

A Cyclic Voltammetric Study of the Redox Reaction of Cu(II) in Presence of Ascorbic Acid in Different pH Media

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(Received: 21 June 2012; Accepted: 26 January 2013)

Abstract

The electrochemical redox behavior of Cu(II), and Cu(II) in presence of ascorbic acid has been investigated at glassy carbon electrode (GCE) in aqueous phosphate buffer solution (PBS) at various pH. In the studied pH range the voltammogram consists of a cathodic and an anodic peak. Cu(II) follows one step two-electron transfer electrochemical redox reaction. The intensities of both cathodic and anodic peak current increase with increasing scan rate that are consistent with Randles-Sevcik equation. The linear behavior of peak current with the square root of scan rate indicates that the electrochemical processes are diffusion controlled. In presence of ascorbic acid both of the cathodic and anodic peak current of Cu(II) is reduced and peak positions are shifted compared to those of Cu(II) alone. These observation suggest that Cu(II) undergoes a strong interaction with ascorbic acid in the studied medium.

Keywords: Cyclic voltammetry, Ascorbic acid, Phosphate buffer, Quasi-reversible.

I. Introduction

Copper (II) is one of the biologically important chemical species that functions as a co-factor in metalloenzymes and metalloproteins¹. It is also regarded as an essential component of different organs such as blood, bones, teeth, nerves, etc. Its imbalance may result anemia, Wilson disease etc., and a number of other diseases in animals². Its redox behavior may play a vital role to maintain its biological activities in association with different biomolecules especially with electron donor atoms at different pH.

Ascorbic acid is a sugar acid with antioxidant properties which is commonly known as vitamin C. It is generally found in all plants, animals and single-cell organisms³. Reptiles and older orders of birds make ascorbic acid in their kidneys. Recent orders of birds and most mammals make ascorbic acid in their liver where the enzyme L-gulonolactone oxidase is required to convert glucose to ascorbic acid⁴. Fat-soluble esters of ascorbic acid with long-chain fatty acids can be used as food antioxidants.

Electrochemical redox reaction of Cu(II) in different supporting electrolytes media in the acidic pH range⁵⁻¹⁰ and basic medium^{11,12} has been investigated because of its application in electrolysis, microelectronics, electroplating, sensors, batteries and biochemical catalytic systems¹³. The mechanism and kinetic behavior of the reduction of aquo-Cu(II) have been investigated using a number of electrochemical techniques, such as dc polarography^{6,10,14}, ac polarography⁶⁻¹⁷, hydrodynamic voltammetry¹⁸⁻²⁰, chronoamperometry at constant potential^{8,21}, and coulometry^{22,23}. Cyclic voltammetric study of Cu(II) in presence of various ligands have also been investigated and reported in details²⁴⁻²⁶. The present study reports the electrochemical redox behavior of Cu(II), and its interaction with ascorbic acid in aqueous phosphate buffer solution.

II. Experimental

Materials

Analar grade copper chloride (CuCl₂·2H₂O) was purchased from Uni Chem, China. For the preparation of phosphate

buffer solution (PBS), potassium dihydrogen orthophosphate (KH₂PO₄) (Merck, Germany), and di-potassium hydrogen phosphate (K₂HPO₄) (Merck, Germany) were procured and used without further treatment. Ascorbic acid obtained from BDH, UK was used as the ligand.

Equipments

A three electrode system consists of glassy carbon electrode (GCE) as the working electrode, Ag/AgCl (satd. KCl) as the reference electrode and platinum wire as the counter electrode were used. Cyclic voltammetric measurement was performed using Computerized Electrochemical System, Model HQ-2040 developed by Advanced Analytics, USA. Solution pH was measured with a pH meter of TOA, Model HM-16S.

Methods

Phosphate buffer solution (PBS) was prepared as follows: 0.1 M KH₂PO₄ and 0.1 M K₂HPO₄ were prepared separately in two volumetric flasks and then the buffer solutions of pH 5.30, 5.82, 6.20, 6.39, 6.59, 6.79 and 7.20 were prepared by mixing requisite volume of the solution, individually. CuCl₂·2H₂O was dissolved in PBS to prepare 1.0, 2.0, 3.0 and 4.0 mM Cu(II) solutions at different pH values. Milli-Q deionized water was used throughout the experiments. GCE was polished with fine alumina powder of 0.3 and 0.05 micron on a wet polishing cloth. For doing so a part of the cloth was made wet with deionized water and alumina powder was sprinkled over it. The GCE was then polished on this surface by pressing softly the electrode against the polishing surface for about 10 minutes. A shiny black mirror like electrode surface was then thoroughly washed with deionized water.

First of all, the cell was filled with desired volume of the experimental solution and the Teflon cap was placed on the cell. The purging glass tube together with reference electrode was inserted through the holes. Under computer controlled stirring, experimental solution was deaerated by purging for at least 10 minutes with 99.9977% pure nitrogen gas. By this way, traces of dissolved oxygen were removed

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from the solution. Solution pH was varied from 5.30 to 7.20 and the scan rate was varied from 25 to 100 mVs⁻¹.

III. Results and Discussion

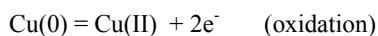
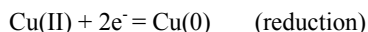
In the present study cyclic voltammetric investigation of Cu(II) in phosphate buffer solution (PBS) at pH 5.30, 5.82, 6.20, 6.39, 6.59, 6.79 and 7.20, and its interaction with ascorbic acid of different molar concentrations (1.0, 2.0, 3.0 and 4.0 mM) at identical condition were carried out at GCE.

Voltammetric response of Cu(II)

The electrochemical redox behavior of 1.0 to 4.0 mM Cu(II) solutions in PBS at different pH (5.30 to 7.20) was investigated at GCE within the potential window of +750 to -570 mV. At more positive or negative potential values only solvent decomposition current was observed.

A typical cyclic voltammogram recorded for 1.0 mM Cu(II) in PBS with scan rate of 100 mVs⁻¹ at pH 5.30 is shown in Fig. 1. In the forward scan a cathodic peak, i_{pc} at about -207.4 mV, and in the reverse scan an intense anodic peak, i_{pa} at about +191.0 mV are observed. In the consecutive redox couple of Cu(II)/Cu(0), the cathodic peak (i_{pc}) results from the reduction of Cu(II) to Cu(0) and the anodic peak (i_{pa}) is for the oxidation of Cu(0) to Cu(II).

The above result suggests that at pH 5.30, Cu(II) undergoes one two-electron transfer redox reaction. It agrees well with the previous study²⁶. The possible mechanism of the redox reaction for the above cyclic voltammogram is as follow:



Effect of scan rate

A series of voltammograms of 1.0 mM Cu(II) at pH 5.30 in PBS at various scan rates such as 25, 50, 75 and 100 mVs⁻¹ were also recorded as shown in Fig. 2. It is found that both cathodic and anodic peak current linearly increases with the increasing of scan rate. The position of the cathodic peak slightly shifted towards the negative potential and the anodic peak shifted a little towards positive direction with the increase of scan rate. These observations suggest a diffusion controlled redox process in PBS medium.

The peak currents for both cathodic and anodic peak are recorded. Almost a linear variation of peak currents with square root of scan rate is observed suggesting that the process is diffusion controlled. Furthermore a plot of peak current vs scan rate for the cathodic and anodic peaks is also linear. This linear behavior demonstrates a combination of diffusion and surface controlled redox system, where the peak currents for adsorbed and desorbed species are

proportional to $v^{1/2}$ and v , respectively^{25,27}. The cathodic and anodic peak potentials (E_p), peak currents (i_p), peak current ratio (i_{pa}/i_{pc}) and peak potential separation (ΔE_p) are compiled in Table 1.

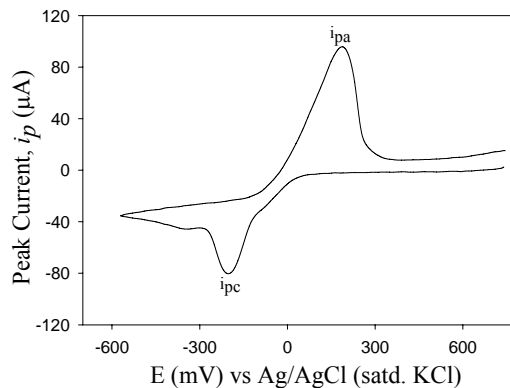


Fig. 1. Cyclic voltammogram response of 1.0 mM Cu(II) in PBS at pH 5.30 with scan rate of 100 mVs⁻¹ at GCE.

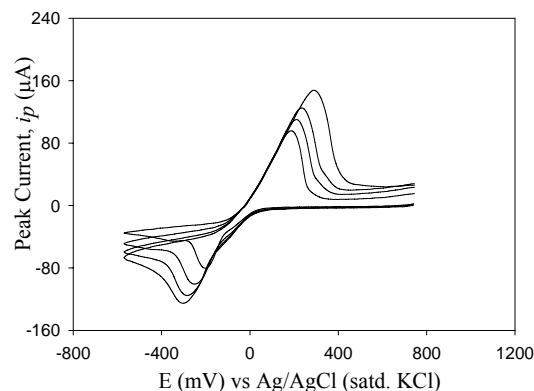


Fig. 2. Cyclic voltammograms of 1.0 mM Cu(II) in PBS with scan rates of 25, 50, 75 and 100 mVs⁻¹ at pH 5.30.

A plot of $\log i$ vs. $\log v$ (Fig. 3) is linear indicating that (i) the process is diffusion controlled^{28,29} and (ii) the peak current is controlled by both charge transfer and mass transport³⁰. The ratio of the oxidation peak current to its corresponding reduction counterpart, (i_{pa}/i_{pc}) is about 1.20-1.09, and the dependence of peak current ratio with scan rate is shown in Fig. 4. The peak current ratio is greater than unity, which corresponds to a quasi-reversible system^{27,31}.

The peak potential separation, ΔE_p is in between 397.44 to 592.92mV. It reveals that the peak potential separation increases with the increasing of scan rate. This may be due to the slow electron transfer kinetics or Ohmic potential (iR_s) drop^{25,32}.

Effect of concentration

The cyclic voltammograms of 1.0, 2.0, 3.0 and 4.0 mM Cu(II) in PBS at 100 mVs⁻¹ are recorded. It is observed that the voltammograms consists of one cathodic and one anodic

peak in the studied concentrations of Cu(II). Both cathodic and anodic peak currents linearly increases with the increasing Cu(II) concentrations.

The rate of diffusion of Cu(II) towards the electrode surface thus increases as the concentration of Cu(II) increases. A gradual increase of peak current with the increase of Cu(II) concentration was observed. This behavior may be due to the presence of a large amount of electroactive species at

higher concentration³³. The system also follows a diffusion controlled mechanism^{27,31}.

Effect of pH on the voltammetric response of Cu(II)

The effect of pH has also been investigated. The studied pHs are 5.30, 5.82, 6.20, 6.39, 6.59, 6.79 and 7.20. The recorded voltammograms for Cu(II) at different pH are shown in Fig. 5.

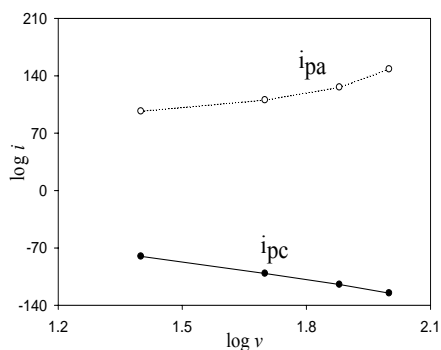


Fig. 3. A plot of $\log i$ vs. $\log v$ for the voltammograms of 1.0 mM Cu(II) in PBS at pH 5.30.

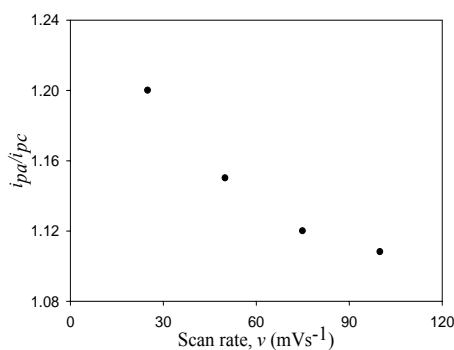
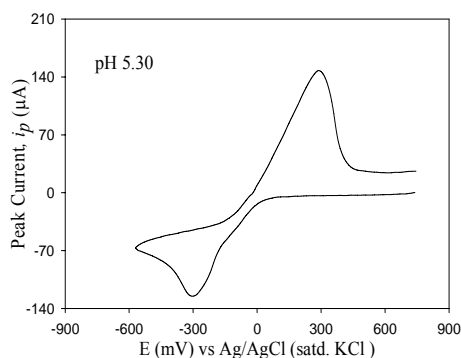
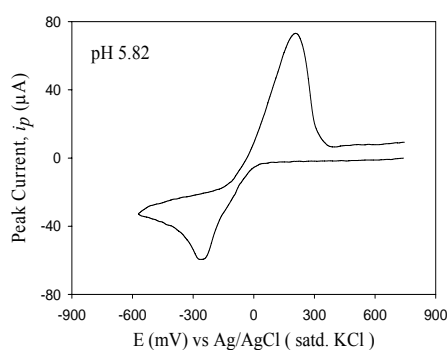


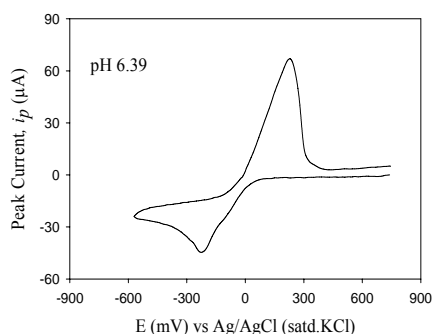
Fig. 4. Dependence of peak current ratio on scan rate of 1.0 mM Cu(II) in PBS at pH 5.30.



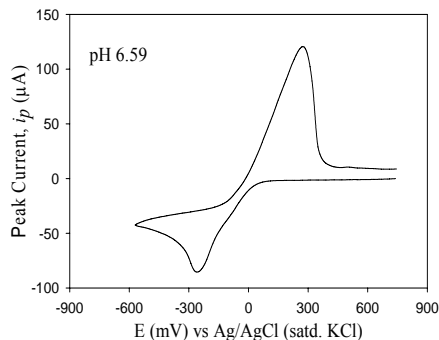
(a)



(b)



(c)



(d)

Fig. 5. Cyclic voltammograms of 1.0 mM Cu(II) with scan rate of 100 mVs^{-1} at pH (a) 5.30, (b) 5.82, (c) 6.39, and (d) 6.59 in PBS at GCE.

Table 1. Data for the effect of scan rate on peak current and peak potential of 1.0 mM Cu(II) in PBS at pH 5.30.

Scan rate (mVs ⁻¹)	SQRT of scan rate	Peak current (μ A)		Peak potential (mV)		$\Delta E_p = E_{pa} - E_{pc}$	i_{pa}/i_{pc}
v	$v^{1/2}$	$(-)i_{pc}$	i_{pa}	$(-)E_{pc}$	E_{pa}		
25	5.00	80.20	96.80	207.44	190.00	397.44	1.20
50	7.07	101.1	110.4	252.44	208.72	461.16	1.09
75	8.66	114.6	126.0	290.24	231.04	521.28	1.10
100	10.00	125.0	148.2	301.4	291.52	592.92	1.19

Table 2. Data obtained from the various voltammograms taken for Cu(II) in PBS at different pH.

Solution pH	CPC, i_{pc} μ A (-)	APC, i_{pa} μ A	CPP, E_{pc} mV (-)	APP, E_{pa} mV	$\Delta E_p = E_{pa} - E_{pc}$	i_{pa}/i_{pc}
5.30	125.0	148.2	301.4	291.53	592.93	1.19
5.82	59.52	73.20	263.0	201.52	464.52	1.23
6.20	82.00	92.53	297.44	235.0	532.44	1.05
6.39	44.16	67.52	226.16	223.48	449.64	1.06
6.59	83.51	117.73	240.0	255.0	495.0	1.42
6.79	19.98	26.24	175.62	118.11	293.73	1.31
7.20	112.66	171.43	186.95	274.27	461.22	1.51

CPC = Cathodic peak current, APC = Anodic peak current, CPP = Cathodic peak potential, APP = Anodic peak potential

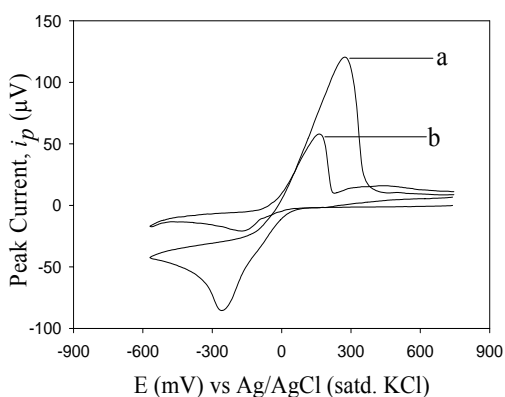


Fig. 6. Cyclic voltammograms of (a) 1.0 mM Cu(II), and (b) Cu(II) in presence of ascorbic acid of molar ratio 1:4 at pH 6.59 in PBS with scan rate of 100 mVs⁻¹ at GCE.

It is observed that at all studied pH the voltammograms show a cathodic and an intense anodic peak. At lower pH both cathodic and anodic peak current are high (Table 2). However, with the increase of pH, the cathodic and the anodic peak current gradually decrease. Moreover, the anodic peak and the anodic peak are shifted toward positive and negative values respectively with increasing pH. It implies that the quasi-reversible electrochemical process is shifted towards the irreversible process.

Cyclic voltammetric response of Cu(II) in presence of ascorbic acid

Cyclic voltammetric response of ascorbic acid in PBS solution at GCE within the potential window of +100 to

+1000 mV was recorded. It exhibits an intense peak in the anodic region while no peak in the cathodic region within the studied potential window. The interaction of Cu(II) with ascorbic acid in PBS has been investigated by electrochemical method. The cyclic voltammograms for 1.0 mM Cu(II), and Cu(II) in presence of various molar concentration of ascorbic acid (e.g., Cu(II)/ascorbic acid 1:1, 1:2, 1:3 and 1:4) at different pH (pH 5.30, 5.82, 6.20, 6.39, 6.59, 6.79 and 7.20) have been recorded. Voltammograms of 1.0 mM Cu(II), and Cu(II) in presence of ascorbic acid of molar ratio 1:4 with scan rate of 100 mVs⁻¹ at pH 6.59 are shown in Fig. 6.

It reveals that in presence of ascorbic acid the anodic and cathodic peak current are drastically reduced compared to that of solely Cu(II). Moreover, the peak potentials for both cathodic and anodic peaks are shifted. These results suggest a strong interaction between Cu(II) and ascorbic acid. The recorded voltammograms for 1.0 mM Cu(II), and Cu(II) in presence of various molar concentration of ascorbic acid (Cu(II)/ascorbic acid 1:1, 1:2, 1:3 and 1:4) at pH 5.30, 5.82, 6.39, and 6.59 are shown in Fig. 7.

At all cases, both cathodic and anodic peak heights of Cu(II) are reduced and the peak potentials are shifted. Nevertheless Cu(II) undergoes complexation reaction with ascorbic acid at various molar concentration and at different pH.

However, the maximum interaction is occurred for 1:4 molar ratio of Cu(II) and ascorbic acid at pH 5.82 and 6.59. This molar ratio might be the suitable condition for the compound formation between Cu(II) and ascorbic acid.

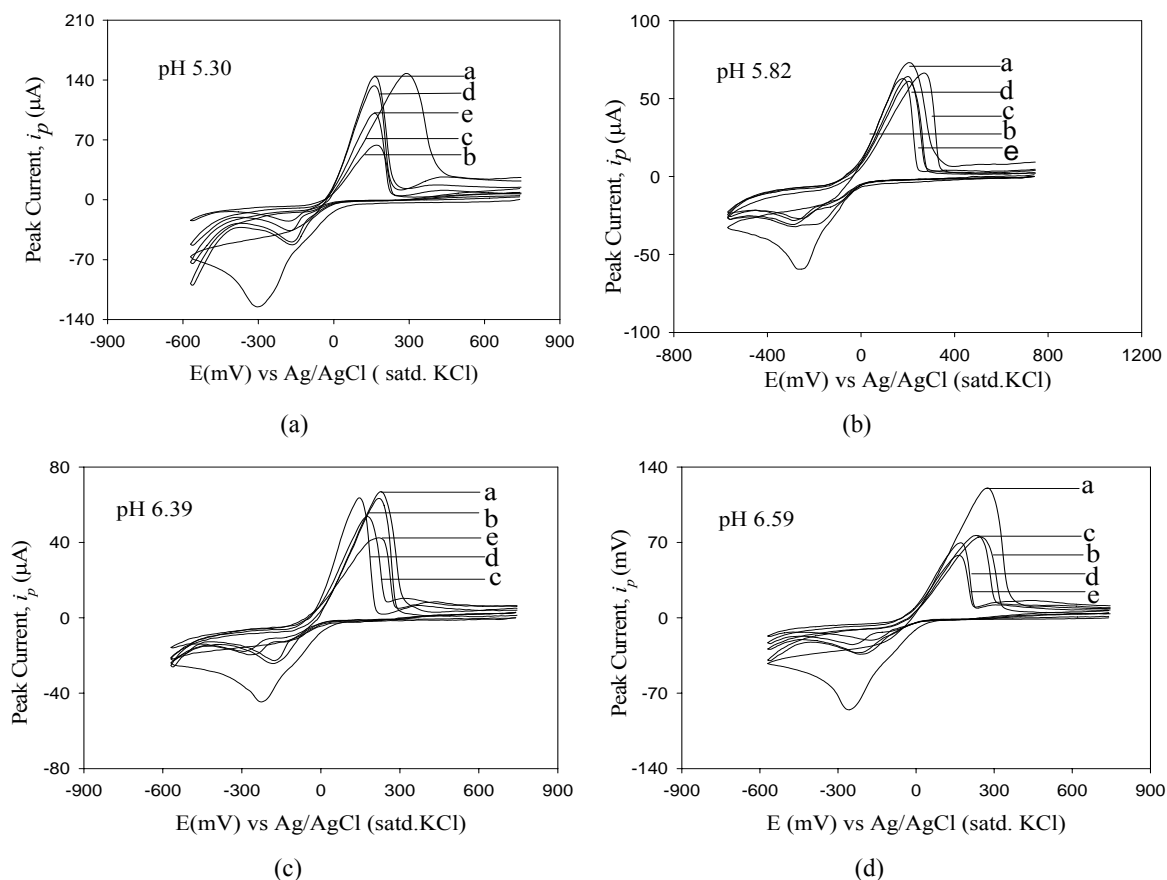


Fig. 7. Cyclic voltammograms of (a) 1.0 mM Cu(II), and Cu(II) in presence of ascorbic acid of molar ratios (b) 1:1, (c) 1:2, (d) 1:3 and (e) 1:4 at pH (i) 5.30, (ii) 5.82, (iii) 6.39 and (iv) 6.59 in PBS with scan rate of 100 mVs^{-1} at GCE.

IV. Conclusion

The electrochemical redox behavior of Cu(II) in aqueous PBS at different pH has been studied. A cathodic and an anodic peak is appeared in the voltammograms that reveals Cu(II) undergoes a one step two-electron transfer electrochemical redox reaction. The linear behavior of peak current against square root of scan rate indicates that the electrochemical process is diffusion controlled. At lower pH the peak current are very high and gradually decreases with the increase of pH. In presence of ascorbic acid both the cathodic and anodic peak current of Cu(II) is reduced and the peak positions are shifted compared to those of Cu(II) alone. These observations suggest that Cu(II) undergoes a strong interaction with ascorbic acid in the studied condition, and the maximum interaction has been occurred for 1:4 molar ratio of Cu(II) and ascorbic acid at pH 6.59.

Acknowledgement

The authors are grateful to the University of Dhaka for financial support.

References

- Bernhard, M. and E. Zattera, 1973. Effects of temperature on the toxicity to the aquatic biota of waste discharge, Proc. 2nd. Int. Congr. On Marine Waste Disposal, *San Remo*, 195.
- White, A., P. Harder and E.L. Smith, 1964. Principles of Biochemistry, 3rd edition, 189.
- Valpuesta, V. and M.A. Botella, 2004. Biosynthesis of ascorbic acid in plants: new pathways for an old antioxidant, *TRENDS in Plant Science*, **9**, 12.
- Stone, I., 1972. The natural history of ascorbic acid in the evolution of the mammals and primates and its significance present day man, *Orthomolecular Psychiatry*, **1**, 82-89.
- Sroka, R. and H. Fischer, 1956. *Z. Elektrochem.*, **60**, 109.
- Kolthof, I.M. and Y. Okinaka, 1959. Cyclic voltammetric studies of pH dependence of Cu(II) reduction, *J. Am. Chem. Soc.*, **81**, 2296.
- Mattsson, E. and J.O.M. Bockris, 1959. Mechanism of the dissolution of copper, *Trans. Faraday Soc.*, **55**, 1586.
- Okinaka, Y., S. Toshima and H. Okinaka, 1964. The effect of uncompensated resistance on the potential-step method, *Talanta*, **11**, 203.

9. Chao, F. and M. Costa, 1968. Mechanism of copper deposition in a sulphate bath containing chlorides, *Bull. Soc., Chim. Fr.*, **10**, 4015.
10. Arvinda, C.L., S.M. Mayanna and V.S. Muralidharan, 2000. Electrochemical studied of pH dependence of Cu(II), *Proc. Indian Acad. Sci.*, **112**, 543.
11. Ambrose, J., R.G. Barradas and D.W. Shoesmith, 1973. Nature and mechanism of anodic film formation on Cu in alkaline phosphate media, *J. Electroanal. Chem.*, **47**, 47.
12. Chander, S. and D.W. Fuerstenau, 1974. Electrochemical studies of copper(II) at glassy carbon electrode, *J. Electroanal. Chem.*, **56**, 217.
13. Huheey, J.E., E.A. Keiter and R.L. Keiter, 2000. Inorganic Chemistry Principles of Structure and Reactivity, 4th edition, Pearson Education, Inc.
14. Brever, B., F. Gutmann and S. Hacobian, 1951. The polargographic determination of antimony, *Aust. J. Sci. Res.*, **4 (A)**, 595.
15. Breyer, B., H.H. Bauer and J.D. Beevers, 1961. Medical chemistry of cardiovascular agents and endocrines, *Aust. J. Chem.*, **14**, 479.
16. Hawkrige, M., Jr. and H.H. Bauer, 1972. Cyclic voltammetric studies of pH dependence of copper(II) reduction in acidic aqueous nitrate., *Anal. Chem.*, **44**, 364.
17. Altermatt, J.A. and S.E. Manahan, 1968. Cyclic voltammetric studies of copper(II) amino acid complexes, *Anal. Chem.*, **40**, 655.
18. Brown, O.R. and H.R. Thirsk, 1965. The differential capacitance of polycrystalline copper in aqueous solution, *Electrochim Acta*, **10**, 383.
19. Bixler, J.W. and W.F. Stafford, 1968. Kinetics and mechanism of the reduction of 1.10-phenanthroline, **40**, 425.
20. Stulikova, M. and F. Vydra, 1973. A spectral and polarographic study of the acid-base, *J. Electroanal. Chem.*, **44**, 117.
21. Tanaka, N., A. Kitani, A. Yamada and K. Sasaki, 1973. Computer-aided measurements of kinetic parameters of electrode reaction, *Electrochim. Acta*, **18**, 675.
22. Tindall, G.W. and S.S. Bruckenstein, 1966. Electrochemical studies of copper at glassy carbon electrode, *Anal. Chem.*, **40**, 1637.
23. Miller, R.W., 1961. Determination of heterogeneous equilibrium constants by chemical stripping, Ph.D. Thesis, The University of Illinois, Urbana, 3.
24. Shaikh, A.A., S.N. Afzal, M.Q. Ehsan and A.H. Khan, 2005. *J. Saudi Chem. Soc.*, **9(2)**, 279-286.
25. Shaikh, A.A., M. Begum, A.H. Khan, M.Q. Ehsan and A.H. Khan, 2006. *Russ. J. Electrochem.*, **42(6)**, 620-625.
26. Shaikh, A.A., J. Firadows, Badrunnessa, S. Serajee, M.S. Rahman and P.K. Bakshi, 2011. Electrochemical studies of the pH dependence of Cu(II) reduction in aqueous britton-robinson buffer solution, *Int. J. Electrochem. Sci.*, **6**, 2333-2343.
27. Bard, A.J. and L.R. Faulkner, 1980. *Electrochemical Methods Fundamentals and Applications*, John Wiley and Sons, New York, 228.
28. Mascus, M., F. Parients, Q. Wu, A. Toffanin, J.P. Shapleigh and H.D. Abruna, 1996. Characterization of the gene encoding nitrite reductase, *Anal. Chem.*, **68**, 3128.
29. Nicolson, R.S. and I. Shain, 1964. Simulation of the electrochemical behavior of multi-redox system, *Anal. Chem.*, **36**, 706.
30. Wang, J., 1948. *Analytical Electrochemistry*, Wiley-VCH, Inc., New York, 1.
31. Brett, C.M.A., and O. Brett, 1998. *Electrochemistry in the presence of convective flow*, **145**, 1994-1999.
32. Zhang, J., 1972. *Electrochemical Methods: Fundamental and Applications*, *Electro Anal. Chem.*, **331**, 945.
33. Christian, G.D., 2004. *Analytical Chemistry*, 6th edition, John Wiley and Sons, New York, USA.