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Optimization of a cerium (IV) carbon paste electrode based on 2-hydroxy-1, 4-naphthoquinon / MWCNTS by using experimental design

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Box–Behnken designs were used as experimental design method to optimize the influence of ingredients of membrane on the electrode performance. A nanocomposite was designed by using *2-hydroxy-1, 4-naphthoquinon* as ion carrier with multi-wall carbon nanotubes (MWCNTs), in order to determination of Ce(IV). Box–Behnken response surface was led to find a model for optimizing the response**.** The best performance was obtained with 5 % wt of lawsone, 10 % wt of MWCNTs, 20 % wt of paraffin oil and 65 % wt of graphite powder. The optimized membrane electrode shows a Nernstian response (15.08±0.2 mV decate^{-1}) toward Ce(IV) ions in linear range from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} with a detection limit of 5.0×10^{-8} mol L^{-1}. The proposed sensor was employed in pH range of 4 to 8 with a fast response time (10 s). The electrode revealed good selectivity with respect to many cations including alkali earth, transition and heavy metal ions. The designed sensor was used as an indicator electrode in potentiometric titration of Ce(IV) with EDTA and also applied for determination of cerium content in real samples.

Keywords: Box-Behnken design, ion selective electrode, multi-wall carbon nanotubes, potentiometry, lawsone

INTRODUCTION

Cerium is the most abundant of the rare earth elements making up about 0.0046 % of the earth's crust by weight. Commercial applications of cerium are abundant. They include catalysts, additives to fuel to reduce emissions and to glass and enamels to change their color. Cerium is considerably distributed in many biological, industrial and environmental systems as a pollutant. Cerium will be dispersed mainly in the environment via the oil production industry. In aquatic animals, cerium causes to damage to cell membranes, which has several negative influences on reproduction and function of nervous system. Cerium is dangerous in the workplace because its gas is inhaled with air and caused the lung embolisms. Especially if it inhalants for a long time, Cerium will cause lung cancer. Finally when it accumulates in the human body, it damages to liver [1-2].

Cerium its application is growing, so there are serious needs to the cerium sensor for measuring of different samples [2-4]. There are some techniques for determination of cerium cation such as inductively coupled plasma-atomic emission spectrometry (ICP-AES), electrothermal atomic absorption spectrometry, spectrofluorometry, ICP-AES/HPLC, stripping voltammetry and inductively coupled plasma-mass spectrometry (ICP-MS), that these methods are time consuming and expensive [3]. But potentiometry methods have many advantages such as, simple, rapid, inexpensive, ease of preparation, relatively fast response, wide linear range and reasonable selectivity.

Carbon paste electrode is one kind of ion selective electrode that has some advantage over other membrane electrodes such as renewability, stable response, low ohmic resistance, no need for internal solution. Because of these merits using of carbon paste electrodes have increased day by day in various fields [5-7].

Lawsone (*2-hydroxy-1*, *4-naphthoquinone*) is a natural pigment that is red-orange dye and exists in henna leaves. Lawsone is also known as hennotannic acid. People have been used lawsone as a natural dye for coloring of hair and hands, for more than 5000 years. Lawsone reacts chemically with a protein in hair and skin (known as keratin), according to a Michael addition reaction, resulting in a strong permanent dye that lasts for a long time.

Lawsone, strongly absorbs ultraviolet light and its extracted aqueous solution, can be effective in tanning of skin and hair, in the absence of sunlight. The structure of Lawsone is shown in Fig. 1 [8, 9].

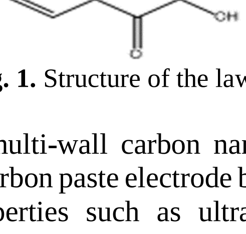

Fig. 1. Structure of the lawsone

Nowadays multi-wall carbon nanotubes use in fabrication of carbon paste electrode because of their interesting properties such as ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or

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semi-metallic behavior and high surface area, ordered structure with high aspect ratio [10].

An experimental design is a plan for assigning experimental units to treatment level and the statistical analysis associated with the plan. The advantages of this method compared to optimization over univariate (one-at-a-time) as follows: faster, more effective and economical. Simultaneous optimization of several variables is possible in this method. Among the experimental design methodologies, Box–Behnken design as a response surface was useful in modeling and optimizing the effective parameters on the electrode performance [11-19].

In this research, we used statistical design of experiment for optimization of a Ce (IV) selective carbon paste electrode which is based on *2-hydroxy-1, 4-naphthoquinon*. The ultimate goal of this research was to study the interaction of factors and modeling the slope of calibration curve as analytical response. So the effect of main factors such as ionophore (lawsone), modifier (multiwall carbon nanotubes), and pH were investigated and optimized.

EXPERIMENTAL

Materials

The graphite powder, with a < 50μm particle size (Merck) along with the paraffin oil (Aldrich) was of high purity and was used for the fabrication of different carbon paste electrodes. The multi-walled carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length was purchased from Research Institute of Petroleum Industry (Iran). Chloride and nitrate salts of the cations were purchased from Merck. Co. The Lawsone (*2-hydroxy-1, 4-naphthoquinone*) were purchased from Sigma–Aldrich. Deionized water was used for preparing all of the solutions

Instrumentation

The electrochemical cell contained a silver–silver chloride double-junction reference electrode (Azar electrode) as a reference electrode and the cerium(IV) sensor as an indicator electrode. The Schematic figure is as follows:

Ag-AgCl (saturated) | sample solution | Carbon paste electrode**.**

After EMF is calculated, calibration curve is drawn by plotting potential, versus, the logarithm of the concentration of the cerium ion. The activities of the ionic species were calculated according to the Debye–Hückel procedure

Carbon paste electrode preparation

Desired amount of *2-hydroxy-1,4-naphthoquinon*, graphite powder, paraffin oil and MWCNT were thoroughly mixed and then transferred into a glass tube, of i.d. 5 mm and a height of 3 cm. After the mixture was uniform as well as possible, to avoid the formation of air gaps, the paste was packed carefully in to the tube. This can prevent an increased in the electrical resistance of the electrode [20]. Then electrical contact was made by inserting a copper wire in to the opposite end. The working surface of the electrode was polished by using soft abrasive paper.Then, the electrode was conditioned for 24 h by being soaked in a 1.0×10^{-3} mol L^{-1} of $(NH_4)_2Ce(NO_3)_6$ solution.

Experimental designs strategy

A Box–Behnken response surface design (RSM) was used for optimizing the significant factors. The results were analyzed using MINITAB 17 for windows.

RESULTS AND DISCUSSION

Potential response of the electrode

The main component of any ion selective electrode is ionophore that influences on its selectivity. With due attention to structure of lawsone, we selected it as ionophore.

So we prepared a number of electrodes and applied them for various metal ions. The curve of potential response of electrode for various ions under identical condition is plotted. Results are shown in Table 1. As can be seen, the slope of the potential versus log[M^{n+}] plot is sub nernstiant for all other ions with narrow linear range.

Ionophore has high selectivity for cerium(IV) ions over other ions. The resulting Ce(IV)-ionophore (lawsone) complex has rapid exchange kinetics and membrane show Nernstian response toward Ce(IV) over a wide concentration range.

Optimization using response surface methodology

Box-Behnken design (BBD) was used in order to analyze levels of factors and study interaction effects between them and optimize parameters. The number of experiments (N) required for development of BBD is defined by Eq. (1).

(1)

In Eq. (1), k is the number of factors and C_0 is the number of central points.

Three factors pH (X_1), ionophore amount (X_2) and the amount of modifier (X_3) were designed in a matrix shown in Table 2 and runs at 15 trials (3 center points) which were shown in Table 3. These factors were chosen in three levels of -1, 0, and 1 for low, middle and high values [21-22].

Table 1. The slopes and r^2 for plot of potential, versus, the logarithm of the concentration of some cations.

Metal ions	Slope, mV decate^{-1}	R^2
Co(II)	17.50	0.9546
Mg(II)	11.29	0.9816
Pb(II)	20.63	0.9707
Cu(II)	37.94	0.9740
Ni(II)	36.60	0.9771
Cd(II)	16.29	0.9638
Zn(II)	18.94	0.9724
Hg(II)	20.14	0.9869
Ce(IV)	14.00	0.9946

Table 2. Factors and levels used in the Box–Behnken design.

Independent value	Symbol	Coded level		
		-1	0	1
pH	X_1	4	6	8
Ionophore, % wt	X_2	5	10	15
Modifier, % wt	X_3	5	10	15

Table 3. Box–Behnken design matrixes.

Trial number	X_1 (pH)	X_2 (ionophore)	X_3 (modifier)	Response (slope, mV decate^{-1})	R^2
1	8	10	15	26.12	0.9731
2	4	15	10	5.20	0.9245
3	6	5	5	21.15	0.9820
4	6	10	10	21.80	0.9763
5	8	5	10	8.00	0.9691
6	6	5	15	26.40	0.9432
7	4	5	10	10.46	0.9685
8	4	10	5	15.08	0.9824
9	6	15	5	32.82	0.9547
10	8	10	5	32.25	0.9730
11	4	10	15	26.80	0.9429
12	6	15	15	26.45	0.9765
13	8	15	10	25.78	0.9132
14	6	10	10	20.05	0.9858
15	6	10	10	21.94	0.9813

The multiple regression analysis on the resulted response led to the following second-order polynomial equation which explains the relation of electrode response (slope, mV.decate^{-1}) with significant factors and interactions.

$$\begin{aligned} Y &= -28.42 + 16.68X_1 + 1.216X_2 - 3.306X_3 - 1.318X_1^2 - 0.1452X_2^2 \\ &+ 0.3629X_3^2 + 0.5760X_1X_2 - 0.4463X_1X_3 - 0.1162X_2X_3 \end{aligned} \tag{2}$$

In Eq. (2), Y is the predicted value of response electrode, X_1, X_2 and X_3 are the coded values of pH, Ionophore amount and modifier value, respectively.

Analysis of variances (ANOVA) was used to study adequacy of the model. It was also tested using Fisher's statistical analysis (Table 4).

Table 4. Analysis of variance for suggested second order model.

Source	DF	Adj SS	Adj MS	F	P
Regression	9	964.936	107.215	64.91	0.000
Residual error	5	8.258	1.652		
Lack-of-fit	3	6.040	2.013	1.82	0.374
Pure error	2	2.218	1.109		
Total	14	973.194			

With due attention to model F value (64.91), we know that model is significant. Since P-value of model was 0.000, so model F value could accuer due to be noise and model has high significance. Result of analysis of variance show that p value for lack of fit (0.374) was not significant and regression was meaningful [11-13]. Coefficient of determination (R^2) appraises goodness of fit for this model, which determines better correlation between the observed and predicted values. In this case, fitting was very well (R^2 = 90 %). Value of adjusted regression coefficient (97.62 %) showed high significant of the proposed model. Also residual should have normal distribution. Normal probability plot was generated using Anderson-Darling test. It performs hypothesis test, which examine whether the observations follow a normal distribution. P-value of test ($0.333 > 0.05$) shows that null hypothesis cannot reject and residual have normal distribution. The interaction between investigated factors is shown in Fig. 2. (a-c). Existence of interaction show that factors may affect on response together. Combined effect is less or greater that of expected for the straight addition of the effect [23-24].

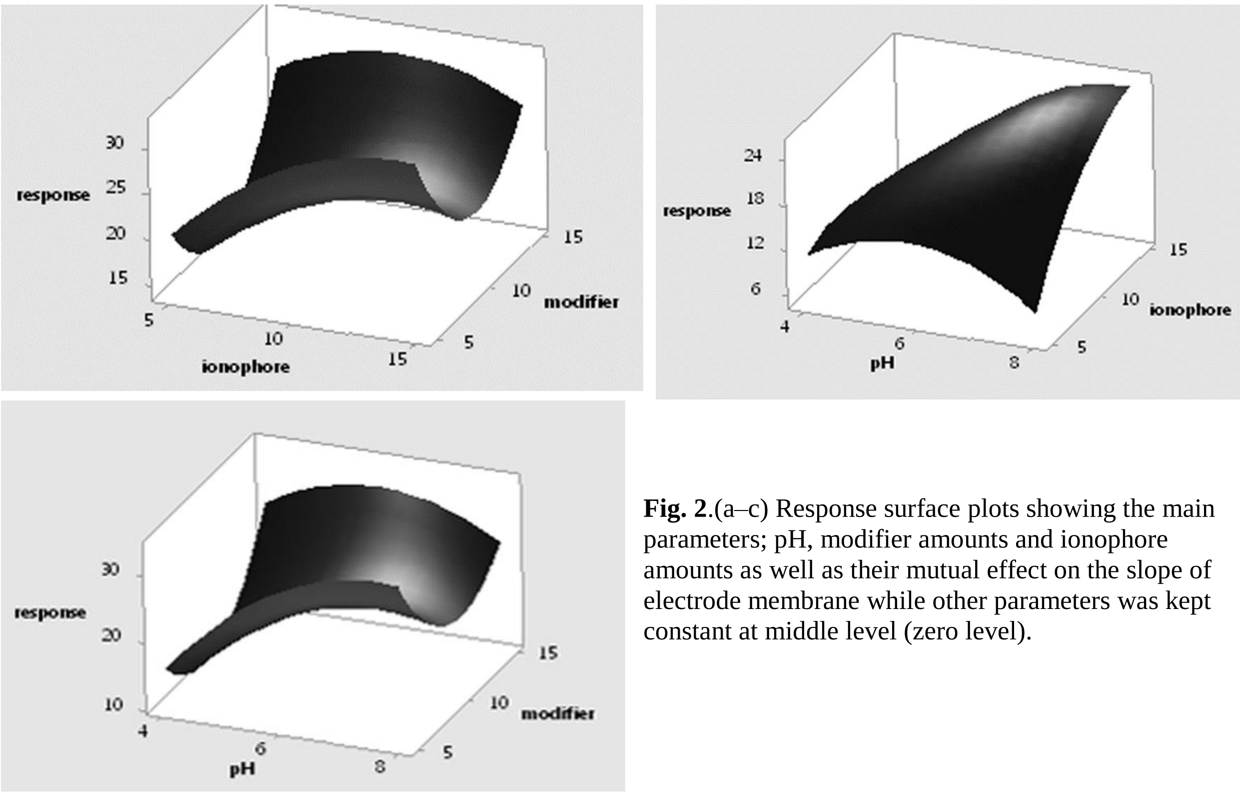

Fig. 2.(a–c) Response surface plots showing the main parameters; pH, modifier amounts and ionophore amounts as well as their mutual effect on the slope of electrode membrane while other parameters was kept constant at middle level (zero level).

Determination of optimal conditions

Response surface plots were drawn as three-dimensional plots of two factors while the other factors were kept constant [25-26]. Also the constant variable is selected at its middle level. (Fig. 2. (a-c)), show the interactions between the pH, modifier and ionophore are significant. Also the best experimental values were given for every parameter by using toolbox in MAPLE. The optimum value for response of electrode (15.08) was obtained when pH, ionophore and modifier were 4, 5 % wt, 10 % wt respectively.

Calibration curve

Solutions with concentration of 1.0×10^{-1}-1.0×10^{-8} of cerium ions were ready and potential of solutions were measured. Potential against thelogarithm of the concentration of cerium ions were plotted. The results are shown in Fig. 3. (a-b).

The results show that the linear range of Ce-CPEs is from 1.0×10^{-2} to 1.0×10^{-7} M. As well as, the detection limit of the CPE was determined by extrapolating the linear portions of the fabricated electrode’s calibration curve [27] and was 5.0×10^{-8} M. The standard deviation for five replicate measurements was ±0.2 mV.

Influence of pH

It is essential to find pH ranges in which electrode works without bothering of the hydrogen ions. For this purpose, the sensor was test by using 1.0×10^{-3} M Ce(IV) solution in the pH range of 2-11. Sodium hydroxide and nitric acid were used to adjust of pH. As can be seen in Fig. 4, potential response remains constant in the pH range of 4 to 8.

The observed drift in EMF at pH values higher than 8 could be attributed to formation of hydroxyl complexes of Ce(IV) ions which cause to reduce the free cerium ions in solution, while drift at pH lower than 4, that arising from protonation of the hetero atoms of ionophore, such as oxygen. As a result, the capability of lawsone to formation of complex with cerium ions decreased in the solution [28].

Response time

The response time of the CPEs was calculated from the average time the CPEs took to produce potential values within ±0.1 mV of their steady-state potentials after successive immersions in a series of solutions, each having a 10-fold concentration difference [29]. In addition, a series of factors affect the response time like, type and speed of stirring, preconditioning of the electrode, the concentration and composition of each solution and temperature. Experiments show the response time of Ce-CPE is less than 15 s

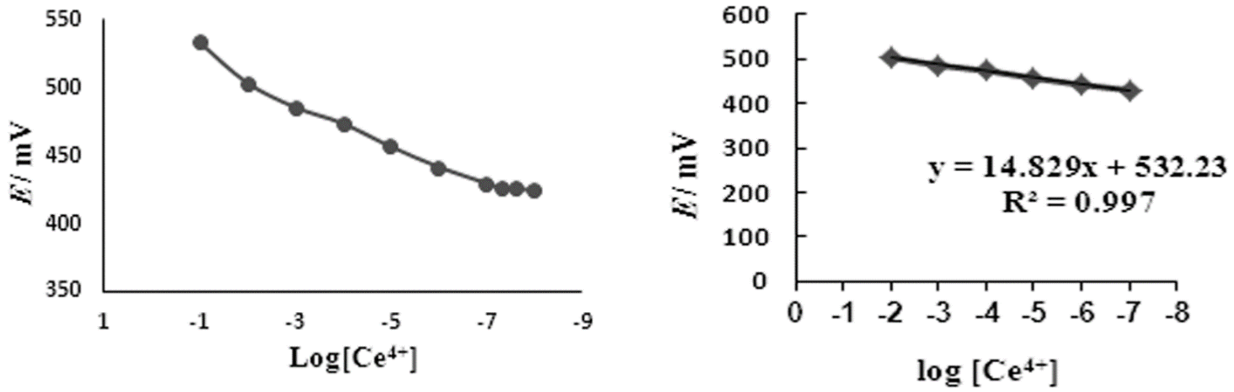

Fig. 3 (a) Calibration curve of cerium selective carbon paste electrode, (b) Dynamic range.

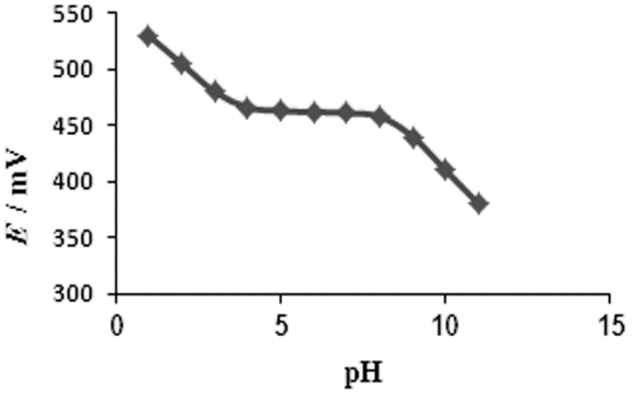

Fig. 4. pH effect on the potential response of the Ce^{4+} modified CPE.

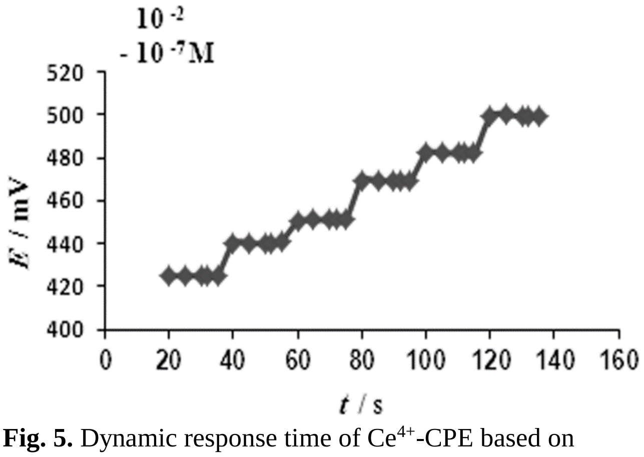

Fig. 5. Dynamic response time of Ce^{4+}-CPE based on Lawsone.

Potentiometric selectivity

Selectivity coefficient explains the effect of interfering ions on response of the ion-selective electrode. In this work, we measured selectivity coefficient by matched potential method [30, 31]. According to this method, a specified activity (concentration) of primary ions is added to a reference solution, and the potential is measured. In other experiment, interfering ions (B) are added to an identical reference solution, until the measured potential matches that obtained before the addition of primary ions. In this method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio:

(3)

In Eq. (3), a_A is primary ion activity (concentration) and a_B is interfering ion activity (concentration).

The resulting selectivity coefficients are listed in Table 5 that show that selectivity coefficient of Ce-CPE in the presence of the various interfering ions is in the order of 1×10^{-2} or less. As a result, there is a good performance of the fabricated CPE toward the Ce(IV) and interaction between Ce(IV) and lawsone is effective.

Table 5. Selectivity coefficients of various ions for cerium selective carbon paste electrode

Interference	*K* $_{MPM}$	Interference	K $_{MPM}$
Cu^{2+}	5.2×10^{-3}	Ca^{2+}	7.7×10^{-4}
Pb^{2+}	5.7×10^{-3}	Zn^{2+}	5.7×10^{-3}
Al^{3+}	6.2×10^{-4}	Ni^{2+}	5.4×10^{-3}
Na^{+}	5.1×10^{-4}	Co^{2+}	5.3×10^{-3}
K^{+}	4.7×10^{-4}	Cd^{2+}	2.3×10^{-3}
Mg^{2+}	6.7×10^{-4}	Hg^{2+}	5.8×10^{-3}
Cr^{3+}	2.0×10^{-2}	La^{3+}	4.2×10^{-2}

Lifetime study

The life time of the designed electrode was studied for a period of 8 weeks. In this period, the sensor was used for one hour per day and the variations in its slope were measured. As can be seen in Table 6, the Ce-CPEs can be used for at least 8 weeks, without significant changes in the slope. After this period, the slope decreases and the detection limit increases. This can be attributed to the loss of lawsone from the CPEs as a result of application over time [32].

Analytical application

To evaluation the practical application of the designed Ce^{4+}-CP electrode, it was used as an indicator electrode to measure the cerium(IV) ion in potentiometric titration of 25 ml 1.0×10^{-3} mol L^{-1} Ce(IV) solution with 1.0×10^{-2} mol L^{-1} EDTA.

As can be seen in Fig. 6, by increasing the amount of EDTA, potential values reduced because of cerium formed complex with EDTA, as a result, the free cerium (IV) concentration decreases in sample solution. So the sharp obtained titration curve proved the performance of this electrode to play a role as an indicator electrode.

To investigate the performance of designed electrodes in measuring of cerium in a real sample, it was used of standard addition method, and results were compared with atomic absorption spectroscopy.

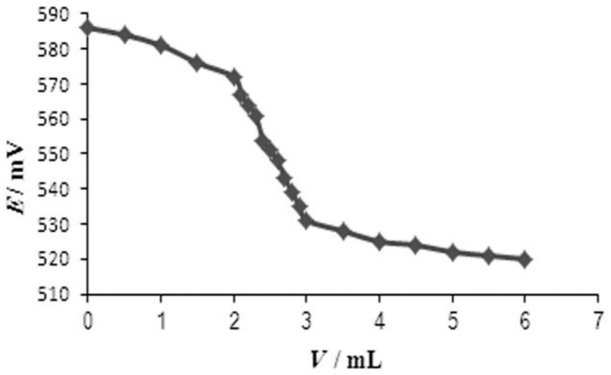

Fig. 6. The curve of titration Ce^{4+} with EDTA.

Peak height for calculation mode and the background correction (deuterium lamp) was applied for atomic absorption during all measurements. As can be seen in Table 7, the cerium contents obtained from triplicate measurements were found to be in satisfactory agreement with those obtained by atomic absorption spectroscopy.

Table 6. Lifetime of Ce(IV) nanocomposite CPE.

Time	Week 2	Week 4	Week 8
Slope	14.71	14.40	13.97
R^2	0.998	0.9969	0.9955

Table 7. Results of cerium determination in real sample.

Sample	Concentration of Ce(IV) mg L^{-1}	Concentration of Ce(IV) mg L^{-1} (added)	Result of ion selective electrode, mg L^{-1}	Result of atomic absorption spectroscopy, mg L^{-1}	Efficiency
Tap water	-	27.41	27.20	27.30	95
Tap water	-	5.48	5.15	5.32	93

CONCLUSION

The new sensor for determination Ce(IV) was built by using *2-hydroxy-1, 4-naphthoquinon* (as carrier) and MWCNT (as modifier). Also Box-Behnken design was used as an efficient method to optimize the main factors for preparation of electrode and test the effect of factors' interaction. The fabricated sensor with optimized structure has many advantages such as wide linear range, low detection limit, fast response time, good selectivity with respect to different metal ions in pH range from 4 to 8. As well as, it was used for determination Ce(IV) sample water and potentiometric titration Ce(IV) with EDTA. To the best our knowledge there is no other report on determination of Ce(IV) with potentiometric electrode.

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