

*Full Paper*

## **Redox Behavior of Biologically Important Fe-Catechol Complexes at Different pH**

**Khan Muhammad Salim Reza<sup>1</sup>, Muhammad Abdul Motin<sup>1,\*</sup>, Muhammad A. Hafiz Mia<sup>1</sup>, Muhammad Matiar Rahman<sup>1</sup>, Muhammad Abdul Aziz<sup>1</sup> and Muhammad Abul Hasem<sup>2</sup>**

<sup>1</sup>*Department of Chemistry, Khulna University of Engineering & Technology (KUET), Khulna 9203, Bangladesh*

<sup>2</sup>*Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna 9203, Bangladesh*

\* Corresponding Author, Tel.:+88 041 769471-5; Ext 515; Fax: +88 041 774403

E-Mail: [abdulmotin75@yahoo.com](mailto:abdulmotin75@yahoo.com) (M. A. Motin)

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**Abstract-** The redox behavior of Fe(III) in presence of Catechol (Cc) has been carried out in buffer solution of different pH, scan rate, variation of Fe(III) concentration and Cc concentration. Uncoordinated Fe(III) or Cc has been found to undergo reversible electrode reaction whereas coordinated Fe-Cc is irreversible. The peak positions of the voltammogram of Fe- Cc shifted with respect to that of free Fe(III) or Cc and also developed a new peak at 0.12 V. The peak current of Fe-Cc decreases significantly compared with that of free Fe(III) or Cc in the same experimental conditions. These behaviors ascribed the formation of complex of Fe with Cc. The complex was formed either by the addition of Cc into Fe(III) or by the addition of Fe(III) into Cc. The effect of pH of Fe-Cc complex was studied by varying pH from 2 to 8.5. The electrochemical oxidation of Fe-Cc is facilitated in lower pH media. The slope of the plots of anodic peak current,  $E_p$  against pH of Fe-Cc complex is 30 mV, indicates that the oxidation of Fe-Cc complexes proceeded via the  $2e^-/2H^+$  processes. The current functions ( $1/\nu^{-1/2}$ ) of the anodic peak of Fe-Cc decreased with the increasing of scan rate demonstrated that the behavior of electrode reaction of Fe-Cc is of ECE type.

**Keywords-** Fe-Catechol Complex, Redox interaction, pH effect, Cyclic voltammetry

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## **1. INTRODUCTION**

The multifunctional activity of many metal complexes has been found to be essential for living organisms. A significant rising interest in the design of electroactive metal ligand complex compounds as drugs and diagnostic reagents is currently observed. Metal complexes with indole derivatives, amino acids, imidazole derivatives, pyridine derivatives, Schiff bases etc. exhibited remarkable biological activity as well as electrochemical activity [1-6]. The organic ligands containing N/S/O- sites provide potential binding sites for metal ions, and any information on their coordinating properties is important to understand the role of the metal ions in biological systems.

Transition metals particularly iron (Fe) and essential trace metals such as Zn, Cu, Ni, Mn etc. are present in animal and human bodies that serve as metalloenzyme or as enzymatic activators. Iron is the most important metal ion usage in hemoglobin for oxygen transport and as an active site for many metalloenzymes. Iron is an essential element in all organisms but its supply is restricted for its low solubility under physiological conditions. For this reason, microorganisms produce low molecular weight chelating agents, called siderophores, that can solubilize iron from the environment by complexing and transporting it to the cell [7-10]. An important structural feature of siderophores is the incorporation of catechol or hydroxamate groups, which are capable of selectively binding iron(III). The high affinity of siderophores for iron makes them useful as drugs to facilitate iron mobilization in humans, especially in the treatment of iron-overloaded diseases [11]. Several mechanisms have been found or proposed for these processes [12,13]. It has been reported that electrochemical behaviors of some biochemically important amino acids and transition metal ions such as Cu, Zn, Fe studied on electrode surface [14-16].

Electroactive metal ligand complex compounds undergo oxidation and/or reduction on the electrode surface within a certain potential range. Their redox behavior can be influenced by the change in pH, substituents, concentration and scan rate. In order to understand the issue of redox behavior of Fe-Cc complexes, an experimental aspect of redox interaction in terms of electrochemical current potential curves analysis is necessary. To our knowledge, a few redox properties analyses have been carried out in Fe with aminoacids, EDTA etc., but the redox interaction analysis of Fe with Catechol at different pH, different scan rate and different concentration has not been analyzed before this work.

## **2. EXPERIMENTAL**

Ferric (III) Chloride, Catechol, Acetic acid, Sodium acetate, Potassium Chloride, Sodium di Hydrogen Ortho Phosphate and Di-Sodium Hydrogen Ortho Phosphate were of analytical grade (E-Merck).

Iron(III) in presence of Cc solutions of different concentrations were prepared at different pH by using acetate or phosphate buffer solutions. The buffer solutions were prepared by dissolving Acetic acid and Sodium acetate (pH 2-7) and by dissolving Sodium di Hydrogen Ortho Phosphate and Di-Sodium Hydrogen Phosphate (pH>7) in deionized water. The pH of the solution was adjusted by further addition of hydrochloric acid, acetic acid, sodium acetate or phosphate salt.

Platinum disks of 1.6 mm in diameter (BASi) were used as a working electrode for voltammetry. The electrode surface was polished with 0.05  $\mu\text{m}$  alumina before each run. The auxiliary electrode was a platinum coil. The reference electrode was an Ag|AgCl electrode (BASi). The working electrode was then polished on this surface by softly pressing the electrode against the polishing surface in the end for 5-10 minutes. The electrode was then thoroughly washed with deionized water. The potentiostat was  $\mu\text{Stat}$  400 (DropSens, Spain). Nitrogen gas was bubbled from the one-compartment cell before electrochemical run.

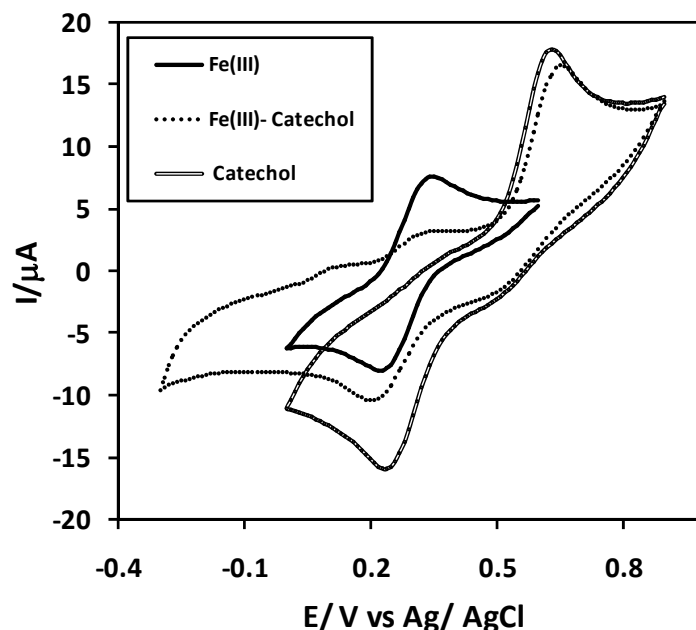
### 3. RESULTS AND DISCUSSION

#### 3.1 Redox behavior of Fe-Catechol System

The redox behavior of Fe-Catechol (Cc) system in buffer solution was performed by Cyclic voltammetry (CV). Fig. 1 (dotted line) shows the CV of Fe(III) in presence of Cc at scan rate 0.1 V/s and pH 2. It shows that the anodic peaks appeared at 0.12 V, 0.33 V and 0.65 V and the corresponding cathodic peaks at 0.21 and 0.50 V, respectively. On the other hand, uncoordinated Fe(III) shows (solid line) one anodic peak at 0.35 V and one cathodic peak at 0.23 V in the same experimental condition (Fig. 1). Uncoordinated Cc (dashed line) shows one anodic peak at 0.63 V and one cathodic peak at 0.24 V in the same experimental condition (Fig. 1).

From the Fig. 1, it is seen that the peak positions of the voltammogram of Fe-Cc is shifted with respect to that of only Fe (III) or only CC. A new anodic peak at 0.12 V also developed with the addition of Cc in Fe (III) solutions. The peak current also decreases significantly compared with that for free Fe (III) or CC in the same experimental conditions. These behavior ascribed the formation of Fe–Cc complex.

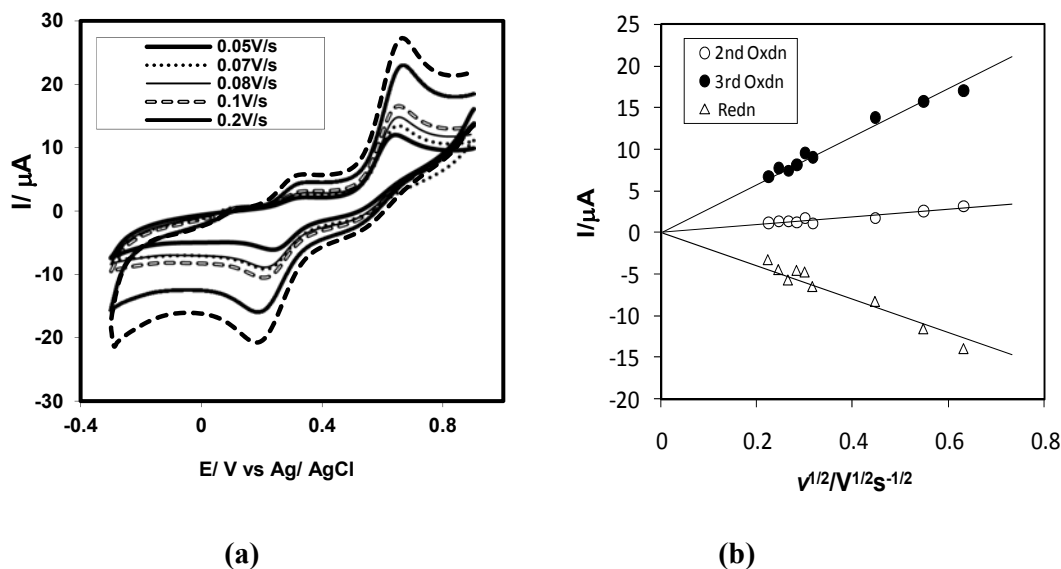
Fig. 2 (a) shows the CV of Fe- Cc in buffer solution (pH 2) at different scan rates. The peak current of both the anodic and cathodic peaks increases with the increase of scan rate. The cathodic peaks are shifted towards left and the anodic peaks are shifted slightly to the right direction with increase in scan rate. Fig. 2 (b) shows plots of the two kinds of the anodic and one cathodic net peak currents of Fe-Cc for first cycle against the square-root of the scan rates where the net current means the second peak subtracted from the first one by the scan-stopped method [18].



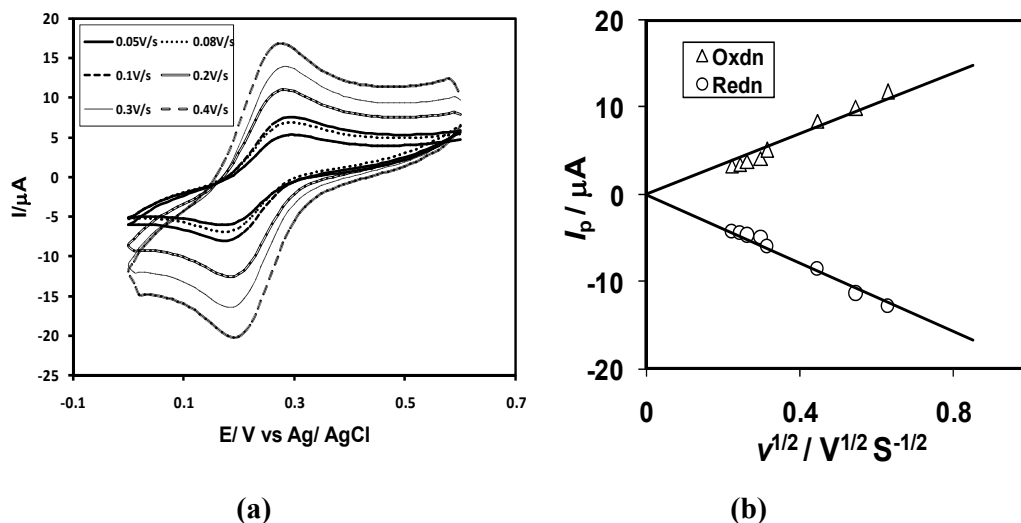
**Fig. 1.** Comparison of Cyclic voltammogram of 2 mM Catechol, 2 mM Fe(III) only and 2 mM Fe(III)- Catechol in buffer solution (pH=2.0) at scan rate 0.1 V/s

The nearly proportionality of the anodic and the cathodic peaks suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process. For second cycle, anodic and cathodic peak current is not a linear behavior of  $i_p$  vs. square root of scan rate suggest that second cycle peak current is affected by chemical complications or polymerization. The CV of uncoordinated 2mM Fe(III) in aqueous solution of 1 M KCl at different scan rates are shown in Fig. 3 (a). Fig. 3(b) shows plots of the anodic and the cathodic net peak currents against the square-root of the scan rates. The proportionality of the anodic and the cathodic peaks also suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process. For uncoordinated Catechol, the anodic and cathodic peak current for redox reaction is also controlled by diffusion.

The corresponding anodic and cathodic peak current ratios ( $I_{pa}/I_{pc}$ ) of Fe-Cc are much lower than one (Table 1). It indicates that voltammetric reactions of Fe-Cc are not reversible at any scan rate. From the Table 1, it is seen that the corresponding peak potential difference are  $>0.1$  V which is higher than theoretical one electron transfer reaction. The measured value is sometimes higher due to uncompensated solution resistance between the reference and working electrodes and non-linear diffusion [19]. The corresponding peak potential separation increases with the increase in scan rate. It indicates that there is a limitation due to charge transfer kinetics or ohmic potential ( $iR$ ) drop [20].



**Fig. 2.** (a) Cyclic voltammogram of 2 mM Fe (III)-6 mM Catechol (1:3) in buffer solution (pH=2.0) at different scan rate. (b) Plots of peak current versus square root of scan rate of Fe (III)-Catechol (1:3) in same condition



**Fig. 3.** (a) Cyclic voltammogram of 2 mM Fe(III) in aqueous solution at different scan rate. (b) Plots of peak current versus square root of scan rate in same condition

For uncoordinated Fe(III), the current ratio is very close to one and independent of scan rate. It indicates that the voltammetric reactions of Fe(III) in aqueous solutions are reversible at any scan rate. The corresponding peak potentials are  $\sim 0.08$  V which is slightly higher than

theoretical one electron transfer reaction. For Catechol, the corresponding anodic and cathodic peak current ratio ( $I_{pa}/I_{pc}$ ) is close to one. It indicates that the voltammetric reactions of Catechol in aqueous buffer solutions are also reversible.

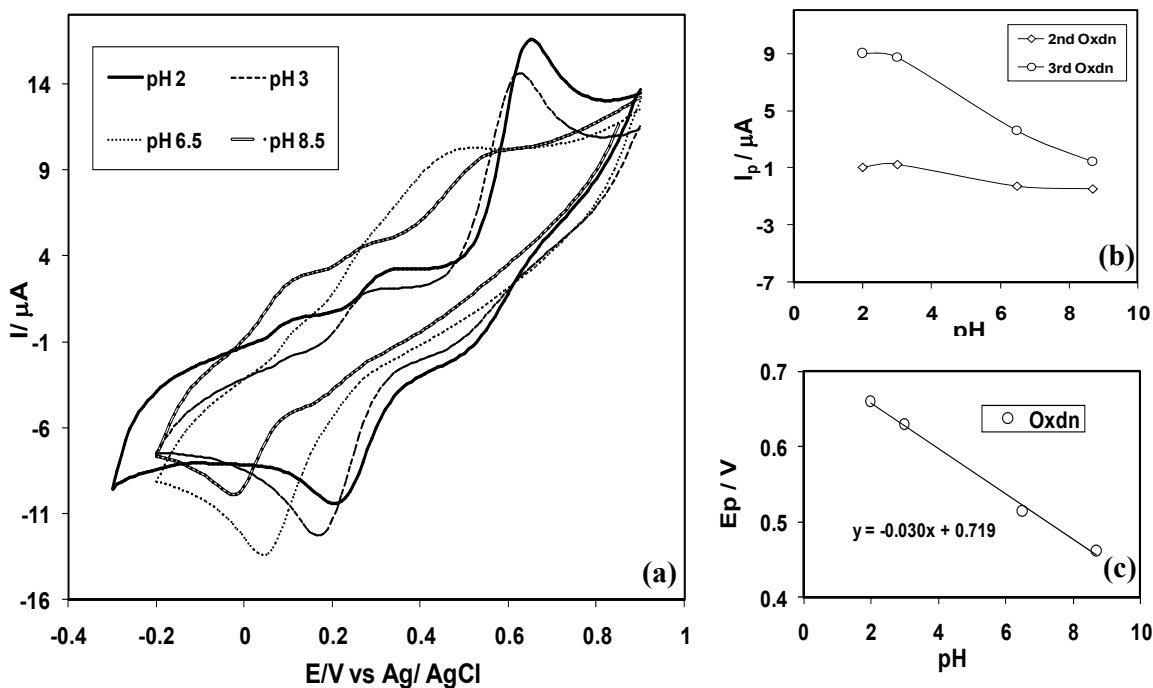
**Table 1.** Peak potential ( $E_p$ ), corresponding peak potential difference ( $\Delta E$ ), peak separation ( $\Delta E_{1/2}$ ), peak current  $I_p$ , corresponding peak current ratio ( $I_{pa}/I_{pc}$ ), of 2 mM Fe(III)–6 mM Catechol (1:3) in aqueous buffer solution (pH=2.0) at different scan rate

$\nu/Vs^{-1}$	$E_{pa2}/V$	$E_{pc}/V$	$E_{pa3}/V$	$\Delta E = E_{pc} - E_{pa}$	$I_{pa}/\mu A$	$I_{pc}/\mu A$	$I_{pa}/I_{pc}$
0.05	0.33	0.24	0.65	0.09	1.10	-3.23	0.341
0.06	0.32	0.22	0.65	0.10	1.30	-4.44	0.293
0.07	0.33	0.22	0.66	0.11	1.28	-7.32	0.175
0.08	0.33	0.21	0.66	0.12	1.21	-4.54	0.267
0.09	0.33	0.21	0.65	0.12	1.67	-4.73	0.353
0.10	0.33	0.21	0.66	0.12	1.06	-9.90	0.107
0.20	0.33	0.19	0.67	0.14	1.74	-8.30	0.209
0.30	0.32	0.17	0.68	0.15	2.55	-11.61	0.220
0.40	0.33	0.17	0.69	0.16	3.15	-14.02	0.225

### 3.2 pH effect of Fe-Cc

Fig. 4(a) shows the comparison voltammogram of Fe-Cc in buffer solution at different pH (2.0, 3.0, 6.5 and 8.5) at scan rate 0.1 V/s. The peak position of the redox couple is found to be dependent upon pH. The peak current is plotted against pH as shown in Fig. 4 (b). From the figure it is seen that the oxidation peak current increased with the decrease in pH. The maximum peak current is obtained at pH 2. This indicates that the electrochemical oxidation of Fe-Cc is facilitated in acid media and hence the rate of electron transfer is faster. The coordination sites of the ligands molecules are increased with decreasing pH that may be favored for the formation of more Fe- Cc complex. In the pH range studied, with the increase of pH, the anodic and cathodic peak potential shifted negatively.

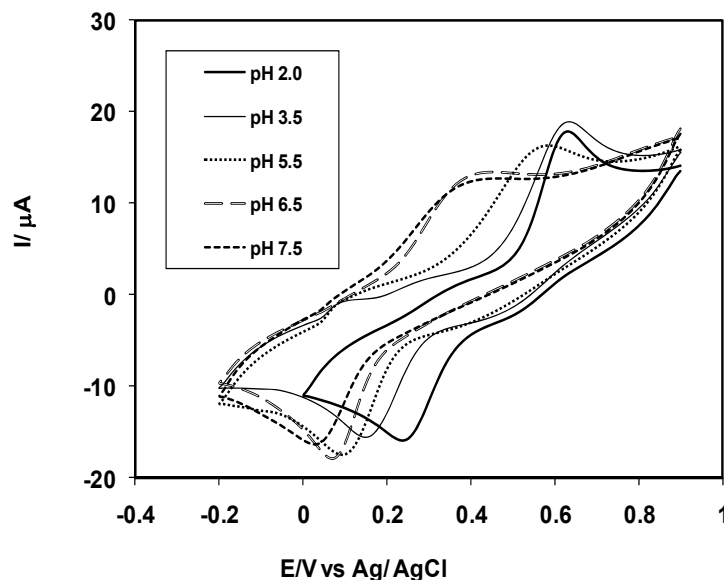
Fig. 4 (c) shows the plot of oxidation peak potential,  $E_p$  values against pH. The slopes of the plot was determined graphically as the anodic peak  $\sim 30$  mV/pH at 0.1 V/s, which is close to the theoretical value for a two-electron, two-proton transfer process. This indicates that the oxidation of the Fe-Cc proceeded via the  $2e^-/2H^+$  processes. This also suggests that during the reaction not only electron but also protons are released from the Fe-Cc complex.



**Fig. 4.** (a) Comparison of Cyclic voltammogram of 2 mM Fe (III)- 6 mM Catechol (1:3) in different pH (2, 3, 6.5, 8.5) at scan rate=0.1 Vs<sup>-1</sup>. b) Plots of peak current, Ip vs pH of Fe (III)-Catechol (1:3) in same condition. c) Plots of peak potential, Ep vs pH of Fe(III)-Catechol (1:3) in same condition

At pH 2, the CV of uncoordinated Fe(III) shows, a anodic peak at potential 0.35 V and corresponding cathodic peak at potential 0.23 V at 0.1 V/s scan rate. Consequently, the anodic peak shifted 0.05 V and cathodic peak shifted 0.05 V positively in buffer solution (pH 2) compared with that of aqueous solution. The anodic and cathodic peak current is almost unchanged with the variation of pH. The corresponding anodic and cathodic peak current ratios are close to one in buffer solution of different pH ascribed that the voltammetric reactions of Fe(III) in buffer solutions are also reversible. The peak currents of free Fe(III) are also controlled by diffusion process in buffer solution of different pH.

Fig. 5 shows the comparison voltammogram of uncoordinated 2 mM Catechol in acetate buffer solution of different pH (3.5, 5.5, 6.5, 7.5) at scan rate 0.1 V/s. The peak current increases with the decrease of pH. The maximum peak current obtained at pH 3.5. This shows that the electrochemical oxidation of Catechol is also facilitated in acid media. In the pH range studied, with the increase of pH, the anodic and cathodic peak potential of Catechol shifted negatively. Consequently, the electrode reaction of Fe-Cc complex and uncoordinated Cc is pH dependent but uncoordinated Fe(III) is pH independent.



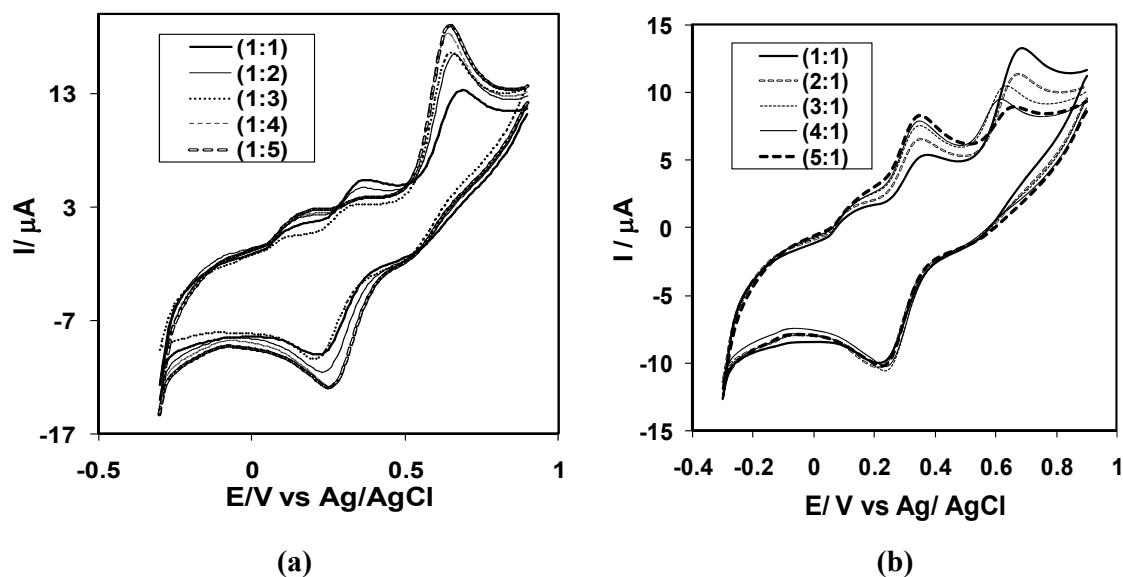
**Fig. 5.** CV of 2 M Catechol (Cc) in acetate buffer solution of different pH at scan rate 0.1 V/s

### 3.3 Concentration effect of Fe(III)-Catechol

Fig. 6 (a) shows the variation of voltammogram pattern by the addition of Catechol into fixed concentration of Fe(III) (1:1 to 1: 5). The anodic peaks shifted negatively and appeared a new peak upon addition of Catechol which indicates the formation of Fe-Cc complex. The current intensity of the new peak increases with the increase of Catechol composition upto certain composition. With the increasing of Catechol composition of 1:1 to 1:5, the first anodic peak current increases, second anodic peak current decreases and third anodic peak current increases (shown in Fig. 6 (a)). After further addition of Catechol, the first anodic peak current is unchanged. This is due to the availability of Fe(III) is limited for the binding of Cc in solution.

In Fig. 6 (b), in contrast, with the addition of Fe(III) composition into fixed concentration of Cc (1:1 to 5:1), the newly appearing first anodic peak current and second anodic peak current increases but the third oxidation peak current decreases. The peak current of the first anodic peak increases with the increase of Fe(III) composition upto certain composition. After further addition of Fe(III), the first anodic peak current intensity is unchanged. It can be assumed that the free ligand Cc concentration is insufficient for the binding of Fe(III) at this concentration. At the above of certain concentration of Fe(III), the second oxidation peak current increases may be due to the increase of free Fe(III) composition and the third oxidation peak current decreases due to the decrease of Catechol composition in solution. This also indicate that the second anodic peak is reflected for Fe(II) and the third anodic peak for Catechol.





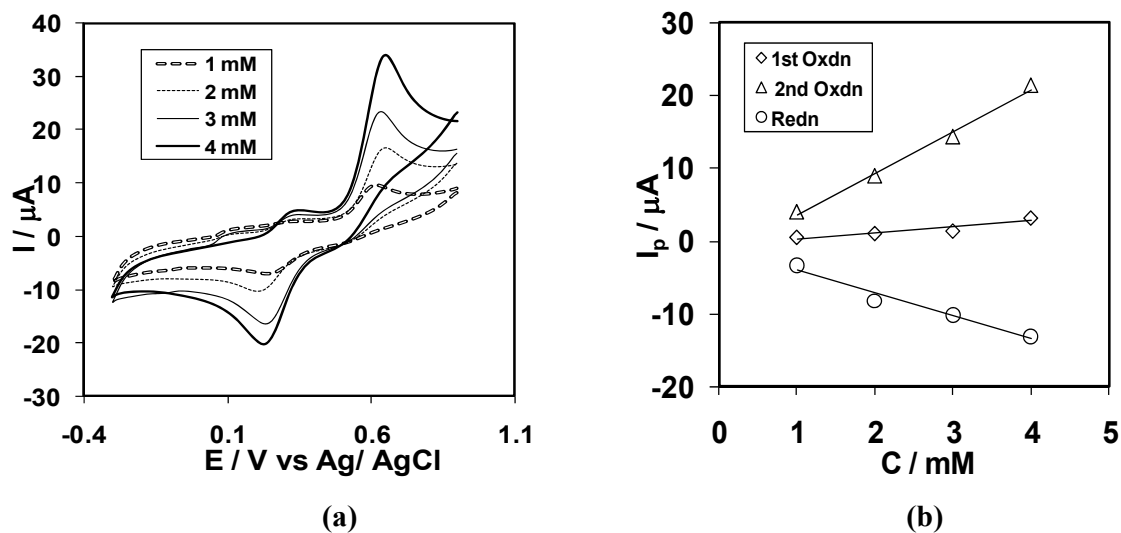
**Fig. 6.** (a) CV of composition change of Catechol with the fixed composition of 2 mM Fe (III) ((1:1), (1:2), (1:3), (1:4) and (1:5)) at pH 2 and scan rate 0.1 Vs<sup>-1</sup>. (b) CV of composition change of Fe (III) with the fixed composition of 2 mM Catechol ((1:1), (2:1), (3:1), (4:1) and (5:1)) at similar condition.

Fig. 7 (a) shows the cyclic voltammograms of increase of concentrations of both the Fe (III) and Cc simultaneously at 0.1 Vs<sup>-1</sup> scan rate. The intensity of the second and third anodic peaks and cathodic peak increases with increasing of both Fe(III)+Cc concentration. Fig. 7 (b) shows the plots of peak currents against concentration of both Fe(III)+Cc species. The relation between Fe-Cc concentration (1, 2, 3 and 4 mM) and cyclic voltammetric anodic and cathodic peak current ( $I_p$ ) is linear. With the increase in concentration there is a gradual linear increase in peak current, which may be due to the presence of a large amount of electroactive species at higher concentration.

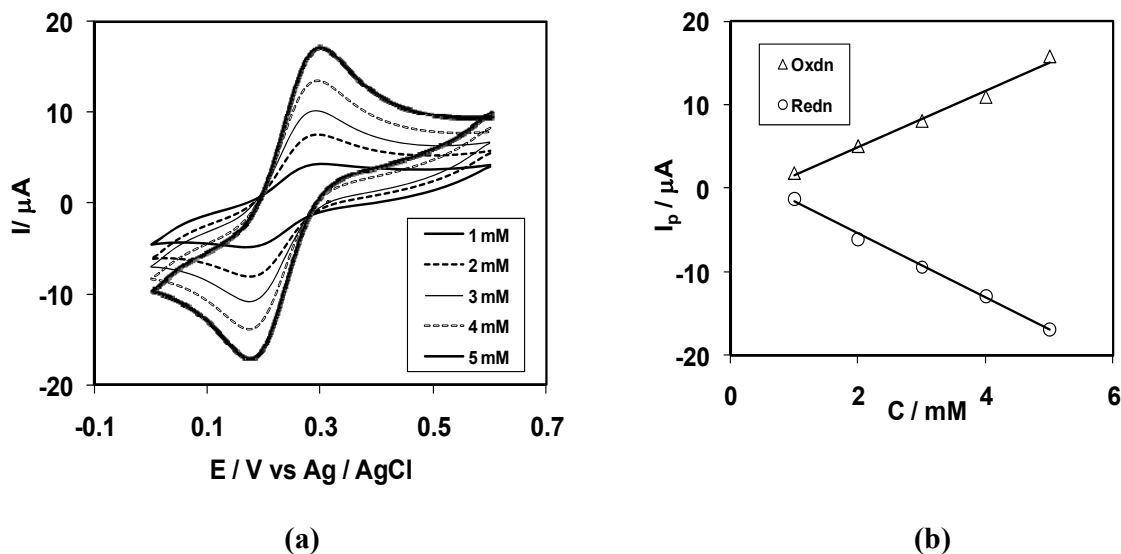
Fig. 8 (a) shows the cyclic voltammogram of different concentrations of the uncoordinated Fe(III) at 0.1 Vs<sup>-1</sup> scan rate. The intensity of the anodic and cathodic peak current increases with increasing of Fe(III) concentration. The effect of concentration can be shown by recording the CV at each concentration (1, 2, 3, 4 and 5 mM) and plotting  $i_p$  vs. concentration for either the anodic peak or the cathodic peak (Fig. 8 (b)). The relation between Fe(III) concentration and cyclic voltammetric anodic and cathodic peak current ( $I_{pa}$ ) is also linear. The linear dependence of peak current of Fe(III) concentration is depicted from the calibration curve shown in Fig. 8 (b).

For the explanation of reaction mechanism of electrode reaction, it is necessary to plot of the current functions ( $1/v^{-1/2}$ ) vs. scan rate. The current functions of third anodic peak

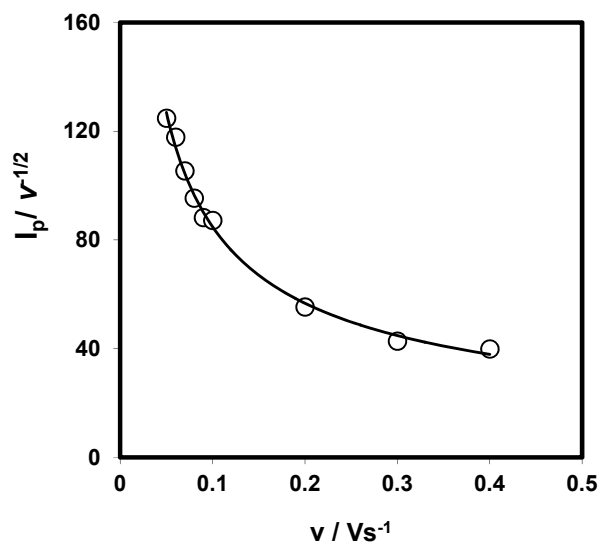
decreased with the increasing of scan rate (Fig. 9). So the behaviors of electrode reaction of Fe-Cc are of ECE type.



**Fig. 7.** (a) Cyclic voltammogram of 2 mM Fe(III)–6mM Catechol (1:3) in buffer solution of pH 2 at scan rate 0.1 V/s. (b) Plots of peak current versus concentration of Fe(III)-Catechol (1:3) in same condition



**Fig. 8.** (a) Cyclic voltammogram of Fe(III) in aqueous solution at scan rate  $0.1 Vs^{-1}$  for concentration 1, 2, 3, 4, 5 mM. (b) Plots of peak current versus concentration of  $FeCl_3$  in aqueous solution at same scan condition



**Fig. 9.** Plots of current function,  $I_p/v^{1/2}$  versus scan rate of 2 mM Fe (III)- 6mM Catechol (1:3) in buffer solution of pH 2

#### 4. CONCLUSION

Cyclic voltammetric studies were used to investigate the interaction behavior of biologically important Fe(III) with Catechol (Cc). The interaction studies have been carried out in variation of Fe(III) concentration, Cc concentration, pH and scan rate. The CV results indicated that uncoordinated Fe(III) or Catechol systems voltammogram are reversible but Fe- Cc systems is irreversible. By the addition of Cc into Fe (III) both the cathodic and anodic peak potentials were shifted and developed a new peak. The development of the new peak or shifted of peak potentials suggested the formation of Fe- Cc complex. The complex was formed either by the addition of Cc into Fe(III) or by the addition of Fe(III) into Cc. The intensities of the peak current were increased with increasing both the concentrations of metal ions as well as ligands. The peak current of Fe- Cc complexes increases with the decrease of pH. The maximum peak current was obtained at pH 2. The electrochemical oxidation of Fe-Cc complexes is facilitated in acid media and hence the rate of electron transfer is faster. The oxidation of the Fe- Cc complex proceeded via the  $2e^-/2H^+$  processes. A linear behavior of  $i_p$  vs. square root of scan rate plot indicated that the electrochemical processes of Fe-Cc complex are diffusion controlled. The current functions ( $1/v^{1/2}$ ) decreased with the increasing of scan rate demonstrated that the behavior of electrode reaction of Fe-Cc are of ECE mechanism.

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