

Preparation of Modified Electrode *in situ* Carbon Paste Electrode supported by Ni(II) Complex for the Electrochemical Removal of Nitrate from Drinking Water

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A new carbon paste electrode modified by NS₂ containing Ni(II) complex was prepared for the electrochemical removal of nitrate ions from drinking water. The tripod ligand NS₂, namely: Hydro {bis(2-isopropylphenyl-2-thioimidazol-1-yl)(5-phenyl-3-methyl-pyrazol-1-yl)}borate, **L**, and its mononuclear Ni(II) complex [LNi-NO₃] were prepared and characterized in the solid state by infrared (FT-IR), thermal analysis (TA) and in solution by conductivity and ¹H NMR. The carbon paste modified electrode was prepared by the immobilization of Ni(II) complex in carbon paste. The prepared electrode was characterized using scanning electronic microscopy (SEM) and cyclic voltammetry (CV). The modified electrode showed only one oxidation peak in the anodic scan at +0.14 V (vs. Ag/AgCl) for the oxidation of Ni(II) complex. Upon addition of nitrate ions, no reduction peaks were observed while the oxidation peak current height for Ni(II) complex was decreased. This decrease in the oxidation peak current can be explained on the basis that a part of Ni(II) complex was consumed in the reduction of nitrate ions to nitrite.

Keywords: Ni(II) complex; Cyclic voltammetry; Carbon paste electrode; Nitrate removal.

1. INTRODUCTION

Environmental pollution is one of the most serious problems in the world. There are different types of environmental pollutions such as air, soil, and water. Water may become contaminated after the use of fertilizer on crops and grass fields or by animal wastes or decaying the organic matter. Nitrate (NO₃⁻) is a water-soluble molecule made up of nitrogen and oxygen. It is formed when nitrogen

from ammonia or other sources combines with oxygenated water. Nitrate is a natural constituent of plants and is found in vegetables at different levels depending on the amount of fertilizer applied and on other growing conditions. Water naturally contains less than 1.0 milligram of nitrate-nitrogen per liter and is not a major source of exposure. Higher levels indicate that the water has been contaminated. Common sources of nitrate contamination include fertilizers, animal wastes, septic tanks, municipal sewage treatment systems, and decaying plant debris. The United States Environmental Protection Agency (EPA) has set the maximum contaminant level (MCL) of 10 mg NO_3^- -N/L (45 mg/L) in drinking water [1]. The same concern in Europe put MCL of 12 mg NO_3^- -N/L in (50 mg/L) drinking water [2]. In 2004 the World Health Organization (WHO) recommends a maximum limit of 50 mg/L for nitrate concentration in drinking water [3]. The increase of nitrate level in drinking water causes algal blooms and depletion of dissolved oxygen causes of methemoglobinemia or "baby blue syndrome" and may be a source of carcinogenic [4]. So, it is very important to control the nitrate level in drinking water. There are many physical and chemical processes were applied for the removal of nitrate from water, such as ion exchange, biological denitrification, chemical denitrification and membrane separation such as reverse osmosis and electrodialysis [4, 5]. Although these methods are effective in removing nitrate ions from contaminated water, some of them not selective [6]. The relatively high capital and operating costs of these processes tends to make them uneconomic.

Removal of nitrate ions based on the electrochemical reduction is a promising route. The electrochemical technology offer different advantages such as the lack of the requirement for chemicals before or after the treatment, no sludge production, small area occupied by the plant and relatively low investment costs [7]. Two main methodologies were used for the removal of nitrate by electrochemical reductions. First: the direct reduction of nitrate (NO_3^-) at the electrode surface to nitrite (NO_2^-), to ammonia (NH_3) or nitrogen gas (N_2). Different electrode materials were used such as copper [8] copper modified electrode [9], composite copper thallium electrode [10], screen printed thick film based on graphite-epoxy composite [11], polypyrrole modified electrode [12], Pd/Sn- modified electrode, Pd/Sn/Au electrode [14], gold electrode [15, 16], Ti/PdO/Co [7], glassy carbon electrode modified with tetraethenated porphyrin [17], tin- modified palladium thin film electrode [18], Rh-modified pyrolytic graphite electrodes [19], platinum electrode [20] and nanostructured copper thin films at disposable pencil graphite electrode [21]. Second: the catalytic reduction via enzymes; the active sites of these enzymes are the catalysts for biochemical reactions. The nitrate ion was converted to nitrogen gas using a mixture of nitrate, nitrite and nitrogen oxide reductase [22]. The enzyme electrodes used for nitrate reduction were used either without modification [22] or modified with different material [4, 23-29]. Modification of enzyme for nitrate removal faced two main problems. First: the commercially available nitrate reductases that are multiredox center enzymes responsible to the biological conversion of nitrate to nitrite are generally not very active and the immobilization method used showed a deactivation of the immobilized enzyme. Second: the redox centers of nitrate reductase are deeply embedded in the protein structure, preventing the direct electron transfer with electrode [24, 30].

Based on this, the aim of this study is to synthesize a monomeric nickel (II) complex, derived from sulfur containing tripod ligand NS_2 , namely: Hydro {bis(2-isopropylphenyl-2-thioimidazol-1-yl)(5-phenyl-3-methyl-pyrazol-1-yl)}borate, **L**. This Ni(II) complex is immobilized on the surface of

carbon paste electrode. The modified electrode is characterized based on scanning electronic microscopy (SEM) and cyclic voltammetry (CV). This modified electrode is applied for the electrochemical removal of nitrate ions from drinking water samples.

2. EXPERIMENTAL

2.1. Materials and methods

All reagents were commercial grade materials and were used without further purification. Graphite powder and paraffin wax were obtained from Sigma-Aldrich. H_3BO_3 , H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 , CH_3COOH , Trizma HCl, and NaOH were obtained from Merck. Double distilled water was used for the preparation of solutions. 3-phenyl-5-methylpyrozole (pz) and N-(2,6-dimethylphenyl)-2-thioimidazole (tim) were prepared according to the reports [31,32]. NMR spectra were recorded on a Bruker Avance DPX 200 Spectrometer, with chemical shifts reported in ppm relative to an internal standard of TMS; IR spectra were recorded from KBr pellets on a Bruker IFS-25 Spectrometer and reported in wave number (cm^{-1}). Elemental analyses were determined by Vario EL analyzer in chemical laboratory. Thermogravimetric (TG) Analysis of Ni(II) complex was performed on Netzsch STA 449F3 with system interface device. The experiment was conducted under nitrogen as the purge gas with a flow rate of 50 ml/min. The range of the temperature studied was from 30 to 1000 °C, at a heating rate of 10 °C/min.

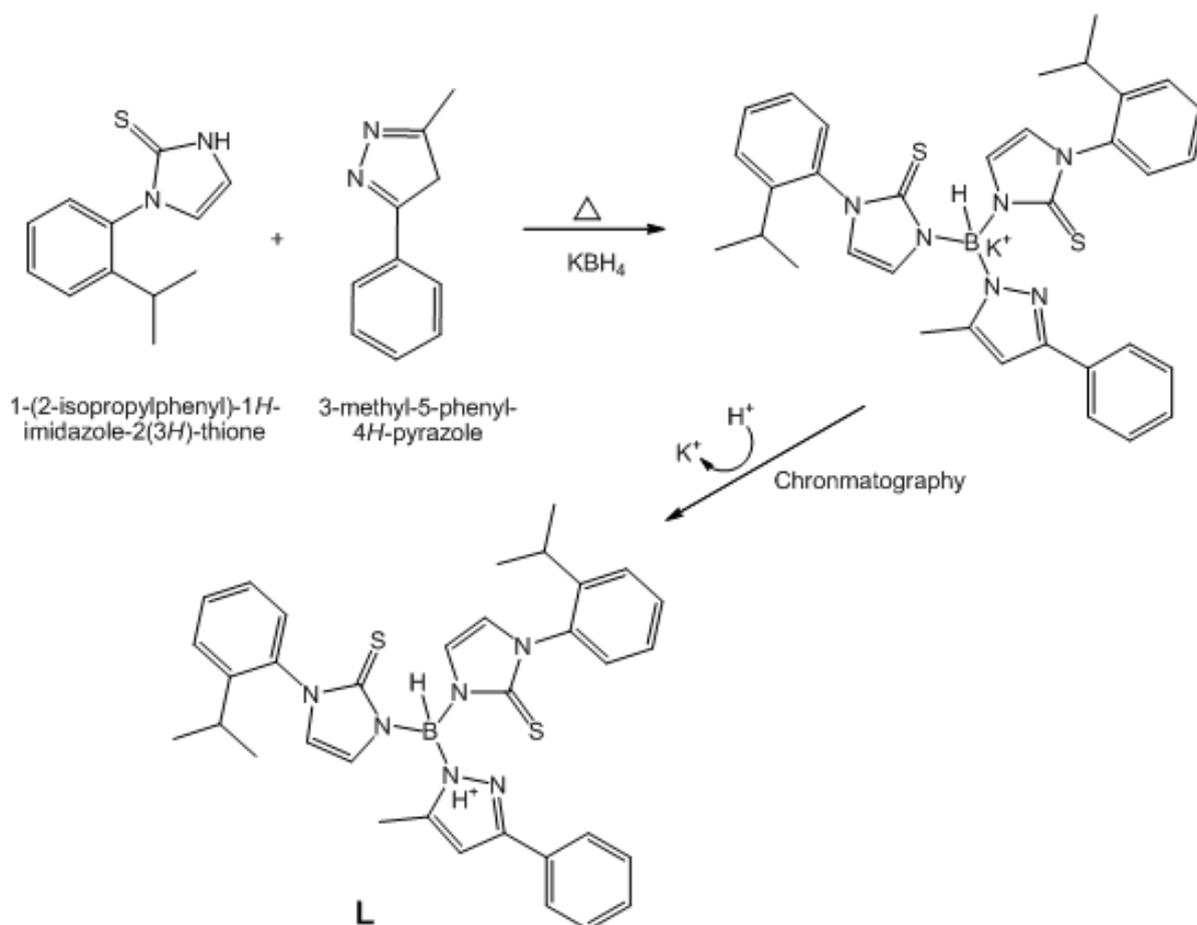
2.2. Syntheses

2.2.1. Synthesis of the ligand L (Scheme 1)

A solution of 2-isopropyl-butyraniline (27.0 g, 0.2 mol) in dry diethyl ether (40 mL) was slowly added to a solution containing a mixture of NaNH_2 (7.8 g, 0.12 mol) and bromoacetal (39.4 g, 0.1 mol) in 60 mL dry diethyl ether. The resulting solution was stirred for 2h under stream of nitrogen. Then, the solvent was removed in *vacuo*, and the residue was heated to 120 °C overnight for completion the reaction. Ethanol (30 mL) was carefully added, followed by water (20 mL). The resulting solution was stirred for one 1h. The remained solid material was extracted from n-hexane and dried with magnesium sulfate, giving 2-(2-isopropyl-lanilin-yl)-1,1-diethoxyethane. Yield: 24.0 g (84.5%). $^1\text{H-NMR}$ (CDCl_3): 1.14(dd, J = 8.6 Hz, 6H), 1.37(s, 6H), 2.56 (t, J = 5.2, 1H), 3.22(d, J = 5.6 Hz, 2H), 3.69(dd, J = 8.6 Hz, 4H), 4.74(dd, J = 5.6 Hz, 1H), 6.61(m, 2H), 7.04-7.17(m, 2H).

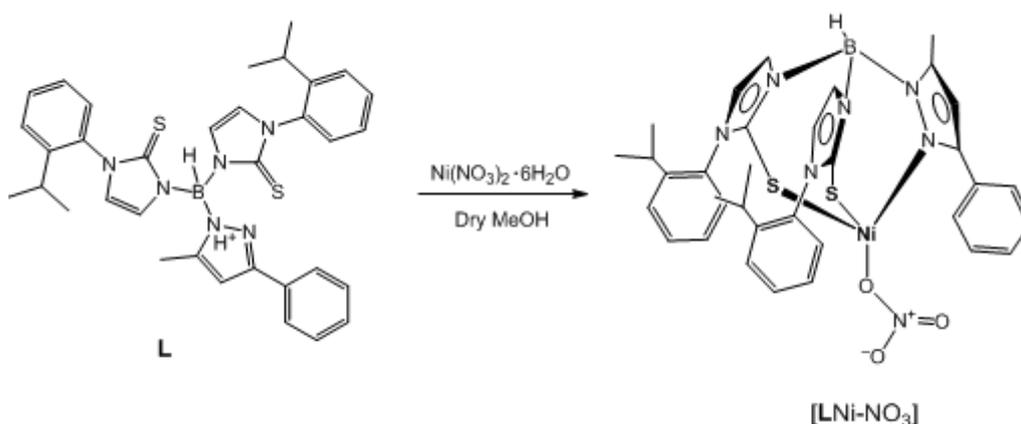
N-isopropyl-2-thioimidazole was obtained as a white crystal in methanol. Yield: 59.3%. M. p. 246 °C (dec). $^1\text{H-NMR}$ (DMSO-d_6): 2.45(d, J = 2.6 Hz, 6H), 2.87(t, J = 5.1 Hz, 1H), 7.15(d, J = 1.5 Hz, 1H), 7.27(d, J = 2.4 Hz, 1H), 7.31(d, J = 2.4 Hz, 1H), 7.52(m, 1H), 7.54(m, 1H), 7.81(d, J = 1.5 Hz, 1H). IR (KBr), $\nu(\text{cm}^{-1})$: 3452.1(w), 3116.4(vs), 2966.1(vs), 2910.8(vs), 1568.1(s), 1494.1(s), 1443.3(m), 1412.3(w), 1315.1(vs), 1291.3(m), 1257.1(vw), 1141.9(vw), 976.2(vw), 914.1(w), 791.5(m), 768.3(m), 732.4(w), 689.3(m), 578.7(m).

A mixture of N-isopropyl-2-thioimidazole (17.44 g, 0.080 mol), 3-phenyl-5-methylpyrazole (9.44 g, 0.06 mol), and potassium boron hydride (2.15 g, 0.04 mol) was ground quickly into a fine powder, and transferred into a 500 mL Schlenk flask. The powder was subjected to vacuum with heating to 100 °C for 2 h. Around 400 mL of newly distilled toluene was added in the flask, and the solution has been refluxed at 160 °C under an atmosphere of nitrogen for one week. The solvent was removed on a rotary evaporator and the residue was dissolved in 50 mL dichloromethane, filtrated through a layer of celite to remove the un-reacted thioimidazole and the possible polymeric byproducts. The filtrate was loaded in a column (Silica gel 60, 30 cm), and eluted by a gradient solvent system (CH₂Cl₂/CH₃COCH₃) to give the ligand L. Yield: 14.27 g (71.0%). M. P. 211 °C. Anal. Calc. for C₃₄H₃₅N₆S₂B₁ (Mr = 603.63): C, 67.65; H, 6.01; N, 13.92; S, 10.62; Found: C, 68.27; H, 6.17; N, 13.49; S, 10.52. ¹H-NMR (CDCl₃): 1.11(d, J = 2.8 Hz, 12H), 2.26(s, 3H), 2.767, 6.21(s, 1H), 6.67(s, 2H), 6.74-6.89(m, 1H), 6.90(s, 2H), 7.05(s, 2H), 7.07-7.25(m, 6H), 7.49(m, 2H), 7.80(s, 1H), 7.83(s, 1H). IR (KBr), ν(cm⁻¹): 3434.3(m), 3138.4(w), 3066.1(s), 2504.8(w, B-H), 1605.1(w), 1548.4(w), 1492.1(s), 1446.9(s), 1416.1(m), 1362.5(vs), 1287.2(m), 1181.3(s), 1153.6(s), 1084.6(vs), 958.7(w), 817.3(vw), 762.5(vs), 735.4(m), 693.8(s), 635.6(vw).

Scheme 1. Synthesis of the ligand **L**

2.2.2. Synthesis of the nickel complex 1 (Scheme 2)

A solution of 87 mg (0.30 mmol) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, dissolved in anhydrous methanol (5 mL) was added to a solution of 181 mg (0.3 mmol) of ligand **L** in 5 mL of anhydrous methanol. The resulting solution was stirred for another 3 h at room temperature and then evaporated to dryness at 40 °C. The residue was extracted with CH_2Cl_2 , filtered, and evaporated to dryness again. Recrystallization from methanol. Yield: 78 mg (76%) of Ni(II) complex as yellowish brown crystals, Anal. Calc. for $\text{C}_{34}\text{H}_{35}\text{N}_7\text{O}_3\text{S}_2\text{BNi}$ [LNi-NO_3] ($M_r = 830.43$): C, 62.19; H, 4.13; N, 11.81; S, 7.72. Found: C, 62.01; H, 4.21; N, 11.73; S, 7.83. IR (KBr), $\nu(\text{cm}^{-1})$: 3439.1(m), 3140(w), 3066.3(s), 2443.5(w, B-H), 1614.2(w), 1549.1(w), 1498.1(s), 1446.3(s), 1390.2(s, $\nu(\text{NO})$), 1372.1(vs), 1191.3(s), 1088(s), 1055(vs), 966.2(w), 821.4(vw), 743.1(m), 695.2(s). Conductivity ($\Omega \text{ cm}^2, \text{ mole}^{-1}$, DMSO): 45.



Scheme 2. Synthesis of nickel(II) complex

2.3. Preparation of unmodified carbon paste electrode (CPE) and carbon paste modified by Ni(II) complex

Unmodified carbon paste electrode was prepared by mixing 65% graphite powder and 35% paraffin wax. Paraffin wax was heated till melting and then, mixed very well with graphite powder to produce a homogeneous paste. The resulted paste was then packed into the end of an insulin syringe (i.d.: 2mm). External electrical contact was established by forcing a copper wire down the syringe. CPE modified with Ni(II) complex was prepared by mixing 60% graphite powder and 30% paraffin wax with 1, 5, 10 and 15% Ni(II) complex. The surface of the electrode was polished with a piece of weighting paper and then rinsed with distilled water thoroughly.

2.4. Electrochemical measurements

Cyclic voltammetry (CV) and square wave voltammetry were performed using an Autolab potentiostat PGSTAT 302 (Eco Chemie, Utrecht, The Netherlands) driven by the General purpose Electrochemical systems data processing software (GPES, software version 4.9, Eco Chemie). Electrochemical cell with three electrodes was used; unmodified carbon paste electrode or carbon paste electrode modified with Ni(II) complex was used as a working electrode, Ag/AgCl was used as a

reference electrode while platinum wire was used as a counter electrode. The pH values were measured using a Metrohm pH-meter with a combined glass electrode. pH values were adjusted using 1 M NaOH solution.

Scanning electron microscopy (SEM; JEOL JSM-6700F), was used to characterize the morphology of bare carbon paste and carbon paste modified electrode by Ni(II) complex.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the ligand *L* and its nickel(II) complex

The ligand **L** was synthesized by the reaction of 3-methyl-5-phenyl-4H-pyrazole (Pz): KBH_4 : 1-(2-isopropylphenyl)-1H-imidazole-2(3H)-thione (Tm^{isopr}) in the ratio of 1.1: 1, 2 in hot toluene. The trick found in this reaction is that the excess pyrazole works as a solvent effect which can reduce the melting points of Tm^{isopr} , and promote the ligand formation. As previously reported, temperature plays a vital role in melting reactions. [33] When it goes above 180 °C, the colour of the reactants turns from white to dark, possibly due to the decomposition of Tm. In this reaction, the temperature was kept around 160 °C. After releasing of hydrogen, the reactions were kept on for 2h for completion. Upon cooling down, the solid is quite difficult to dissolve in low polaric solvents like CH_2Cl_2 and CHCl_3 . The residue is possibly the polymeric by-products and in solution, there are more unreacted tim and pz as shown by TLC. The ligand was further purified by cation exchange, forming $[\text{HB}(\text{Tm}^{\text{isopr}})_2(\text{Pz}^{\text{Ph,Me}})]$. A hydrogen ion is attached on the nitrogen atom of pyrazole, like the way of most lipids. The proton could be replaced when ligand **L** coordinates to nickel ion. It is reasonable that the alkalic crude ligands react with the acidic silica gel during purification, which leads to substitution of potassium ion with proton. This result overcomes the scare of boron bonds diassociation on silica gel.

Recently, we have prepared a series of thiolate zinc(II) complexes [33-37]. The ligand **L** was used to emulate the NS_2 coordination environment provided by the two cysteine and one histidine protein residues in some sulfur-containing zinc(II) enzymes. The nickel(II) complex $[\text{L-Ni}(\text{NO}_3)]$ was prepared in a high yield by treating the ligand with an equimolar amount of nickel(II) nitrate hexahydrate in absolute methanol. The resulting Ni(II) complex was isolated and recrystallized from $\text{MeOH}/\text{CH}_2\text{Cl}_2$. The $\nu(\text{B-H})$ absorption band of nickel(II) complex at 2443 cm^{-1} was shifted around 100 cm^{-1} to lower energy relative to that of the free ligand. The presence of two very intense bands at 1088 and 1055 cm^{-1} were assigned to $\text{C}=\text{S}$ terminal stretching. These bands are generally used to confirm the presence of thiolate ligand in the complex. The detected bands at 966 and 821 cm^{-1} were suggested to be C-S stretches. The low intensity band at 524 cm^{-1} , a breathing mode of the heterocycle NS_2 complex, and the bands below 500 cm^{-1} , were assigned to angular deformation and both Ni-S and Ni-N stretching modes. These shifts may result from changes in the electronic state where the $\text{C}=\text{S}$ bond loses its double bond character when the ligand coordinates *via* the thione sulfur. The shifts in the bands between the free ligand and the complexes result from electronic shifts within the ligand. It also exhibits $\nu(\text{NO})$ absorption band of the nitrate anion at 1390 cm^{-1} . The complex behaves as 1:1 electrolyte with molar conductance value of $45\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$. This suggests that the NO_3^- ion is bound directly to the nickel ion in solution.

The thermogravimetric analysis of Ni(II) complex indicates that the decomposition of the complex proceeds in four main stages. Typical TG-DTG curve of Ni(II) complex is presented in Figure 1. The big mass loss and broad peak are observed in the TG and DTG curves, respectively. The course of the DTG curve showed four endothermic peaks at 417, 573, 691, and 820 K. Mass loss in the beginning of the second stage is slow and becomes rapid as decomposition proceeds. The first step is at 417 K; with a constant weight loss of 34.35% due the loss of one molecule of 2-isopropylphenylthioimidazole and one molecule of nitrogen dioxide (Calc. 35.18%). The second step is at 573 K and is accompanied by a total mass loss of 28.67% due to the loss of one molecule of 2-isopropylphenylthioimidazole (Calc. 30.10). The third step is at 691 K; with a constant weight loss of 16.33% due the loss of one molecule of isopropylbenzene (Calc. 16.60%). The rest of the molecule decomposes in the fourth step leading to the formation of mixture of NiO and B₂N₃, as final solid product (Found 17.20 %; calc. 18.31%).

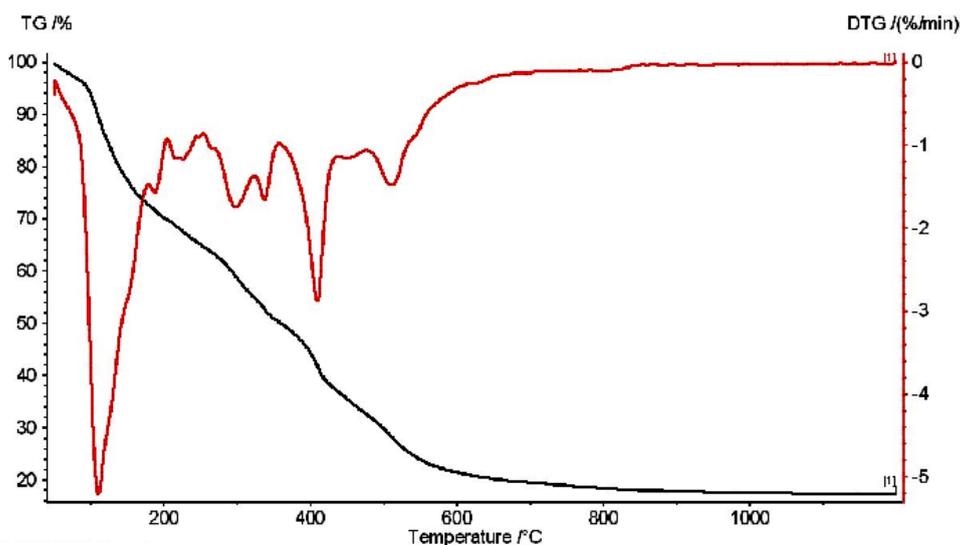


Figure 1. Typical TG-DTG curve of Ni(II) complex.

3.2. Characterization of carbon paste electrode

Scanning electron microscopy (SEM) was used to characterize the morphology of the bare carbon paste electrode and carbon paste electrode modified with Ni(II) complex. Fig. 2a (i) represents the SEM morphology for the prepared electrode. The SEM image of the bare carbon paste electrode showed a microstructure with a discontinuous grain growth with a large unclear crystal structure. Also the surface structure of the bare carbon paste electrode shows that the graphite particles are covered by a very thin film of paraffin wax. Fig. 2.a (ii) shows that the surface of carbon paste electrode modified by Ni(II)- complex is relatively homogeneous and more smoother than the carbon paste.

Qualitative analysis of the Ni(II) complex in the electrode composition was used to clarify the presence of Ni atoms and its distribution in the composition of the prepared electrodes by making

EPMA maps for Ni as illustrated in Fig. 2b. From these maps, it can be seen that Ni atoms are present in the electrode composition and dispersed homogeneously through carbon atoms.

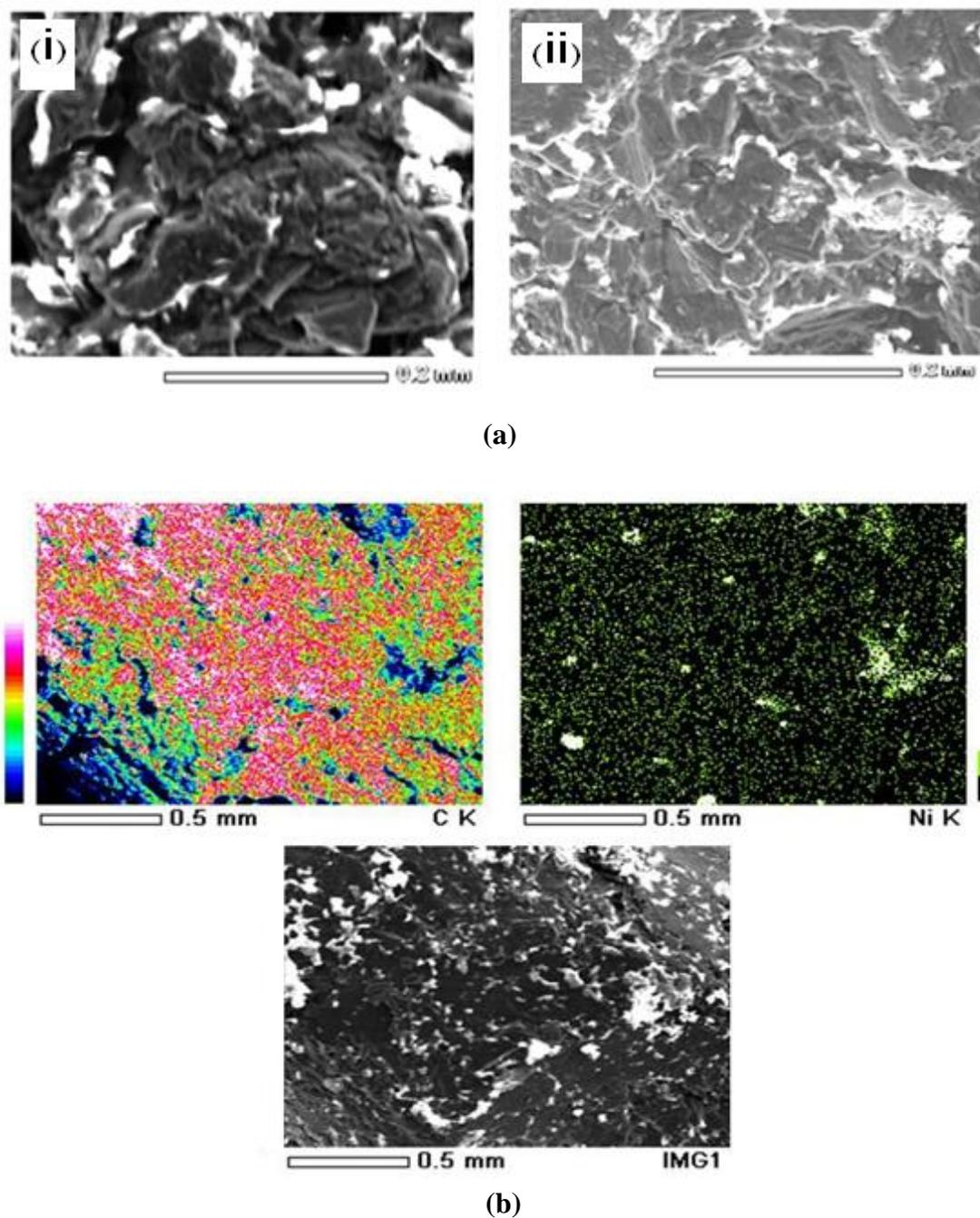
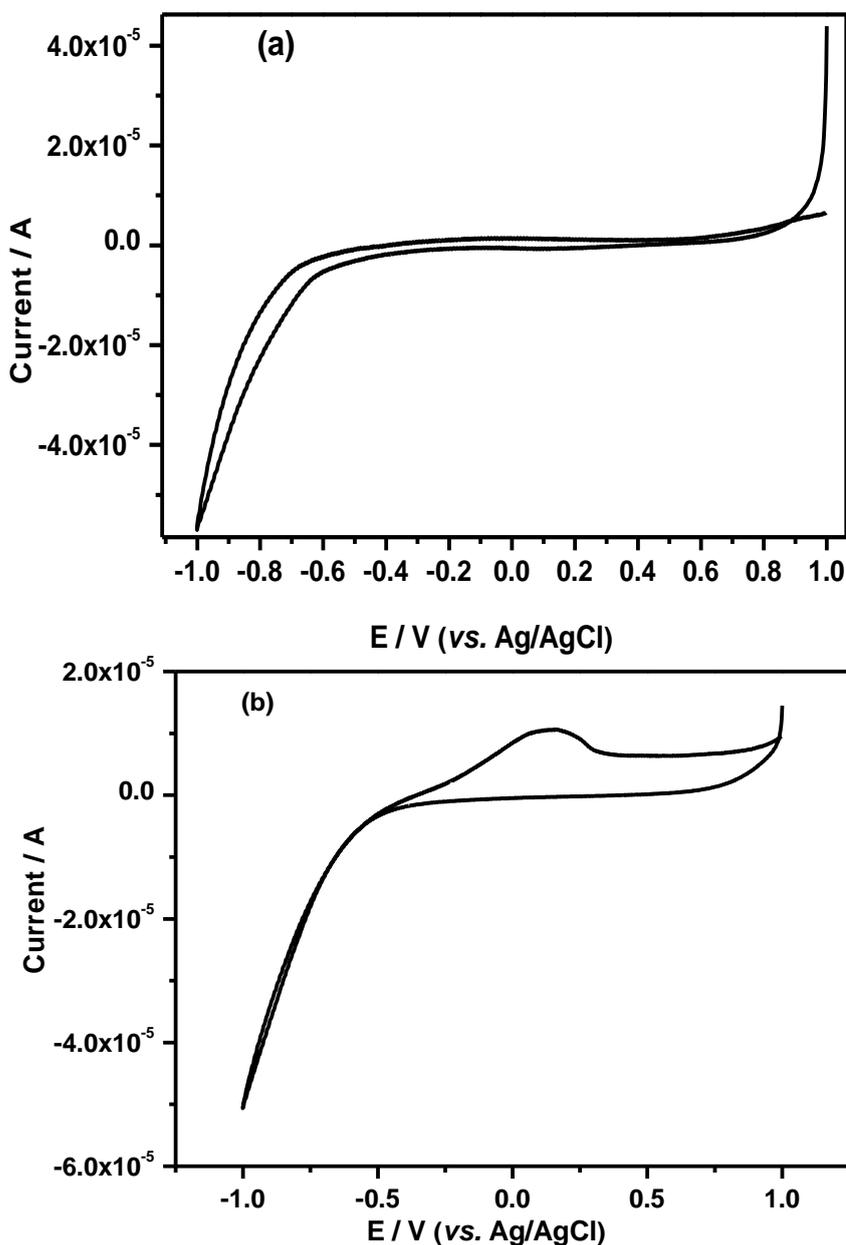


Figure 2. (a) SEM micrographs for a bare carbon paste electrode surface (i) and carbon paste electrode modified with Ni(II) complex (ii). (b) Microstructure maps for Ni constituent in carbon paste electrode modified with Ni(II) complex.

3.3. Cyclic voltammetry

Cyclic voltammetry was used to study the electrochemical behavior of the bare carbon paste electrode and carbon paste electrode modified with Ni(II) complex. The electrochemical behavior of the prepared electrode was examined in a potential range from +1.0 to -1.0 V (vs. Ag/AgCl) using a potential scan rate of 100 mV s^{-1} . Fig. 3a shows the cyclic voltammograms for a bare carbon paste electrode and Fig. 3b shows carbon paste electrode modified with Ni(II) complex using phosphate buffer pH 7. A bare carbon paste electrode did not show any signal in the studied potential range while carbon paste electrode modified with Ni(II) complex showed an oxidation peak at $\sim +0.14 \text{ V}$. This oxidation peak may be due to the irreversible oxidation of Ni(II) to Ni(III) (Fig. 3b). By increasing the amount of Ni(II) complex concentration from 1 to 15 %, the oxidation peak current increased. So carbon paste modified by 15 % of Ni(II) complex was used for further studies. Fig. 3c shows the effect of nitrate addition on the electrochemical oxidation peak of Ni(II), by increasing nitrate concentration the oxidation peak of Ni(II) decreased.



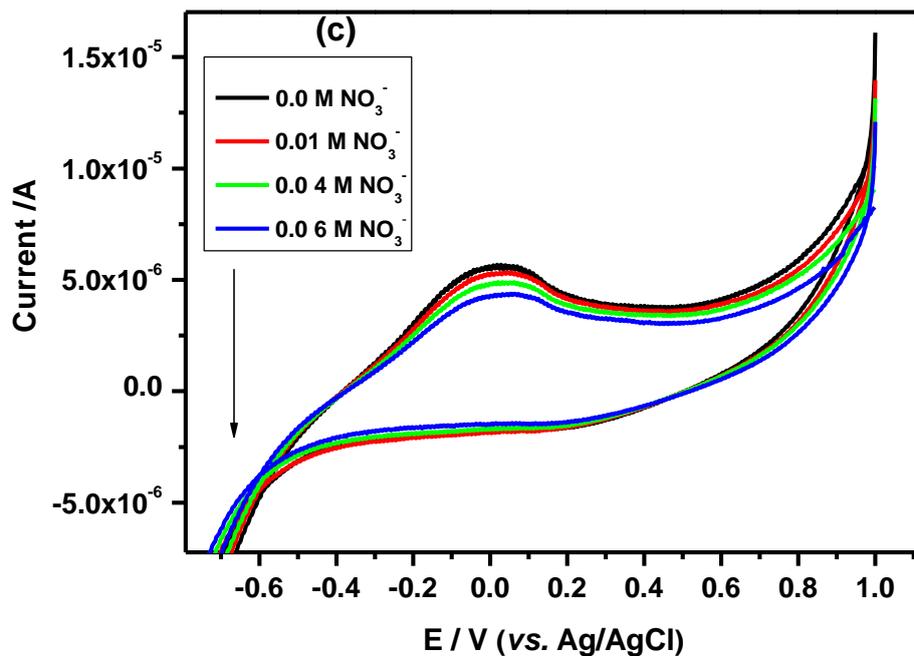
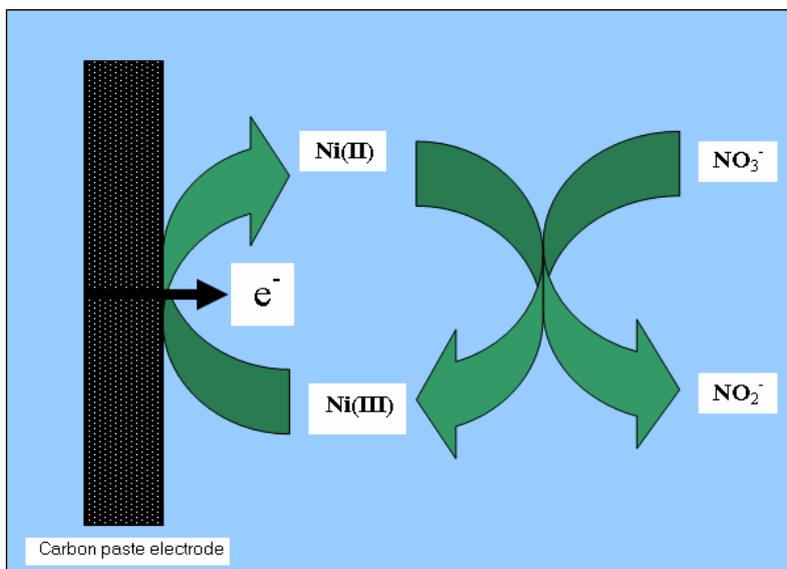


Figure 3. Cyclic voltammetric response for: (a) bare carbon paste electrode (b) carbon paste electrode modified with Ni(II) complex and (c) b in the presence of different nitrate concentrations, using phosphate buffer pH 7.

The decrease in the oxidation peak can be explained by the following scheme:



In the presence of Ni(II) complex, the nitrate ions were reduced to nitrite ions and Ni(II) ions oxidized to Ni(III) ions leading to the decrease of Ni(II) concentration on the carbon paste.

3.4. Effect of supporting electrolyte and pH

The effect of pH on the electrochemical reduction of nitrate using carbon paste electrode modified with Ni(II) complex was studied using cyclic voltammetric techniques in the pH range of 2.0 to 11.7 using 0.1 M Britton-Robinson buffer. The oxidation peak of Ni(II) showed the highest peak current and best peak shape at pH 7.0

The effect of supporting electrolytes was also investigated to study the electrochemical reduction of nitrate. Different supporting electrolytes were examined such as sodium phosphate, sodium acetate, sodium perchlorate, borate, sodium sulfate, Trizma HCl and Britton-Robinson buffer. Carbon paste electrode modified by Ni(II) complex showed an oxidation peak in Britton-Robinson, sodium phosphate and Trizma HCl buffers. The highest peak current and the best peak shape for the oxidation of Ni(II) complex was observed using phosphate buffer. So for further work a phosphate buffer pH 7 was selected for further studies.

3.5. Effect of potential scan rate

The effect of potential scan rate on the electrochemistry of carbon paste electrode modified by Ni(II) complex was studied using phosphate buffer pH 7. The oxidation peak currents increased linearly by increasing the scan rate values from 10 to 100 mV/s. The oxidation peak currents were proportional to the square root of the scan rate ($v^{1/2}$) (Fig. 4), which, indicates that the electron transfer reaction is diffusion controlled [38]. The linear regression equation was $I_p \text{ (A)} = 2.95 \times 10^{-6} + 2.167 \times 10^{-6} v^{1/2}$ with a 0.988 correlation coefficient and 7.45×10^{-8} standard deviation (SD).

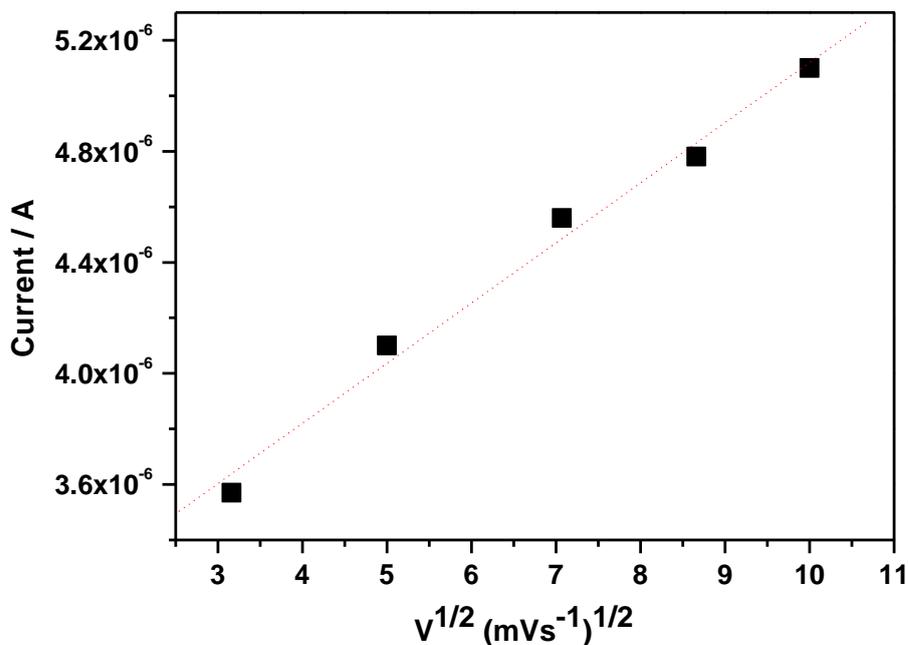


Figure 4. Plot of anodic peak current I_p against $v^{1/2}$ for carbon paste electrode modified with Ni(II)-complex in phosphate buffer pH 7 at various scan rates: 10, 25, 50, 75 and 100 mVs^{-1} .

3.6. Electrochemistry of nitrate at screen printed gold electrodes and the efficiency of nitrate reduction with time

Screen printed electrodes were previously used for the electrochemical determination of different analytes [39-40]. The electrochemistry of nitrate was studied at screen printed gold electrode using cyclic voltammetric techniques in phosphate buffer pH 7 as a supporting electrolyte. Nitrate showed two irreversible redox peaks, the first one in the cathodic direction at + 0.6 V (vs. Ag/AgCl) and the second one in the anodic direction at + 1.2 V (vs. Ag/AgCl) (Fig. 5a). The first peak due the reduction of nitrate to nitrite and the second peak due to the oxidation of the produced nitrite to nitrate according to the following scheme:



The effect of time on the reduction peak current of nitrate using phosphate buffer pH 7 was examined from 0 to 20 minutes. The reduction peak current of nitrate increased with time as shown in Fig. 5b.

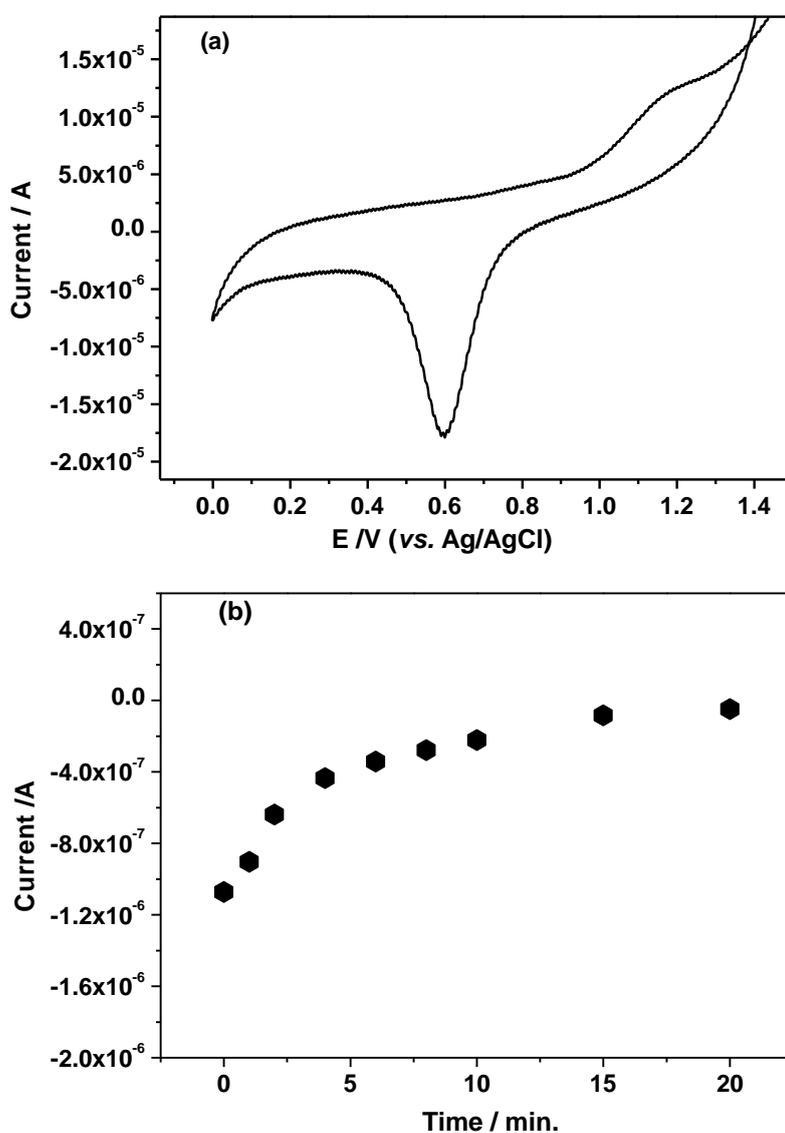


Figure 5. (a) Cyclic voltammogram for nitrate ions in phosphate buffer pH 7 at screen printed gold electrode (b) nitrate ion concentrations as a function of time (from 0 to 20 min.)

3.7. Effect of time on the removal of nitrate in the presence of carbon paste electrode modified with Ni(II) complex

The effect of carbon paste electrode modified by Ni(II) complex on nitrate concentration with time was examined by two different methods. The first method by measuring the decrease in the oxidation peak current of Ni(II) complex. The effect of incubation time was studied from 0 to 20 minutes. Fig. 6 showed the decrease in the oxidation peak current of Ni(II) by increasing the incubation time and the decrease was sharply in the first 2 minutes and become nearly stable after this time.

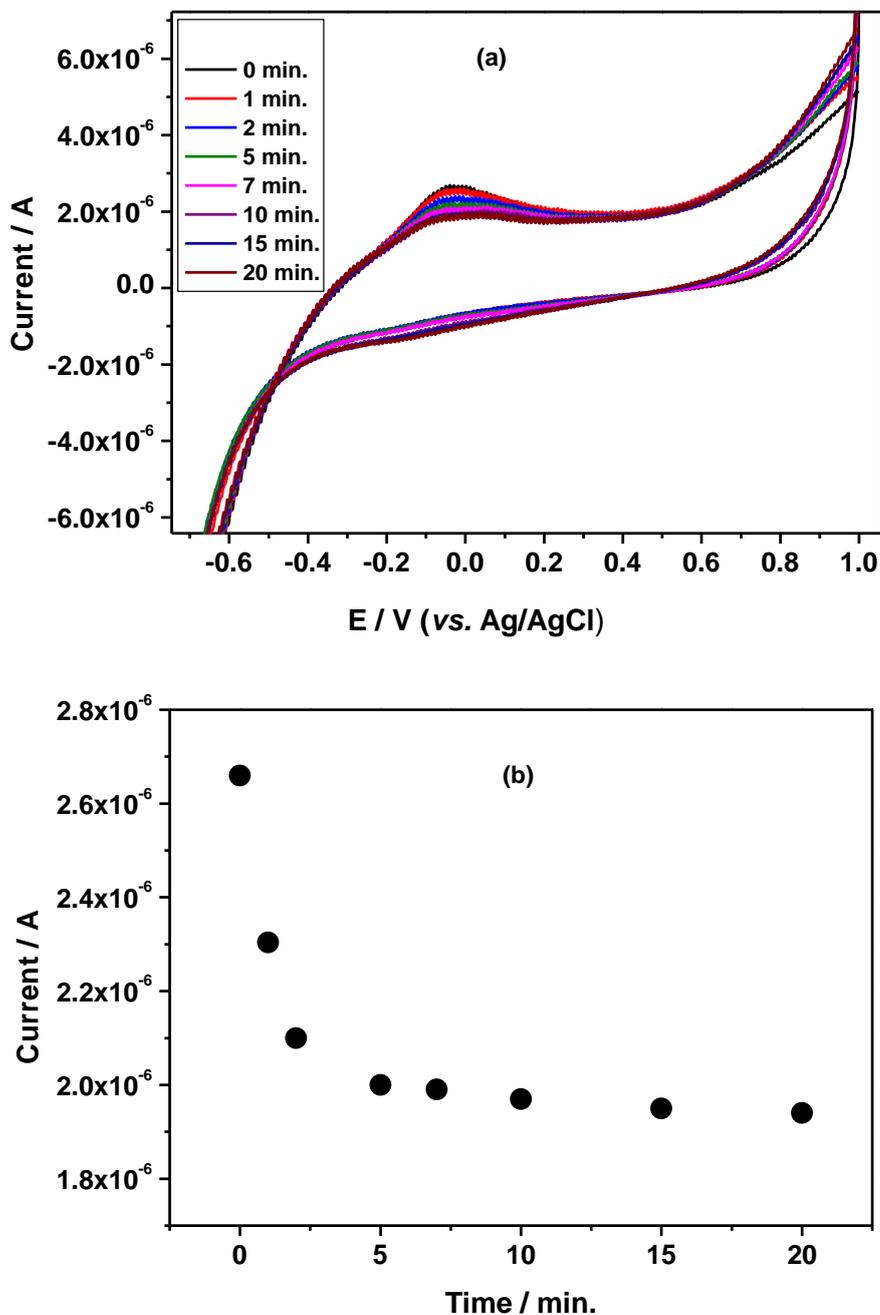


Figure 6. (a) Cyclic voltammograms for carbon paste electrode modified with Ni(II) complex recorded at different times, (b) current- time relationship.

The second method used to follow the nitrate concentration was a home made electrochemical cell. The cell contains carbon pate electrode modified by Ni(II) complex, where water passed over the electrode and after that water passed through the electrochemical cell containing screen printed gold electrode as a working electrode and Pt wires as a reference and counter electrodes to detect the nitrate concentration.

Fig. 7 showed the effect of carbon pate electrode modified by Ni(II) complex on the peak current and peak potential of nitrate on the cathodic and anodic direction with different time intervals. The reduction peak current of nitrate decreased sharply during the first 2 minutes and after that the peak current becomes nearly stable Fig. 7a. This result showed a good agreement with the result obtained by the first method (Fig. 6b). The peak potential for the reduction of nitrate was shifted to positive direction. The effect of time on the oxidation of the produced nitrite in the presence of carbon pate electrode modified by Ni(II) complex was also investigated. The peak current decreased sharply during the first 2 minutes and after that become nearly stable (Fig. 7b), while the oxidation peak potential shifted to more positive value.

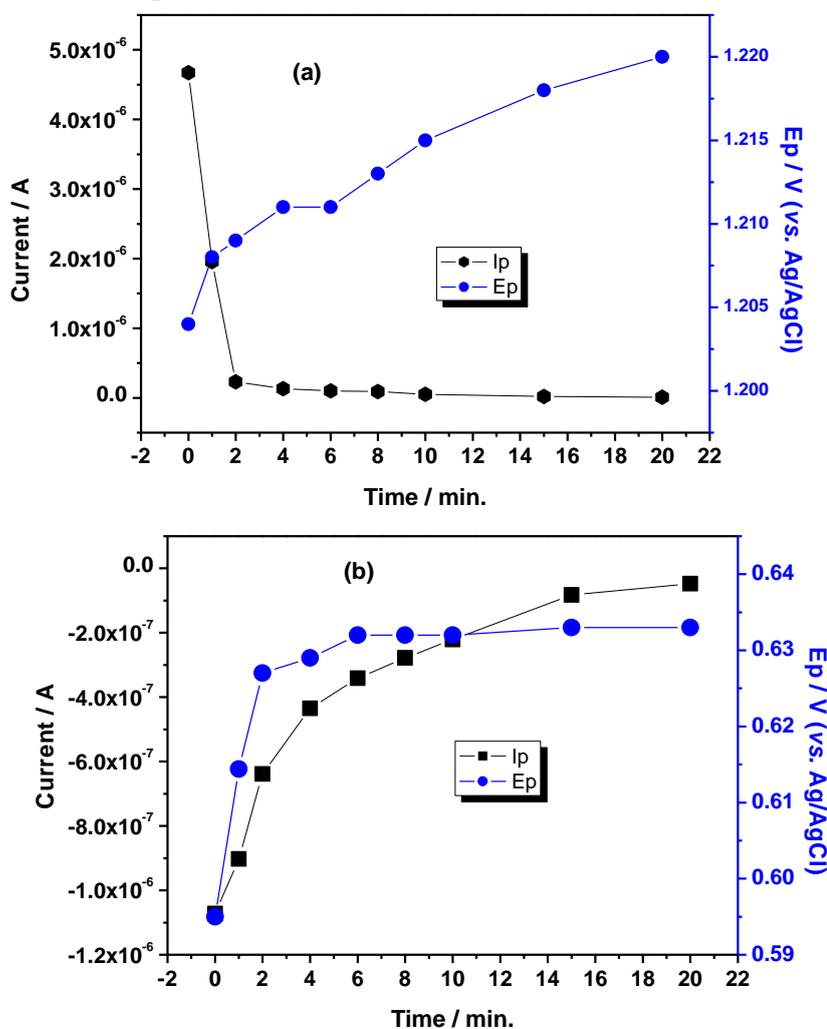


Figure 7. (a) The effect of time on the peak current and peak potential for the reduction of nitrate and (b) the effect of time on the peak current and peak potential for the reoxidation of the produced nitrite.

3.8. Analytical applications

The proposed method was applied for the removal of nitrate from different groundwater samples. The nitrate concentration was measured before and after immersion of carbon paste electrode modified by Ni(II) complex for 5 minutes using screen printed electrode using the above mentioned conditions. The resulted data was summarized in Table 1.

Table 1. Nitrate concentrations in different water samples before and after treatment.

	Nitrate conc. before treatment (mg/L)	Nitrate conc. after treatment (mg/L)
Sample 1	97.5	13.7
Sample 2	189.8	18.5
Sample 3	134.8	25.2
Sample 4	73.9	17.5
Sample 5	215.2	21.8

4. CONCLUSION

A new tripod ligand NS_2 , namely: Hydro {bis(2-isopropylphenyl-2-thioimidazol-1-yl)(5-phenyl-3-methyl-pyrazol-1-yl)}borate **L** was synthesized and characterized. Its mononuclear Ni(II) complex was prepared and characterized in the solid state by using FT-IR, elemental and thermal analyses and in solution by using conductivity and 1H NMR. The obtained Ni(II) complex was immobilized in carbon paste. The carbon paste modified electrode was characterized by SEM and cyclic voltammetry (CV). The electrochemical behavior of the carbon paste modified electrode showed an oxidation peak due to the oxidation of Ni(II) ions to Ni(III) ions. The oxidation peak current for Ni(II) decreased in the presence of nitrate ions due to the consumption of Ni(II) in the reduction of nitrate ions.

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