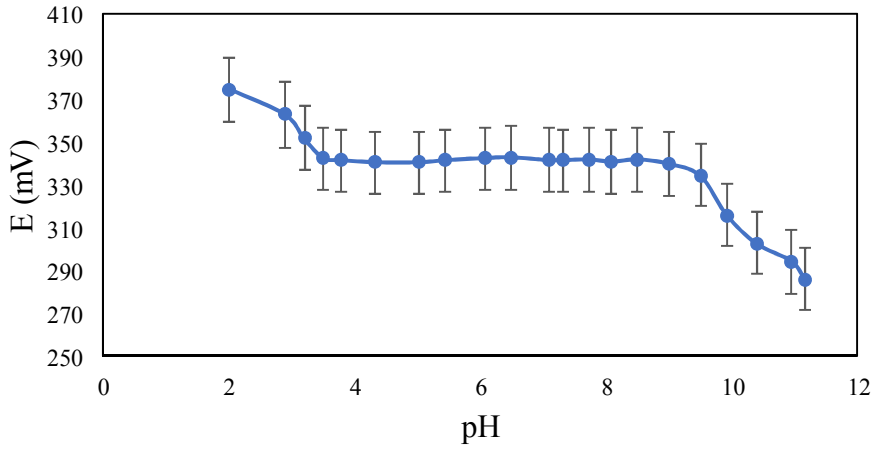


Figure 6. The chart of pH effect on the Mg/CPE.

Effect of dynamic response time

The response time is a vital factor in the analytical application of electrodes. This factor was defined as the time required for the electrode potential to reach 90% of the final value after being immersed in a series of solutions with a concentration difference of 10-fold [43]. As seen in Figure 7, response time was about 10s at the range of 1×10^{-5} to 1×10^{-1} M for Mg/CPE. In this study, repeatability and reproducibility were assessed, too. Repeatability and stability were obtained by examining the response of an electrode for five consecutive weeks. On the other hand, reproducibility was gained via checking the answer of the five electrodes on one day. The relative standard deviation (RSD) for five successive tests of response Mg/CPE was 2.1 and while the electrode stayed at room temperature, Mg/CPE retained 98% of its initial response after a week and 95% after five weeks. Results indicated that prepared Mg/CPE has acceptable reproducibility and good stability.

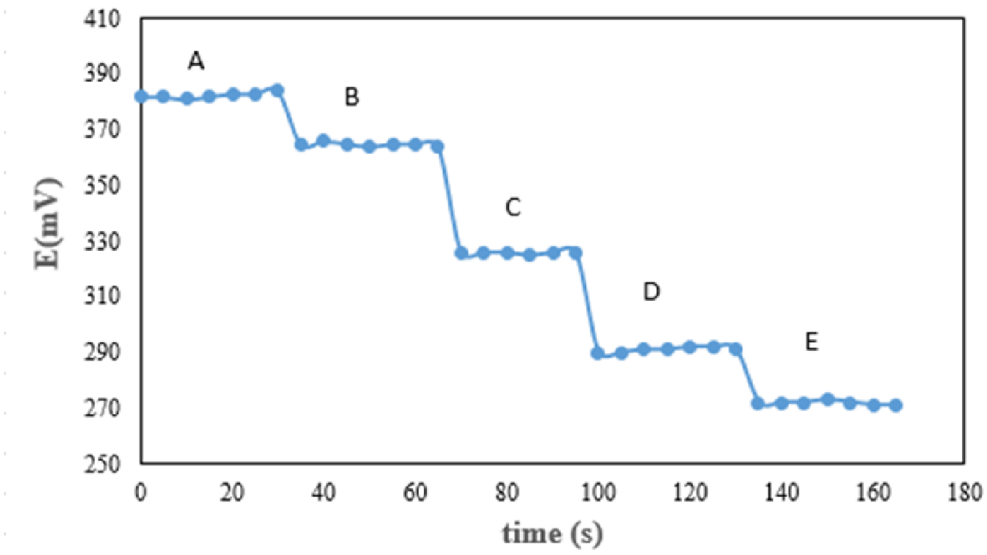


Figure 7. The chart of Dynamic response time for Mg/CPE. (A: 1.0×10^{-5}, B:1.0×10^{-4}, C: 1.0×10^{-3}, D:1.0×10^{-2}, E:1.0×10^{-1} M).

Selectivity

We applied matched potential method (MPM) to research the effect of interfering ions on the response of the electrode. According to this method, a certain concentration of the primary ion was added to the reference solution (1.0×10^{-5} M of Mg^{2+}), and the potential was determined. In the other paper, interfering ions (X) was gradually added to a similar solution, until to be observed the same potential changes. Table 5 designed the selectivity coefficients of Mg/CPE.

Table 5. Selectivity coefficients ($K^{MPM}_{Mg^{2+}}$) of MCPE.

J(Interfering ion)	$K^{pot}_{Ag,J}$
Hg^{2+}	4.10×10^{-4}
Mn^{2+}	1.56×10^{-3}
Ni^{2+}	8.91×10^{-3}
Co^{2+}	1.02×10^{-3}
Cd^{2+}	1.32×10^{-4}
Cu^{2+}	1.06×10^{-4}
Ag^{+}	1.40×10^{-3}
Zn^{2+}	2.65×10^{-2}
Pb^{2+}	1.02×10^{-3}

$k_{MPM\ Mg2+,\ X} = a_{Mg}/a_{X,}$ X= interfering ion

Potentiometry titration

To investigate the method performance, potentiometry titration was used to evaluate the efficiency of the method. Mg/CPE was applied as an indicator electrode in titration with EDT. The potential changes were measured during the addition of 1.0×10^{-2} M EDTA solution to 10.0 mL of 1.0×10^{-3} M Mg^{2+} solution. According to Figure 8, Mg/CPE can be used in measuring Mg^{2+} ions.

Real sample analysis

We studied the determination of Mg^{2+} in real samples such as river and tap water. As Table 6 shows, via spiking different concentrations of magnesium ions into the matrix of river water and tap water, an acceptable recovery percentage was obtained. The results also showed good accuracy and reproducibility. The potentiometry method by carbon paste electrode as indicator electrode was a routine and simple method for measuring alkaline and alkaline earth elements. Results for Mg^{2+} had shown in Table 6.

Table 6. Evaluation of the efficiency of Mg/CPE compared to tap and river water samples.

Matrices	Added (mol/L)	Founded(mol/L)	(%RR)	Relative standard deviation(%RSD)
Tap water	0	-	-	-
	2.0×10^{-3}	2.01×10^{-3}	100.5 %	**±3.2**
	1.0×10^{-5}	1.02×10^{-5}	102.0%	**±1.5**
River water	0	-	-	-
	2.0×10^{-3}	1.99×10^{-3}	99.5 %	**±1.9**
	1.0×10^{-5}	0.98×10^{-3}	98 %	**±2.4**

Experimental Method Verification

The relative standard error (RSE) is a parameter to express the accuracy of the obtained data. The RSE had calculated via the slope obtained from the experiment and comparison of software.

$$\text{RSE},\% = \frac{\text{Actual value} - \text{Predicted value}}{\text{Predicted value}} \times 100$$

The optimum values of carbon paste have a non-significant difference between predicted and actual values. The model is acceptable as the RSE is very small.

Comparison of this work with other works

For studying the performance of this sensor with previous sensors, some properties such as sensing agent, Nernstian slope, Linear range, Response time, pH range in between 2008 to now were examined.

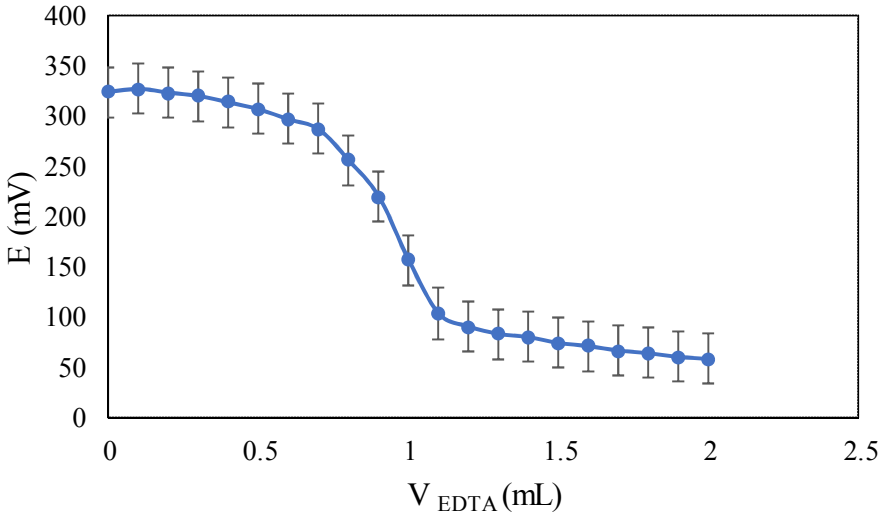


Figure 8. The titration graph for 10 mL of Mg^{2+} aqueous solution by 1.0×10^{-2} M EDTA in the presence of Mg/MCPE as indicator electrode.

A summary of the most relevant sensors for this task had given in Table7. Compared to other sensors, this sensor has an exceptional Nernst slope, suitable linear range, and short response time. The linear range is comparable to many other sensors. Although in a small number of sensors, a much higher linear range has been reported [44, 45]. On the other hand, the present work has advantages such as easy operation, cheap materials, fast response (short response time) and long lifetime, and superior sensitivity.

Table7. Comparison of performance of prepared sensor with other sensors previously provided.

Sensing Agent	Nernestian slope (mV/decade)	Linear range	LOD	Response time	pH range	year	[Reference]
Schiff base chitosan and 5-nitro isatin	29.567	1×10^{-5} - 1×10^{-1}	1.4×10^{-5}	10 s	3.51-9.0	-	This work
Chitosan Schiff base	29.83	1×10^{-8} - 1×10^{-3}	4.4×10^{-9}	10 s	3.5-9.0	2020	[44]
Methyl phenyl semi carbazone	28.4	1×10^{-8} - 1×10^{-1}	1.7×10^{-9}	<10 s for $\geq1.0\times10^{-3}$ and <15 s for $\geq1.0\times10^{-6}$	1.0-9.5	2013	[45]
Magnesium salycilate	28	1×10^{-5} - 1×10^{-1}	-	-	4.0-9.18	2014	[46]
polypyrrole doped with Titan yellow dye	28.27	1.0×10^{-5}– 5.0×10^{-2}	6.28×10^{-6}	<10 s	4.5-8	2014	[47]
5,10,15,20-tetrakis(2-furyl)-21,23-dithiaporphyrin	30 ±1.0	9.2×10^{-6}– 1.0×10^{-1}	8.0×10^{-6}	15 s	4-8.4	2011	[48]
4,5-Bis(benzoylthio)-1,3- dithiole-2-thione (Bz2dmit)	29.2	1×10^{-5} - 1×10^{-1}	1×10^{-5}	<10 s	3.5-9	2008	[49]

Conclusion

This Mg/CPE is composed of MWCNT as a modifier, Schiff base chitosan and 5-nitro isatin as an ionophore in a membrane, and additionally carbon and paraffin. MWCNTs are one of the carbon materials because the high surface-to-volume ratio increased mechanical and chemical stability and electrical conductivity. CPEs have numerous advantages over other electrodes, including low ohmic resistance, constant response and easy renewability. The Results presented Mg/CPE with a combination percent of Graphite 55: Paraffin 27.5: Ligand 11.5: MWCNT: 6.25 as convenient for the measuring of Mg^{2+} in a wide linear dynamic range. Acceptable selectivity was obtained that distinguishes the electrode from pre-made electrodes. Further research is needed to reduce costs, increase linear range, and use new and specific modifiers that are selective to a particular species.

Acknowledgments

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