Multiwall Carbon Nanotubes Modified Carbon Paste Electrode for Determination of Copper(II) by Potentiometric and Impedimetric Methods

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Abstract

A chemically modified carbon paste electrode with multiwall carbon nanotube (MWCNT) was prepared and used as a sensor for Cu\textsuperscript{2+} ion. The unique chemical and physical properties of CNT have paved the way to new and improved sensing devices. A central composite chemometrics design was applied for multivariate optimization of the effects of three significant parameters (Graphite powder ($X_1$), MWCNT ($X_2$) and Ionophre ($X_3$)) influencing the response of the electrode. In the optimized conditions, the electrode exhibits a Nernstian slope of 30.1 mV/decade in a linear range between $1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M over a wide pH range (2.0-6.5). Importantly, the effect of the MWCNT on the performance of electrode was investigated by impedance technique, that showed the MWCNT helps the transduction of the signal in carbon paste electrode and the charged transfer resistance ($R_{ct}$) was reduced. The impedimetric results indicated that the linear concentrations range was $1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$ M and in comparison with potentiometry, the pH range increased to 2.0-7.5.

Article history:
Received 13/7/2012
Accepted 28/10/2012
Published online 1/12/2012

Keywords:
Multiwall carbon nanotube
Carbon paste electrode
Electrochemical impedance
Response surface methodology
Central composite design
1. Introduction

The importance for trace analysis for copper arises primarily in environmental and biological sciences since copper, is an essential element and is also toxic at high concentration [1, 2]. Copper is one of the most widespread elements in the environment of industrialized countries. Due to many applications of copper in industry [3], in many biological systems [4], and in medicinal and environmental samples, researchers have attempted to develop sensors for copper determination with high selectivity and sensitivity [5-11].

Recently, the development and application of chemically modified electrodes (CMEs) as electrochemical sensors, have received considerable attention. Among these electrodes, carbon-paste electrodes (CPEs) have been widely used as suitable matrices for the preparation of the modified electrodes mainly due to their advantages over membrane electrodes such as easy renewability, stable response, low ohmic resistance, no need for internal solution and compatibility with various types of modifiers [12-15]. The operation mechanism of chemically modified carbon paste electrodes depends on the properties of the modifier which is used for selectivity towards the target species [16, 17].

Nowadays, CNTs have been a suitable candidate for the modification of electrodes due to their significant mechanical strength, excellent electrical conductivity, high chemical stability and their high surface area [14, 16, 18-20]. The modified electrode with multiwall carbon nanotubes (MWCNTs) for use in analytical sensing exhibit low detection limit, high sensitivity and fast response due to the signal enhancement provided by high surface area, low overvoltage, and rapid electrode kinetics [21].

Graphite powder, MWCNT and ionophore are the parameters which influence on electrode response significantly. To optimize the amounts of these parameters, response surface methodology (RSM) [22] was applied. Response surface methodology is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response [23]. The methodology allows us identify and statistically evaluate the effects and interactions of the parameters and their roles in the efficiency of the treatment process. Moreover, this technique has several advantages over one-variable-at-a-time method including a reduced number of experiments, time consuming, cost-effective, and generation of large amounts of information from a small number of experiments [24].

Nowadays, electrochemical impedance spectroscopy (EIS) has played an essential role in the characterization of many types of sensors. EIS has been used to provide information on various fundamental processes that occur at the electrode–electrolyte interface [25, 26]. This method is a non-destructive steady-state technique that involves the application of signals of very low amplitude (either of potential or current) around a stationary reference state and the linear response of the system is measured over a range of frequencies. The linear frequency response analysis makes EIS very useful for studying electrochemical systems exhibiting complex non-linear behavior [27, 28].

The present work is focused on fabrication of multiwall carbon nanotube modified carbon paste electrode for determination of copper (II) and investigation of the response mechanism of the
proposed electrode by potentiometry and electrochemical impedance spectroscopy. Also central composite experimental design (CCD) was applied to fit a relevant mathematical function, and to estimate the quality of the fitted model. To the best of our knowledge, there is no previous report in literature on the use of modified carbon paste electrode with multiwall carbon nanotube and electrochemical impedance spectroscopy for determination of Cu (II).

2. Experimental
2.1. Materials

Pure graphite powder (particle size <50 μm) from Merck, high viscose paraffin oil (density = 0.88 kg L⁻¹) from Merck and multiwall carbon nanotube (10–40 nm diameters and 1–25 μm length) from Fluka, NaTPB from Aldrich and N, N'-bis(3-methylsalicylidene)-p-diphenylene methane diamine as ionophore were used for the preparation of the carbon paste electrode (CPE). Also, Copper nitrate was obtained from Merck. Hydrogen chloride (HCl) and sodium hydroxide (NaOH) were used for pH adjustment. Doubly distilled water was used for preparing of all solutions.

2.2. Synthesis of ionophore

The target Schiff-base, N,N'-bis(3-methylsalicylidene)-p-diphenylene methane diamine was synthesized from o-cresol in two steps according to the following procedure: Firstly, we were synthesized 2-hydroxy-3-methyl benzaldehyde by dissolving o-cresol (1.08 g, 10 mmol) in anhydride trifluoroacetic acid (10 mL) under N₂ atmosphere. Then hexamethylene tetramine (1.4 g, 10 mmol) was added to the mixture in one portion. The reaction mixture was refluxed until all starting cresol was converted and the mixture was then cooled to room temperature. The cooled solution was poured into 4 M HCl (30 mL) and stirred for 15 min. The product was extracted with CH₂Cl₂ (2 × 30 mL). The combined organic layer dried by Na₂SO₄ and the solvent was evaporated. The yellow residue was purified by column chromatography to give the pure product as yellow liquid:

2-hydroxy-3-methyl benzaldehyde, bp = 208 °C, IR (KBr, cm⁻¹) 750 (m), 1085 (s), 1145 (s), 1293 (s), 1670 (s), 1745 (s), 2765 (m), 2895–2990 (m), 3500–3600 (m, br); 1H NMR (CDCl₃, ppm) δ: 1.95 (s, 3H), 6.2–6.6 (d, 2H), 6.8 (s, 1H), 9.3 (s, 1H), 10.9 (s, 1H) was produced.

Then 2-hydroxy-3-methyl benzaldehyde (1.36 g, 10 mmol) was dissolved in methanol (10 mL) and then 4,4'-bis(aminophenyl)methane (0.99 g, 5 mmol) was added to the mixture solution. The resulting mixture was refluxed and stirred for 30 min. The reaction mixture was cooled to room temperature and the resulting precipitate was filtered and washed with cold methanol. The product was recrystallized from methanol to give Schiff base; N,N'-bis(3-methylsalicylidene)-p-diphenylene methane diamine (4.08 g, 94% yield) as orange yellow crystals (mp = 175-177 °C); IR (KBr, cm⁻¹) 800 (m, vinylic CH), 1140 (s), 1200 (s), 1300 (s, C=O), 1520 (s), 1550 (s, Ar C=C), 1635 (s, C=N), 2970 (m, CH), 3055 (w), 3400–3500 (m, br, phenolic OH); ¹H NMR (CD₂COCD₃, ppm) δ: 2.1 (s, 6H), 2.8 (s, 2H), 6.4–7.6 (m, 14H), 8.5 (s, 2H), 13.5 (s, 2H); MS (m/z) = 436: (M⁺ +2), 435 (M⁺ +1), 434 (M⁺), 300, 224, 165, 121 (base peak), 106, 97, 71.
2.3. Construction of the MCWNT modified CPE

General procedure for preparation of CPE-CNT is as flowing: graphite powder, MWCNT, ionophore and paraffin oil with appropriate weight mixed well usually with a mortar and pestle until a uniformly wet paste was obtained. The paste was then packed into the end of a glass tube (usually: 3-5 mm internal diameter and 3-10 cm long). Electrical contact was made by inserting a copper wire into the glass tube at the back of the mixture. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper. The electrode was finally conditioned by soaking in a solution of Cu$^{2+}$ ion. The time of conditioning and the concentration of Cu$^{2+}$ ion solution were optimized and the obtained results were respectively 8 h and 1.0 ×10$^{-2}$ M Cu$^{2+}$ ion solution.

2.4. EMF measurements

Potentiometric measurements were performed using a digital pH-ion meter (Zag Chimi, Iran, model 162). The representative electrochemical cell for the emf measurements was as follows:

Hg | Hg$_2$Cl$_2$, KCl (sat’d) | Cu$^{2+}$ (x M) | Carbon Paste Electrode | Cu

All measurements were carried out while sample solution stirred using a magnetic stirrer. The performance of the electrodes was examined by measuring the emfs of the analyte ion solutions in the concentration range from 1.0×10$^{-8}$ to 1.0×10$^{-1}$ M Cu$^{2+}$ ion solution.

2.5. Impedance measurements

EIS measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system with PGSTAT 302 boards (Eco Chemie B.V., Utrecht, Netherlands). The system operated on a PC using FRA software. The utilized three-electrode system was composed of three electrodes: An Ag/AgCl electrode (from Metrohm Co.) as reference electrode, carbon paste electrode as working electrode, and a platinum electrode (from Azar El. Iran) as counter electrode. All measurements were done while sample solution was quite static. EIS spectra were collected at the open circuit potential (OCP) using a sinusoidal excitation signal amplitude of 0.35 V through a frequency domain from 200 kHz down to 200 Hz with 40 frequency points. By fitting the obtained experimental data with the Randles equivalence circuit [29], the $R_{ct}$ and $C_{dl}$ values have been calculated. Data analysis for the impedance measurements was performed using the Z-View 2.1 software.

2.6. Design of experiment using central composite design

CCD for three independent variables was employed to optimize the amounts of factors which affect the electrode response. Three significant factors, namely graphite powder ($X_1$), MWCNT ($X_2$) and ionophore ($X_3$) amounts were studied at 3 levels with 3 replicates at the central point using faced-centered design. The range of values of each of the three independent variables was defined as shown in Table 1. Furthermore, Table 2 shows the experimental design matrix derived from CCD.

The design is a three-level full factorial with $2^f$ factorial points, perfected with additional $n_0$ center and $2f$ axial (star) points. The factorial points represent a first-order model, while center points, set to the midpoint of each factor range,
provide information about curvature existence and calculate the pure error \([23, 30]\). In addition, axial points allow estimation of the pure quadratic properties of the model \([22, 31]\). Here, the total number of experiments for the three independent variables is: \(23 + (2 \times 3) + 3 = 17\).

Table 1 Independent variables and their levels for CCD.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Name</th>
<th>Factor Level</th>
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<tr>
<td></td>
<td>Powder Graphite</td>
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<tr>
<td>X₁</td>
<td>60</td>
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</tr>
<tr>
<td>X₂</td>
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<td>6</td>
</tr>
<tr>
<td>X₃</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2 Central composite design consisting of experiments for the study of three experimental factors in coded levels with experimental results.

<table>
<thead>
<tr>
<th>Run NO.</th>
<th>Coded level of variables</th>
<th>Response Slope /mV</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1 1 1</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>-1 -1 -1</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>1 -1 -1</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>0 1 0</td>
<td>37</td>
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<tr>
<td>5</td>
<td>1 -1 0</td>
<td>39</td>
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<td>6</td>
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<td>15</td>
<td>0 0 -1</td>
<td>26</td>
</tr>
<tr>
<td>16</td>
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<td>26</td>
</tr>
<tr>
<td>17</td>
<td>0 0 -1</td>
<td>27</td>
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</tbody>
</table>

After running the 17 trials and obtaining the responses, it is customary to fit a mathematical equation to investigate the relationship between response and process variables. By RSM, a quadratic polynomial equation was used to predict the response. The mathematical model describing the data for three CCD is the following second-order polynomial function:

\[
\text{Response} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3
\]

(1)

Where \(X_1\), \(X_2\) and \(X_3\) are independent variables, \(\beta_0\) the intercept coefficient, \(\beta_1\), \(\beta_2\), \(\beta_3\), the linear terms, \(\beta_{11}\), \(\beta_{22}\), \(\beta_{33}\), the squared terms and \(\beta_{12}\), \(\beta_{13}\), \(\beta_{23}\), represent the interaction terms. The coefficients of the response surface Equation (1) were calculated by least squares regression using Minitab.v.16 software. In order to investigate the significance of each of the factors and the model fitness, analysis of variance (ANOVA) was applied. The P-values are used to determine the significance of each of the factors. Generally, the fisher’s \(F\) statistic value with low probability P-value indicates high significance of regression model \([32]\). The model fitness is justified by determining the coefficient \(R^2\).

3. Results and discussion

3.1 Interaction of the ionophore and \(\text{Cu}^{2+}\)

In order to investigate the interaction mechanism of ionophore and \(\text{Cu}^{2+}\) ion, UV-Vis spectroscopy was used. The UV-Vis spectra of the ionophore and the mixture solution of ionophore and \(\text{Cu}^{2+}\) ion were shown in Fig. 1. As shown in this figure, decreasing in absorbance density and shifting in wavelength of the mixture solution of ionophore and \(\text{Cu}^{2+}\) ion spectrum indicate that the relatively good interaction between ionophore and \(\text{Cu}^{2+}\) ion was occurred.
Fig. 1. The UV/VIS absorption spectra of the ionophore $1.0 \times 10^{-5}$ M and mixture solution of ionophore $1.0 \times 10^{-5}$ M and Cu (NO$_3$)$_2$ $1.0 \times 10^{-5}$ M.

3.2. Central composite experimental design

In order to optimize three independent variables, which influence on the electrode response, namely the amounts of graphite powder ($X_1$), MWCNT ($X_2$) and ionophore ($X_3$), central composite design with quadratic model was applied. The Nernstian slope of 29.58 mV/decade was studied as response. That experimental plan enables to obtain the following second order polynomial model by applying multiple regression analysis:

\[
\text{Slope} = 32.5549 + 2.6400X_1 + 0.2200X_2 + 4.6600X_3 + 7.4789X_1^2 - 6.2211X_2^2 - 0.7211X_3^2 - 1.7750X_1X_2 - 2.5500X_1X_3 - 0.9000X_2X_3 \quad (2)
\]

The quality of the model developed could be evaluated from their coefficients of correlation ($R^2$, adjusted-$R^2$ and predicted-$R^2$). The values of $R^2$, adjusted-$R^2$ and predicted-$R^2$ are respectively 98.65%, 96.91% and 83.87%. The value of $R^2$ for Equation (2) is 98.65% which means that the model is representative, because just about 1.35% of all deviations cannot clarify by the proposed model. The value of $R^2$ which is very close to one suggests that the predicted data from the model are comparable with experimental data with sufficient degree of accuracy [33]. The predicted responses were plotted versus the calculated one (Fig. 2) which denotes the predicted values are very closer to experimental results and the residual values are low.

Fig. 2. Relation between experimental and predicted slope values using Equation (2).

Table 3 shows the analysis of variance (ANOVA) for Equation (2). As mentioned before the P-values were used to determine the significance of each variable. Generally, P-values smaller than 0.05 signify that the model terms have a significant effect on the response at confidence level of 95% [31]. Interpreting the P-values for each variable demonstrate that the $X_1$, $X_3$, $X_1^2$, $X_2^2$, $X_1X_2$, $X_1X_3$, and $X_2X_3$ are significant and affective model terms.

3.3. Response surface and determination of optimal conditions

When a polynomial representation of a response surface is obtained, the experimenter often is interested in determining the factor levels that provide an optimum response [34]. In order to calculate the optimal points, the first derivative of the mathematical function, which describes the response surface, was equaled to zero. The
optimum conditions obtained, are: graphite powder (0.062 g), MWCNT (0.006 g) and ionophore (0.005 g).

The 3-dimensional (3D) response surface plots were drawn to illustrate the effects of the independent variables and combined effects of each independent variable upon the response variable. The response surface plot is the theoretical 3-dimensional plot showing the relationship between the response and the independent variables [35]. For instance, the response surface and counter plots for slope as a function of graphite powder ($X_1$) and MWCNT ($X_2$) were shown in Fig. 3.

The effect of MWCNT on the performance of the electrode

Electrochemical impedance spectroscopy was applied to investigate the influence of MWCNT on carbon paste electrode. So impedance measurements were done on the carbon paste electrode in presence and absence of MWCNT. When MWCNT was used in fabricating of electrode, charge transfer resistance was less than when wasn't used it ($R_{ct}$ with MWCNT: 35.515 Kohm, $R_{ct}$ without MWCNT: 185.704 Kohm). The reason of this observation is that the presence of MWCNT was caused increasing in conductivity of the electrode surface. The complex plane plot of this study (Fig. 4) confirms obtained results.

![Graph showing response surface and counter plots](image)

**Table 3.** ANOVA for response surface quadratic model (response: Nernstian slope).

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
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<th>P</th>
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<td>6.480</td>
<td>6.480</td>
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<td>0.90</td>
</tr>
</tbody>
</table>

**3.4. The effect of MWCNT on the performance of the electrode**

Electrochemical impedance spectroscopy was applied to investigate the influence of MWCNT on carbon paste electrode. So impedance measurements were done on the carbon paste electrode in presence and absence of MWCNT. When MWCNT was used in fabricating of electrode, charge transfer resistance was less than when wasn't used it ($R_{ct}$ with MWCNT: 35.515 Kohm, $R_{ct}$ without MWCNT: 185.704 Kohm). The reason of this observation is that the presence of MWCNT was caused increasing in conductivity of the electrode surface. The complex plane plot of this study (Fig. 4) confirms obtained results.

![Graph showing complex plane plot](image)

**3.5. Investigation of the electrode response**

The response of the electrode prepared with optimum values of graphite powder (0.062 g), MWCNT (0.006 g) and ionophore (0.005 g) was investigated by measuring its potential in copper (II) nitrate solutions prepared in the concentration range of $1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$ M.
Fig. 4. Complex plan plots of the carbon paste electrode with and without MWCNT. (Points and lines indicate the experimental and fitting data, respectively).

A typical calibration plot is shown in Fig. 5, which depicts a Nernstian slope of 30.1 mV per decade in a linear range from $1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M.

Fig. 5. Calibration plot of Cu$^{2+}$-MWCNT-modified-CPE at concentration range of $1.0 \times 10^{-8}$ to $1.0 \times 10^{-3}$ M Cu(NO$_3$)$_2$.

In order to investigate the response of the proposed carbon paste electrode by EIS, the concentration range of $1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$ M copper(II) nitrate solutions was used. As illustrated in Fig. 6 (a), the linear range extended to $1.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$ M. The Warburg impedance [36, 37] appeared at low frequencies showing diffusional transport of an electroactive species to the electrode surface. Moreover, further evaluation, the diagrams of the $R_{ct}$ and $-\log C_{dl}$ versus the -logarithm of the copper(II) nitrate concentration are depicted in parts (b) and (c) of Fig. 6, respectively.

Fig. 6. (a) Complex plan plots of the electrode at concentration range of $1.0 \times 10^{-10}$-1.0×$10^{-1}$ M Cu(NO$_3$)$_2$, (b) diagram of the $R_{ct}$ and (c) diagram of $-\log C_{dl}$ versus the -log of the copper (II) nitrate concentration.

3. 6. The influence of pH

The effect of pH on the potential response of the electrode was studied for $1.0 \times 10^{-4}$M Cu(NO$_3$)$_2$ solution in the pH range of 1.5–10.0. The potential of the electrode was determined as a function of pH and the results presented in Fig. 6 (a). It is seen from Fig. 7 (a) that the potential was constant and quantitative in the pH range of 2.0–6.5. Outside this range, considerable potential deviations were seen. At the pH higher
than 6.5 due to the formation of some hydroxy complexes of Cu(II) ions in solution, the potential sharply decreased. On the other hand for a pH of less than 2.0, the change of potential may be related to the response of the electrode to hydrogen ions [1].

![Fig. 7](image)

**Fig. 7.** (a) Effect of pH on the response of Cu$^{2+}$-MWCNT-modified-CPE at 1.0×10$^{-4}$M Cu(NO$_3$)$_2$. (b) Complex plan plots of the Cu$^{2+}$-MWCNT-modified-CPE at different pH values with an external solution concentration of 1.0×10$^{-4}$M Cu(NO$_3$)$_2$; (c) diagram of the $R_c$ and (d) diagram of $-\log C_{dl}$ versus pH.

Also, to investigate the effect of pH on the response of the sensor using EIS, the experiments were examined at external solution concentration of 10$^{-4}$ M Copper(II) Nitrate. The Nyquist plot related to this measurement (presented in Fig. 7 (b)), imply that no considerable change observes in the impedance spectra. In order to more study, $R_{ct}$ and $-\log C_{dl}$ versus pH changes were plotted in Fig.7 (c), which illustrates that over the pH range of 2.0-7.5 charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$) are relatively constant (Fig. 7 (d)).

### Table 4. Selectivity coefficients for Cu (II) carbon paste electrode.

<table>
<thead>
<tr>
<th>Interference ion</th>
<th>$K_{pot}$ (FIM)</th>
<th>$K_{pot}$ (SSM)</th>
</tr>
</thead>
<tbody>
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<td>Na$^+$</td>
<td>10$^{-4}$×1.35</td>
<td>10$^{-4}$×1.04</td>
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<tr>
<td>K$^+$</td>
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<td>10$^{-4}$×2.51</td>
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<tr>
<td>Ag$^+$</td>
<td>10$^{-4}$×2.15</td>
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</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>10$^{-4}$×1.74</td>
<td>10$^{-4}$×2.8</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>10$^{-4}$×4.23</td>
<td>10$^{-4}$×3.16</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>10$^{-4}$×2.15</td>
<td>10$^{-4}$×3.75</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>10$^{-4}$×2.15</td>
<td>10$^{-4}$×6.3</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>10$^{-4}$×3.24</td>
<td>10$^{-4}$×3.24</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>10$^{-4}$×1.86</td>
<td>10$^{-4}$×1.73</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>10$^{-4}$×4.28</td>
<td>10$^{-4}$×8.7</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>10$^{-4}$×2.62</td>
<td>10$^{-4}$×2.8</td>
</tr>
</tbody>
</table>

### 3.7. Determination of selectivity coefficients

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of other cations [38]. The potentiometric selectivity coefficients ($K_{ni}$) [39] for a variety of cations were obtained using the separate solution method (SSM) [40] and fixed interference method (FIM) [41]. In Table 4 the selectivity coefficients for the proposed sensor are presented. According to the results, a good
selectivity of the Cu\(^{2+}\)-modified carbon paste electrode over most interfering ions was achieved.

4. Conclusion
In this paper, a novel modified carbon paste electrode for the detection of copper (II) have constructed. MWCNTs and newly synthesized Schiff base as the effective modifier materials, was used to fabricate modified electrode. Central composite design (CCD) under Response Surface Methodology (RSM) was used to optimize the electrode components (graphite powder, MWCNT and ionophre). The constructed electrode at optimum condition (graphite powder (0.0618 g), MWCNT (0.006 g) and ionophore (0.005 g)) displayed the Nernstian slope of 30.1 mV in linear concentration range of 1.0 \times 10^{-6} M to 1.0 \times 10^{-1} M over a wide pH range (2.0-6.5). Moreover, the behavior of the proposed electrode was investigated using EIS technique. Compared with potentiometry, the impedimetric results showed an increase in linear concentration range (1.0 \times 10^{-7} M to 1.0 \times 10^{-1} M) and in the applied pH range (2.0-7.5).

Acknowledgements
We gratefully acknowledge the support of this work by Payam Noor University (PNU) of Ardakan center, IUT Research Council and Excellence in Sensors.

References