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Full Paper

Introduce of Minoxidil as a Very Selective ligand for Ultra Trace Detection of Copper Ion by Adsorptive Stripping Voltammetric Method

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Abstract- A new method is presented, for the determination of copper, based on adsorptive stripping voltammetry of the complex of copper with minoxidil at a hanging mercury drop electrode (HMDE). The most suitable operating conditions and parameters, such as pH, accumulation potential, deposition time, ligand concentration and scan rate, were selected. The calibration graph for copper (II) was linear over the concentration range of 0.5 to 700 nM; the detection limit of the method was 0.09 nM. The interferences of some common ions were studied and the method was found suitable for determination of copper (II) in water and drug samples. Moreover, by using of the proposed method, there is a considerable improvement in the detection limit, linear dynamic range and deposition time, compared to the methods other than adsorptive stripping voltammetry for the determination of copper.

Key words- Minoxidil, Adsorptive Stripping Voltammetry, Copper Ion

1. INTRODUCTION

In the recent years introducing of simple, selective, sensitive and inexpensive methods for determination of trace metal ions in various samples is the most important goal in the field of analytical chemistry [1]. The general requirements for an ideal analytical method include: (I) fast response times of instruments for the acquisition of necessary information on a real-time or near real-time basis; (II) no or minimum requirement for sample preparation; (III) achievement to the low detection limits; (IV) achievement to the highest selectivity; and (V) cost-effective analysis [2]. Standard methods such as flame atomic absorption spectrometry (FAAS) [3], electro thermal atomic absorption spectrometry (ETAAS) [4], flame emission spectrometry (FES) [5], and inductive coupled plasma-mass spectrometry (ICP-MS) [6] are time consuming, expensive, not accurately reliable for the determination of ultra trace concentrations of metal ions, suffer from serious matrix interferences and require adequate expertise. Beside, the electrochemical methods including anodic, cathodic and adsorptive stripping voltammetric techniques, in comparison to techniques involving atomic spectroscopy offer some important advantages such as: the instrumentation is relatively inexpensive, speed of analysis, easy to handle, the voltammetric responses for metal ions is highly sensitive, get lower detection limits, and the determination is given with good precision and accuracy [7-9]. But, due to the formation of intermetallic compound in amalgams, covering of nearest anodic and/or cathodic peaks, lack of specific chelating agents, susceptible to matrix effects and other interferences, these methods are not very selective rather than atomic spectroscopic methods [10]. In this regards, introduce of very selective ligands is well established as an efficient strategy to enhancement of selectivity of adsorptive cathodic stripping voltammetry (AdCSV) for determination of interest metal ions. Copper is an essential constituent of enzymes and play an important role in biological systems. Since the concentration of copper is extremely low in various natural samples, a sufficiently selective and sensitive method for the reliable determination of copper would be of great interest. Several adsorption voltammetric methods with different chelating agents such as: 8-hydroxyquinoline [11], cathecol [12], thiourea [13], phenanthroline [14], N-phenylcinnamohydroxamic acid [15], pyrogallol red [16], cupferron [17], α-benzylmonooxime [18] and salicylaldehyde thiosemicarbazone [19] were introduced for determination of copper. These ligands have advantage of sensitivity, but all these reagents have the disadvantage of poor selectivity for copper determination especially in the presence of Fe, Cd, Pb, Zn and Ni [11-16], and or have small linear dynamic ranges [14-16]. Pournaghi-Azar used BAE [bis-(acetylacetone)- ethylendiimine] as chelate to determine copper by differential pulse anodic stripping voltammetry, but an extraction step was adopted using dichloromethane as the solvent, which complicated the analysis procedure [20]. Ensafi used α-benzylmonooxime to determine copper by differential pulse cathodic voltammetry, but the chelate was a reactive agent and could not be exposed in air for a long time [21].

Menek et al., studied the electrochemical behavior of Cu(II)–5-Br-PADAP complex, but did not used it to determine copper in real samples [22]. However, there are not very selective chelating reagents for adsorptive cathodic determination of copper. In this work, we introduced a very selective ligand for adsorptive stripping voltammetric determination of copper at ultra trace level. The procedure is based on reduction of the complex of copper with minoxidil after accumulation at the surface of a hanging mercury drop electrode. It was found that there was not any inter-metallic effect between copper and common metal ions in this system.

2. EXPERIMENTAL

2.1. Reagents

All reagents used were analytical reagent-grade and double distilled water was used throughout. Minoxidil solution, 1.0×10^{-2} M, was prepared by dissolving of 0.0209 g of the compound (Sigma-Aldrich) in a binary mixture solution of water and ethanol (9:1 v/v) in a 10-mL volumetric flask. 100 mL stock solution of 1×10^{-3} M of copper was prepared by dissolving 0.02416 g Cu $(NO_3)_2 3H_2O$ (Merck) in double distilled water. The Britton-Robinson (B.R) buffer solution was prepared from H_3PO_4, CH_3COOH and H_3BO_3 with total concentration of 0.01 M for voltammetric measurements and 0.03 M for Spectrophotometric study.

2.2. Instruments

Electrochemical experiments were carried out using a polarograph VA 797 Computrace (Metrohm). Measurements were carried out with a hanging mercury drop electrode (HMDE), in a three-electrode arrangement. The auxiliary electrode was a wire of platinum with a considerably larger surface area than that of HMDE. A silver-silver chloride (KCl 3 M) was used as reference electrode. Stirring was carried out by a large Teflon rod with 2000 rpm speed. Solutions were purged with high purity nitrogen for 3 min prior to each experiment, and it was performed under a nitrogen atmosphere. A Metrohm-827 digital pH-meter was used for pH measurement. Absorbance spectra were recorded using an hp spectrophotometer (Agilent 8453) equipped with a pettier (Agilent 89090A).

2.3.Voltammetric measurements

Ten milliliters of 0.01 M B.R buffer solution (pH=10), containing 1.5×10^{-4} M minoxidil was pipetted into the voltammetric cell. The solutions were purged with water-saturated nitrogen for 3.0 min in the first cycle and 10 s for each successive cycle. The preconcentration (adsorption) potential (-50 mV) was applied for 50 s to a fresh mercury drop while the solution was stirred. The stirring was stopped for period of 5 s (equilibration time)

and then, the potential was scanned from 0.0 V toward more negative values (-1.0 V) using differential pulse (DP) modulation (Pulse amplitude , 50 mV; pulse time 40 ms; voltage step 5.0 mV; voltage step time 0.1 s; resulting in a scan rate of 50 mV s^{-1}). Each scan was repeated three times with a new drop for each analyzed solution and the mean of these voltammograms obtained.

2.4.Preparation of drug sample

For drug sample, 0.0137 g sample of Mega-Tron tablet (taken from five powdered tablets), labeled with amount of 1 mg per tablet, was completely dissolved in 2.0 ml of 0.1 M HNO_3 on a water bath, and the mixture was cooled and filtered through filter paper (Watman No.1). The filtered mixture was diluted to 10 ml. 10 µl of this solution was transferred in to the electrochemical cell containing 10 ml of B.R buffer (pH=10).

3. RESULTS AND DISCUSSION

Minoxidil, 2,4-diamino-6-piperidinopyrimidine-3-oxide (MXL) Fig.1 is the most common active anti-alopecia and baldness drug and also recently used in combination with other drugs for treatment of hirsutism and acne.

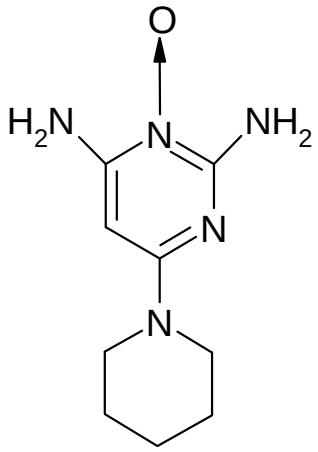
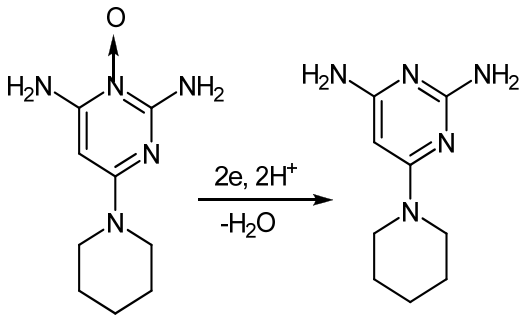


Fig. 1. The structure of 2,4-diamino-6-piperidinopyrimidine-3-oxide (Minoxidil)

In our previous work, the irreversible electrochemical behavior of MXL in an acidic solution has been reported [23]. According to this report, MXL is electro-inactive in alkaline solutions and its reduction mechanism is as follows:



3.1. Spectrophotometric study of interaction of copper with minoxidil

MXL has two amine groups and can be used as a complexing agent. In order to determined the affinity of MXL to form a complex with metal ions, the complexation of MXL with a wide range of metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Al^{3+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, U^{6+}, Cu^{2+}, Sn^{2+}, Bi^{3+}, Ag^{+}, and Hg^{2+} in aqueous solution with pH=10 were studied by spectrophotometric titration. In this procedure, the spectra of a series of solutions containing a constant concentration of ligand (5.0×10^{-5}M) at a fixed ionic strength of 0.03 M of B.R buffer (pH=10.) and varying amount of metal ions (1.0×10^{-2} M) was obtained at 25 ºC. The results revealed that only the copper has a significance effects on MXL spectrum (Fig. 2a). As can be seen, the complexation was accompanied by a shift of the absorption and of the MXL (286 and 265 nm) solution towards lower wavelengths (282 and 261 nm) with a hyper chromic effect (n–π* transition) due to its complexation with copper ion [24]. The absorbance *vs*. $[Cu^{2+}]$/[MXL] mole ratio plot obtained at a wavelength of 265 nm is shown in (Fig. 2b).

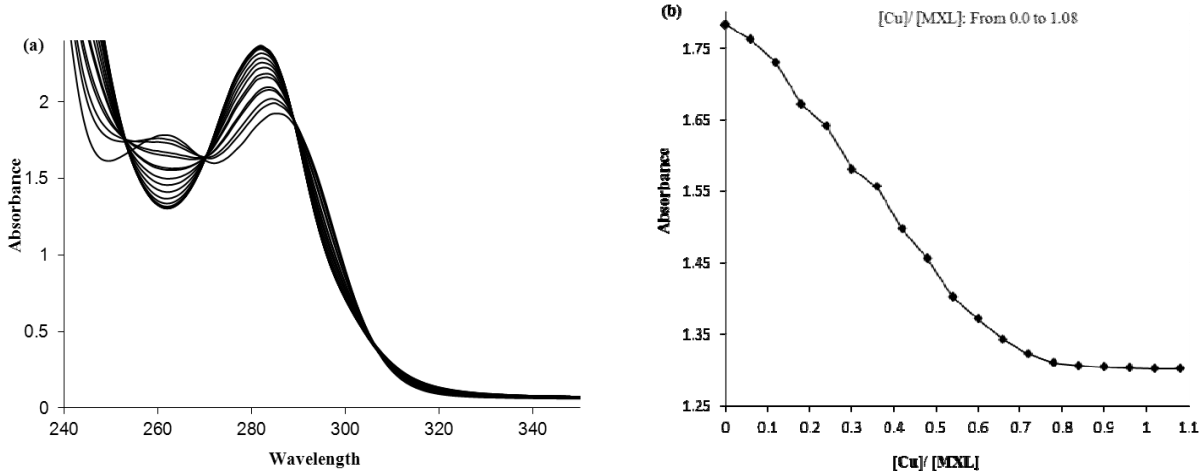


Fig. 2. (a) Absorption spectra of complexation of MXL (5×10^{-5} M) in B.R buffer (pH=10) solution in the presence of varying concentrations of copper(II) ion at 25ºC; (b) the mole ratio plot of $[Cu^{2+}]$/[MXL] at a wavelength of 286 nm

As it is seen the absorbance mole ratio plot revealed a distinct inflection point at $[Cu^{2+}]/[MIN]$ molar ratio of 0.5 emphasizing the formation of 1:2 complex in solution. Based on literature survey on amine derivatives complexation ML_2 complex was proposed wherein, the metal ion is coordinated via amine groups [25]. This main structure may be surrounded by other free ligands such as water or oxygen that are presented in the MXL structure. Thus, the structure that was shown in Fig. 3 is proposed for complex formed between MXL and copper ion. According to our previous work [24], the overall equilibrium constant of the resulting complex between Cu^{2+} and MXL was calculated as follows.

When two MXL interacts with Cu^{2+}, it forms a1:2 complex as follows:

$$Cu + MXL \overset{K_1}{\leftrightarrow} Cu - MXL \tag{1}$$

$$K_1 = \frac{[Cu-MXL]}{[MXL][Cu]}$$

$$Cu - MXL + MXl \overset{K_2}{\leftrightarrow} Cu - (MXL)_2 \tag{2}$$

$$K_2 = \frac{[Cu-(MXL)_2]}{[Cu-MXL][MXL]}$$

The mass balance equations are written as Eqs. (3) and (4).

$$C_{MXL} = [MXL\,] + [Cu - MXL\,] + 2[Cu - (MXL\,)_2] \tag{3}$$

$$C_{Cu} = [Cu] + [Cu - MXL\,] + [Cu - (MXL\,)_2] \tag{4}$$

Substitution of Eqs. (1) and (2) into Eqs. (3) and (4) and rearrangement yields Eq. (5).

$$K_1K_2[MXL\,]^3 + [k_1(1 + K_2(2C_{Cu} - C_{MXL}))][MXL\,]^2 + (1 + K_1(C_{Cu} - C_{MXL}))[MXL\,] - C_{MXL} = 0 \tag{5}$$

The observed absorbance of solution is also given by:

$$A_{obs} = \varepsilon_{MXL}\,[MXL\,] + \varepsilon_{Cu-MXL}\,[Cu - MXL\,] + \varepsilon_{Cu-(MXL)_2}[Cu - (MXL\,)_2] \tag{6}$$

Where ε value is the molar absorptivity of the species denoted. For evaluation of the formation constant from the absorbance–mole ratio data, a non-linear least-square curve-fitting program KINFIT was used. The program is based on the iterative adjustment of

calculated absorbance to the observed values. Adjustable parameters are stepwise equilibrium constants of all complexes present and the corresponding molar absorptivity. The procedure used for the evaluation of K_1 and K_2 values from the data is as follows. The free MXL concentrations, [MXL], were calculated by means of a Newton–Raphson procedure. Once the value of [MXL] had been obtained, the concentrations of other species involved are calculated from the corresponding mass balance equations by using the estimated values of the formation constants at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values of the absorbance or the conductance for all experimental points was minimized. The output of program KINFIT comprises the refined parameters, the sum of-squares and the standard deviation of the data. The log K_1=5.3 and log K_2=3.4 were obtained for the proposed complex.

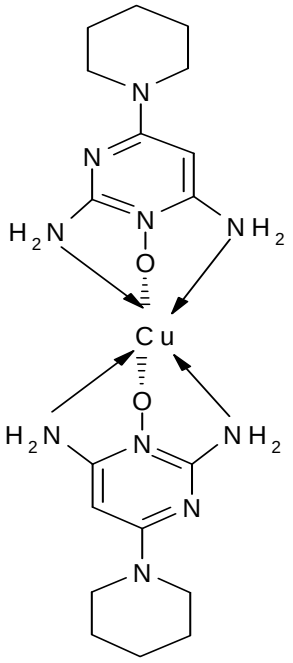


Fig. 3. The proposed structure of Cu-$(MXL)_2$ complex

3.2. Adsorptive Characteristics of the Cu –MXL Complex

Preliminary studies of the electrochemical behavior of Cu (II) and its complex with MXL were performed by cyclic voltammetry. Fig. 4 shows the cyclic voltammograms obtained for 0.5 μM copper (curve a) and its complex with 10 μM MXL (curve c) in an unstirred solution of 0.01 M B.R buffer (pH=10). The forward potential scan commences at an initial potential of 0.0 V, and its direction was reversed at -1.0 V. The closeness of the oxidation to the reduction peak potentials showed that the redox process for copper ion (curve a, peaks

separation of 35 mV) is reversible and correspond to the of M^{2+}/M process, while a complicate behavior was observed for its complex with MXL (curve b) that may be due to the M^{2+}/M^{+} and M^{+}/M redox reactions. Also, the shift in the peaks potential of copper complex relative to that of metal ions are due to formation of coordinated compound between metal ions and ligand. As can be seen the ligand is electro-inactive in the studied potential window (curve a). The observed tailing in the cathodic peak of copper –MXL system reveals the adsorption of complex on the surface of the electrode. Furthermore, the cathodic peak current of complex was higher than anodic peak current and thus, reduction peak current was selected for monitoring of copper ions in solution. In order to achieve a high sensitive method for copper ions determination the selection of a proper electrochemical technique is of great importance. Therefore, differential pulse stripping voltammetry (DPSV) as a sensitive method was selected and used for further investigation. Thus the DP stripping voltammograms of Cu- MXL system at the surface of HMDE was recorded. Fig. 5 displays a differential pulse cathodic stripping voltammogram (curve c) of Cu-MIN system at pH=10 after 10 s accumulation at -0.280 mV. The blank solution (MXL plus buffer) does not show any peak current in this potential range (curve b). While the solid bold line display the cathodic stripping voltammogram of 5.0×10^{-7}M of Cu^{2+} ion in the absence of MXL. As can be seen from Fig. 5 the peak potential of reduction of Cu^{2+} ion was shifted and its peak current was increased when its voltammogram recorded in the presence of MXL (curve c). This reduction current increased linearly with increasing metal concentration. Comparison of the voltammogram shows that the height of the metal ion peak depends on the presence and absence of MXL. Reducing the peak current of Cu-MXL system in the presence of Triton X-100 confirms the adsorption phenomena on the surface of the electrode [9].

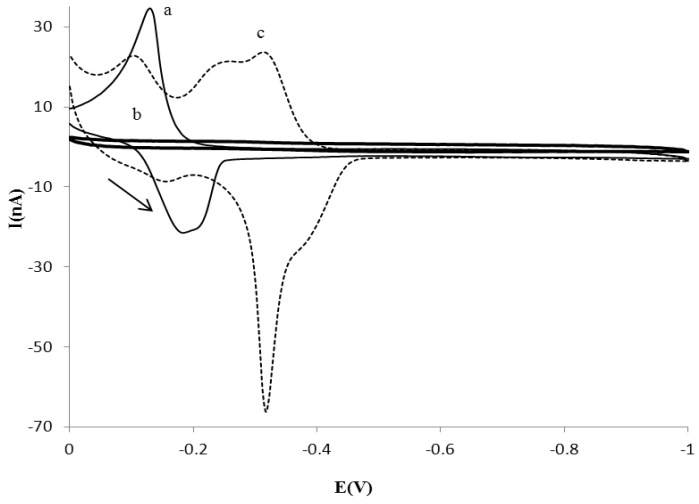


Fig. 4. Cyclic voltammogram of 5.0×10^{-7} M of Cu (a, solid line), 1.0×10^{-5} M of MXL (b, bold line), Cu-MXL (c, dote line); B.R buffer pH=10, and scan rate 60 mV s^{-1}

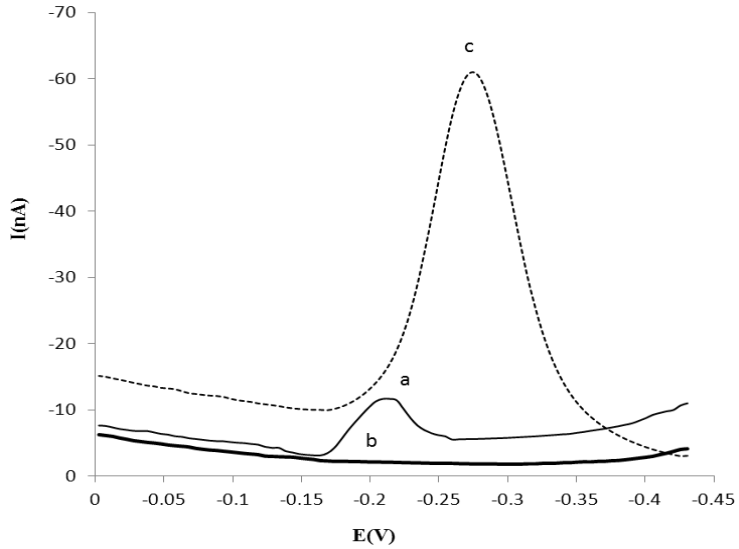


Fig. 5. Adsorptive cathodic stripping voltammogram of 5.0×10^{-7} M of Cu (a, solid line), 1.0×10^{-5} M of MIN (b, bold line), and Cu-MXL (c, dote line); the accumulation time 10 s, accumulation potential 0.0V, B-R buffer pH=10, and scan rate 40 mV s^{-1}

3.3. Optimization of Parameters

3.3.1. Effect of pH and supporting electrolytes

As the MXL has two amine groups, there is a competition between protons and Cu^{2+} for the binding sites in the ligand molecule. Therefore, the influence of pH on the stripping peak of Cu^{2+} was investigated in the range of 8-12 for a solution containing 1.0×10^{-5} M MXL and 5.0×10^{-7}M Cu^{2+}in B.R buffer (Fig. 6a). Maximum peak current was achieved at pH of 10.0. This value offering a compromise between the complexing amine groups and the hydrolysis of the Cu^{2+} ions that occur in alkaline medium. In other words, in lower pH of 10 the amine groups were protonated (pK_a=9.2) [26], and at pH higher than 10, the reduction is maybe attributed to the precipitation of copper hydroxides. Also the effects of different types of buffers such as Borate, ammonium-ammonia and B.R on peak current of Cu^{2+} were investigated. Maximum peak current was achieved in B.R due to a better stability of the complex formation in this buffer. Copper yielded small peaks in ammonium and or borate buffers due to its competitive complexation in solution by ammonium or borate ions.

3.3.2. Effect of Accumulation Potential

The effect of accumulation potential on the peak current of MXL was examined over the range of 150 to -150 mV. As can be seen in (Fig. 6b), the peak current increased by changing potential from 150 to -50 mV, due to increased the accumulation of Cu-MXL on the surface of the electrode. Thus -50 mV was selected as an accumulation potential.

3.3.3. Effect of MXL Concentration

The effect of MXL concentration on the sensitivity of proposed method was also studied. The obtained results (Fig. 6c) show that the cathodic stripping peak current of MXL-Cu complex increased with increasing the MXL concentration up to 15×10^{-5} M, and leveling off at higher concentrations. An optimum MXL concentration of 15×10^{-5} M was selected for further experiments.

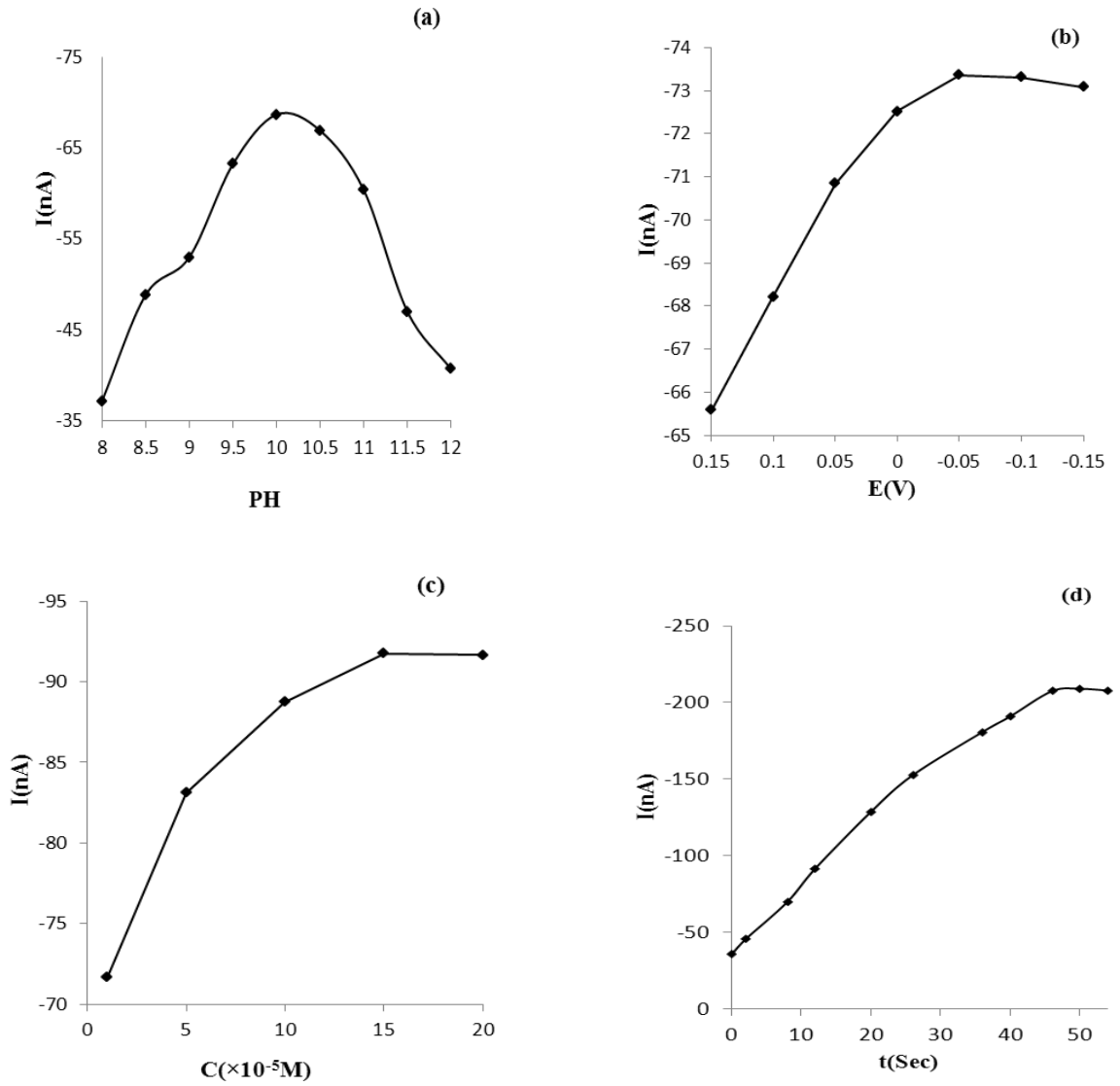


Fig. 6. Effect of (a) pH on peak current of 5.0×10^{-7} M of Cu ion, other conditions are as in Figure 4; (b) Accumulation potential at pH=10, other conditions are as in Fig. a; (c) MIN concentration on peak currents of Cu at pH 10 and accumulation potential=-50 mV, other conditions are as in Fig. b; (d) Accumulation time in the presence of 15×10^{-5} M of MIN, pH 10, E_{ac}= -50V, and scan rate 40 mV s^{-1}

3.3.4. Effect of Accumulation Time

The extent of preconcentration depends on the length of time over which the adsorption is allowed to proceed. The longer the accumulation time, the more Cu-MXL complex is adsorbed and the larger the peak current. The peak increases almost linearly at first and then curve level off toward the time axis (Fig. 6d). In our previous works, the same behavior was observed and we believed it may be attributed to the equilibrium attainment at the electrode surface–solution Interface [28]. We found an optimal deposition time of 50s.

3.3.5. Effect of Scan Rate

Other condition that affects the adsorptive response of the complex is scan rate; therefore, the influence of scan rate on the peak current of the complex was examined over the range 20 to 70 mV s^{-1}. The results showed that the peak current increases slightly at first up to 50 mV s^{-1} and then decreased for greater values of scan rate. Thus 50 mV s^{-1} was selected for the study.

3.4. Interference Studies

As mentioned above the most novelty of this work is introduced of a high selective complexing reagent (MXL) for adsorptive cathodic stripping voltammetry (AdCSV) of copper ion at optimum conditions. Therefore, the evaluation of the selectivity of the method is very important. To check the selectivity of the proposed stripping voltammetric method the influence of many ions on the determination of copper was examined. Interference was taken as the level causing an error in excess of 4%. The results of this study are summarized in Table1. From the results, it can be concluded that the method is free from interferences of foreign ions. It was found that only iodide, bromide and thiocyanate interfered in the determination of copper. The interference of anions can be eliminated easily by the addition of nitric acid 5.0 M to the solution containing copper plus potential interference anion and then heated to dryness. Then, the residual dissolved in water and copper contents were measured by the recommended procedure [20]. Many proteins and enzymes that are present in the biological materials can also interfere with the determination of trace copper by AdCSV due to competition with the added ligand, MXL. This competitive effect was modeled by addition of EDTA, as shown in Fig. 7. The complex of Cu(II) with EDTA forms in the solution and does not adsorb onto the HMDE. At EDTA concentrations 25-fold lower than that of MXL the peak of copper starts to decrease greatly and is completely suppressed at EDTA concentration equal to that of Cu^{2+}. This indicates a relatively low stability of the complex Cu–MXL and the necessity to destroy the organic substances prior to analysis. Like study was reported by Sucia et al., [27].

3.5. Linear Ranges and Detection Limits

Under the selected conditions (Briton-Robinson buffer, pH=10, accumulation potential -50 mV, accumulation time 50 s, scan rate 50 mV s^{-1}) the reduction peak current of copper complex yields well-defined concentration dependence (Fig. 8). To verify the linear relationship between peak current and metal concentration, one calibration graph was constructed under optimum conditions and after 50 s accumulation time. The result of this study (correlation coefficient greater than 0.99) indicated that the current-concentration relationship was linear in the concentration range of 0.5 to 700 nM for copper with a linear equation of I(nA)=-0.394C(nM)-11.72. The detection limit (3s) [28] of 0.09 nM was obtained for copper. The relative standard deviation of the method for 10 replicate determinations of 0.1, 1 and 6×10^{-7} M Cu(II) is 3.7, 3.6 and 2.6%, respectively.

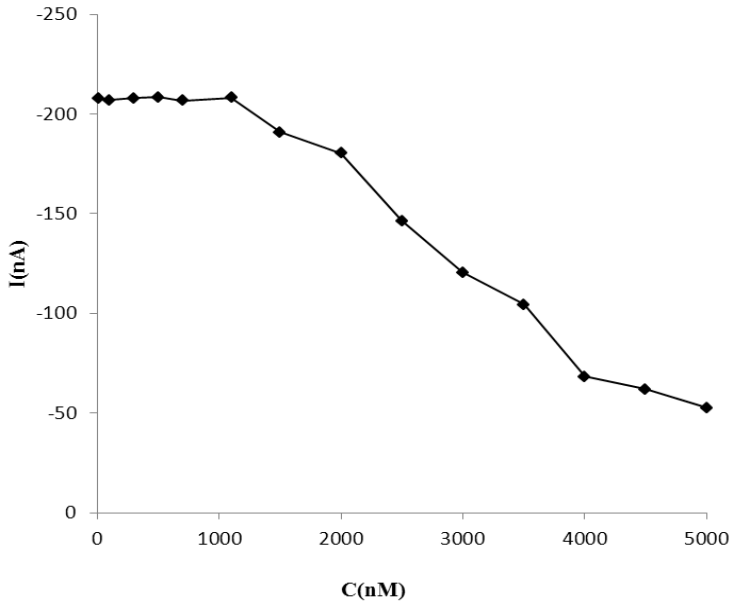


Fig.7. The effect of EDTA on peak current of Cu-MIN in optimum conditions

Table 1. Tolerance limit to foreign ions on the recovery of 5.0×10^{-7} M Cu(II)

Ions	**Tolerance limit $M_{Foreign\ ions}/M_{Cu2+}$**
K^+, Na^+, Li^+,Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Tl^+	2500
Cl^-, F^-	2000
Mn^{2+}, Cd^{2+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Ni^{2+}	1800
Co^{2+}, Pb^{2+}, Hg^{2+}, Hg_2^{2+}, Pd^{2+}, Fe^{2+}, Fe^{3+}	
Ag^+, SO_4^{2+}, HPO_4^{2-}, Cr^{6+}, As^{3+},	1500
I^-, Br^-, SCN^-	500

Table 2. Determination of copper in water and drug samples

Sample	$Cu^{2+}\times10^{-8}$M Added	$Cu^{2+}\times10^{-8}$ M Found	RSD %(n=5)	$Cu^{2+}\times10^{-8}$M Found by AAS
Karage River	0.0	4.71±0.14	1.8	4.63± 0.08
	2.0	6.68±0.15	1.7	
	4.0	8.75±0.14	1.9	
Zayandeh roud River	0.0	3.42±0.14	2.3	3.94± 0.11
	2.0	5.46±0.13	2.1	
	4.0	7.47±0.12	1.9	
Gharasoo River	0.0	4.52±0.14	1.8	4.45±0.13
	2.0	6.47±0.12	1.7	
	4.0	8.48±0.16	1.7	
Mega- Tron (tablet)	0.0	1.52±0.05	2.0	1.56±0.05
	5.0	6.58±0.14	1.9	
	10.0	11.53±0.19	1.8	

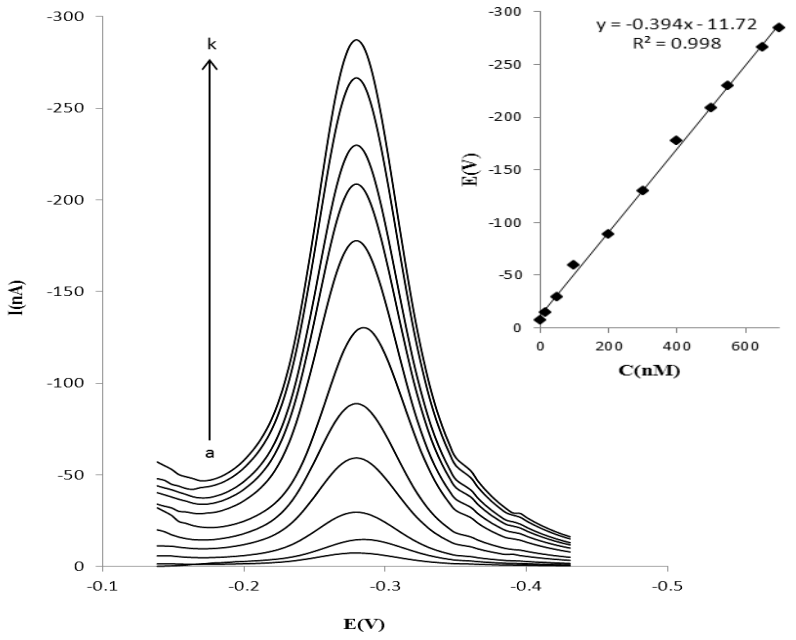


Fig.8. Differential pulse cathodic stripping voltammograms of 0.1 M B-R buffer solution (pH=10) containing different amount of Cu ions (a) 0.5, (b) 15,(c) 50,(d) 100,(e) 200,(f) 300, (g) 400,(h) 500,(i) 550,(j) 650and (k) 700×10^{-9}M at optimum conditions

3.6. Determination of copper in river water and in drug sample

For the water samples, three water samples given from the Karage river (Karage), Zayandeh Roud river (Isfahan) and Gharasoo river (Kermanshah) were analyzed. Each sample was filtered using filter paper (Whatman No.1) and then digested by UV irradiation for 2 h before analysis to destroyed organic matter. Then, into 10 ml of each sample, 2 ml of nitric acid was added and the samples heated up to dryness. Then the residue dissolved in 10 ml of water. The analysis was performed by the recommended procedure, with a standard addition method. The results of the analysis are shown in Table 2. In conclusion the present study describes an effective means for the determination of ultra trace levels of copper. The use of minoxidil offers an attractive alternative to other ligands [11-19] and pyrogallol red [16-25, 27-32].

Table 3. Some critical points in present work compared with some previous works performed by adsorptive stripping voltammetry applied for determination of copper

Ligand	LOD $ngmL^{-1}$	D. R $ngmL^{-1}$	t_{Accu}(s)	Reference
N-Phenylcinnamohydroxamic acid	0.030	0.64–64	180	[15]
Bis (acetylacetone) ethylenediimine	1.020	3.18–63.6	600	[20]
DMG and catechol (mixed)	0.030	0.03–6.35	60	[31]
Pyrogallol red	0.300	2.0–70	90	[32]
Nuclear fast red	0.200	1.0–100	180	[33]
Calcein blue	0.010	0.02–15	90	[34]
Morin	0.600	0.20–130	60	[35]
Chromazorul S	0.050	0.10–32	50	[36]
Cyclopentanone thiosemicarabzone	0.200	0.1–99.8	150	[37]
Benzotriazolate	0.190	0.19–50.8	120	[38]
Adenine	0.030	0.10–2.60	120	[39]
Zincon	1.100	2.0–220	30	[40]
2,7-PADN	0.510	0.6–64.0	240	[41]
Thiosemicarbazide	0.007	0.01–90.0	60	[42]
Minoxidil	0.005	0.03–44.48	50	This work

4. CONCLUSION

This study presented very selective ligand (minoxidil) for ultra trace determination of copper using adsorptive differential pulse stripping voltammetry. It has been shown that, after proper optimization of the experimental conditions, this method was suitable for determination of copper at sub-nM levels with satisfactory selectivity. The data presented in

Table 3 shows that the proposed scheme of analysis offers a practical potential for determination of ultra trace amount of copper with high selectivity and sensitivity, simplicity and speed that have not been present together in the previously reported anodic and adsorptive cathodic stripping voltammetric methods [11-19, 29-42]. This method was used for determination of copper in different water and drug samples with satisfactory results.

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