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Electrochemical assessment of the reduction priority of Cu^{2+}, Cd^{2+}, and Ag^{+} at different pH in the presence of cysteine by cyclic voltammetry

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Abstract

This study explores the electrochemical reduction behavior and complexation priority of Cu^{2+}, Cd^{2+}, and Ag^{+} ions in the presence of L-cysteine across a pH range of 1.0 to 6.0 using cyclic voltammetry. L-cysteine, a biologically significant thiol-containing amino acid, forms coordination complexes with transition metal ions via its -SH, $-NH_2$, and -COOH functional groups. The voltammetric analysis reveals pH-dependent changes in peak potential and peak current, indicative of metal-ligand interactions. At low pH (1-2), Cu^{2+} exhibits the strongest complexation with cysteine, as evidenced by significant suppression of its cathodic peak current. From pH 3 to 6, Cd^{2+} shows the most pronounced peak current suppression, reflecting the formation of stable Cd-cysteine complexes. Ag^{+}, in contrast, demonstrates relatively weak complexation throughout the pH range. The observed complexation trend follows the order $Cd^{2+} > Cu^{2+} > Ag^{+}$, consistent with thermodynamic stability data and Pearson's HSAB theory. The findings emphasize the critical role of pH in modulating ligand nucleophilicity and complex stability, with implications for metal ion speciation, bioavailability, and electrochemical sensing applications.

Keywords: L-cysteine, pH, reduction priority, complexation, metal ion

Introduction

The redox behavior of biologically and environmentally relevant metal ions in the presence of sulfur-containing ligands such as L-cysteine has been extensively studied due to its significance in bioinorganic chemistry, toxicology, and electrochemical sensor development. Cysteine, a thiol-containing amino acid, plays a vital role in coordinating metal ions through its thiol (-SH), amine ($-NH_2$), and carboxylic (-COOH) functional groups, forming stable metal-ligand complexes that influence both biological pathways and environmental mobility [1-3]. Transition metals like copper (Cu^{2+}), cadmium (Cd^{2+}), and silver (Ag^{+}) show high affinities toward thiol donors and participate in redox-active interactions with cysteine, resulting in metal-cysteine complexes with distinct electrochemical characteristics [4-6]. Cu^{2+} is an essential trace element involved in enzymatic catalysis and redox regulation [7], while Cd^{2+} and Ag^{+} are non-essential and toxic at low concentrations, often linked to heavy metal poisoning and antimicrobial resistance mechanisms [8, 9]. The interaction of these ions with cysteine directly influences their bioavailability, toxicity, and redox activity, necessitating detailed studies of their reduction behavior under varying physicochemical conditions [10, 11]. Cyclic voltammetry (CV) has emerged as a powerful tool for investigating the redox properties of metal-ligand complexes. It allows rapid assessment of reduction potentials, complex stability, electron transfer kinetics, and the influence of environmental parameters such as pH [12-14]. The presence of cysteine significantly alters the voltammetric behavior of Cu^{2+}, Cd^{2+}, and Ag^{+} due to the formation of coordination complexes that shift the reduction peaks and modify current responses [15]. These shifts provide valuable insights into metal-ligand binding strength and electrochemical priority, particularly when assessed over a pH gradient [16]. The solution pH plays a crucial role in governing the speciation and binding mode of cysteine with metal ions. At lower pH values, protonation of the amino and thiol groups reduces the ligand's nucleophilicity, whereas at higher pH, deprotonation facilitates stronger coordination and enhanced redox interactions [17, 18]. By varying pH, one can observe changes in peak potential and current, which reflect the strength and stability of metal-cysteine complexes. Comparative studies across a range of pH values allow the deduction of a reduction priority order among Cu^{2+}, Cd^{2+}, and Ag^{+}, with potential implications in environmental remediation, biosensor design, and understanding biochemical metal trafficking pathways [19, 20]. This study aims to investigate the reduction behavior and priority order of Cu^{2+}, Cd^{2+}, and Ag^{+} ions in the presence of L-cysteine across different pH conditions using cyclic voltammetry. The work provides mechanistic insights into how cysteine modulates the redox properties of these metal ions and identifies their relative electrochemical reducibility in acidic to near-neutral environments.

Materials and Methods

Chemicals and Reagents

Analytical grade reagents with a purity of ≥99%, including silver nitrate ($AgNO_3$), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 2H_2O$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), L-cysteine, sodium hydroxide (NaOH), glacial acetic acid (CH_3COOH), phosphoric acid (H_3PO_4), and sodium acetate (CH_3COONa), were used in this study. All solutions were prepared using double-distilled water. Stock solutions of metal salts and L-cysteine were freshly prepared and diluted as required. The reagents were used without further purification. A 0.1 M sodium acetate buffer with pH adjusted between 5.0 and 7.0 was employed for all electrochemical experiments.

Instrumentation and Electrochemical Measurements

Voltammetric experiments were conducted using a PhadkeSTAT-20 potentiostat with Squidstat software. A three-electrode setup was used: glassy carbon as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The working electrode was polished with alumina, rinsed, and dried before use. Cyclic voltammetry was performed at room temperature to study the redox behavior of Cu^{2+}, Cd^{2+}, and Ag^{+} in the presence of cysteine. Suitable potential ranges were selected to observe the metal-cysteine complex reduction and oxidation.

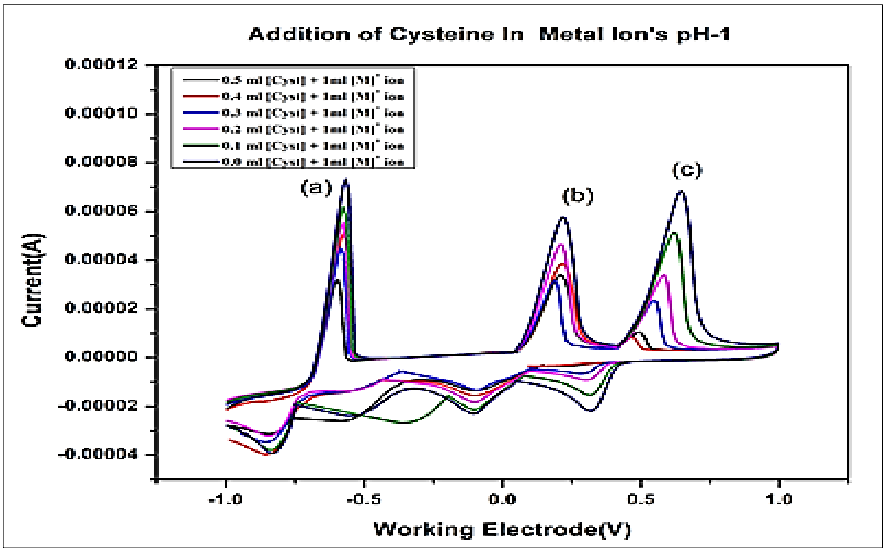
Electrochemical Procedure

Cyclic voltammetry (CV) was used to investigate the redox behavior of Cu^{2+}, Cd^{2+}, and Ag^{+} individually and in combination, in the presence of L-cysteine under varying pH conditions. Voltammograms were recorded in the potential range suitable for each metal's redox transitions (typically between -0.2 V and -1.2 V vs Ag/AgCl). Scan rates were maintained at 100 mV/s unless stated otherwise. Each metal ion was tested alone and then in equimolar mixtures with cysteine to observe shifts in peak potential (E_p) and changes in peak current (I_p), which reflect complex formation and electrochemical reactivity. Experiments were repeated at different pH levels (1.0 to 6.0) to assess the influence of protonation-deprotonation on metal-cysteine interaction.

All voltammograms were analyzed to determine the onset potential, peak potential (E_p), and peak current (I_p) of reduction waves. Reduction priority was established by comparing the cathodic peak shifts and current suppression or enhancement in the presence of cysteine. Greater shift toward negative potential and reduced peak current were interpreted as indicators of stronger complexation and lower electrochemical reducibility. All experiments were conducted at ambient temperature (25 ± 2°C) and repeated three times to ensure reproducibility. The average values were used in comparative analysis.

Results

At pH 1 and pH 2: At pH 1**,** the cyclic voltammograms revealed three distinct cathodic peaks corresponding to the reduction of Ag^{+} (-0.55 V), Cu^{2+} (+0.25 V), and Cd^{2+} (+0.75 V). As cysteine concentration increased from 0.0 to 0.5 mL, a notable suppression in peak currents was observed for all three metals, indicating the formation of metal-ligand complexes that decreased the availability of free metal ions for reduction. Interestingly, at cysteine volumes above 0.3 mL, the peak current for Cu^{2+} slightly increased, suggesting the electrochemical reduction of Cu-cysteine complexes. Among the metals, Cu^{2+} exhibited the most pronounced shift, signifying stronger complexation, followed by Ag^{+} and Cd^{2+}. This behavior is attributed to the partial protonation of cysteine's thiol and amine groups under acidic conditions, which still retain sufficient nucleophilicity to coordinate metal ions.



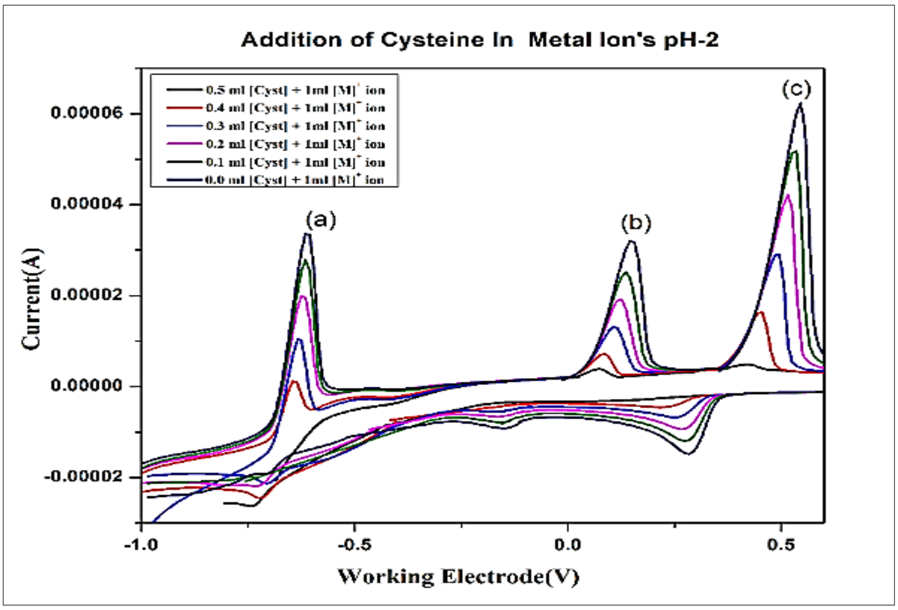
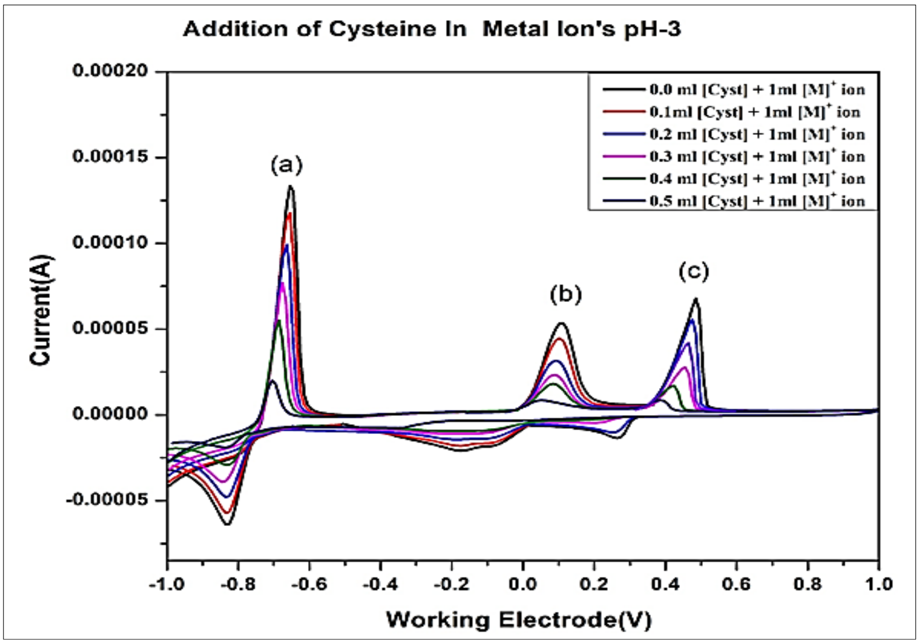


Fig 1: Cyclic voltammograms showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behavior of metal ions (Ag^+, Cu^{2+}, Cd^{2+}) at pH 1 and pH 2 in acetate buffer.

At pH 2, similar peaks were observed at -0.55 V (Ag^+), +0.15 V (Cu^{2+}), and +0.55 V (Cd^{2+}), but with a more consistent and progressive decrease in current across all metals upon cysteine addition. The suppression was more significant for Cu^{2+} and Cd^{2+} compared to Ag^+, indicating stronger interactions with cysteine. This can be explained by the increased deprotonation of cysteine's functional groups at pH 2, enhancing its ability to form stable complexes. Thus, the trend in complexation affinity shifts slightly, following $Cu^{2+} > Ag^+ > Cd^{2+}$ at pH 1 and $Cu^{2+} > Cd^{2+} > Ag^+$ at pH 2.

At pH 2 and pH 3: At pH 3, differential pulse voltammograms recorded in acetate buffer revealed well-defined cathodic peaks for Ag^+, Cu^{2+}, and Cd^{2+}, with increasing cysteine concentration (0.0-0.5 mL) leading to a clear suppression of peak currents. This behavior indicates the progressive formation of metal-cysteine complexes, which reduce the concentration of free metal ions available for electrochemical reduction. Among the three, Cd^{2+} exhibited the most significant current decrease**,** followed by Cu^{2+} and Ag^+, establishing a complexation strength order of $Cd^{2+} > Cu^{2+} > Ag^+$**.** The moderate acidity at pH 3 enhances the nucleophilicity of cysteine due to partial deprotonation of it's -SH and $-NH_2$ groups, thus facilitating more effective coordination.



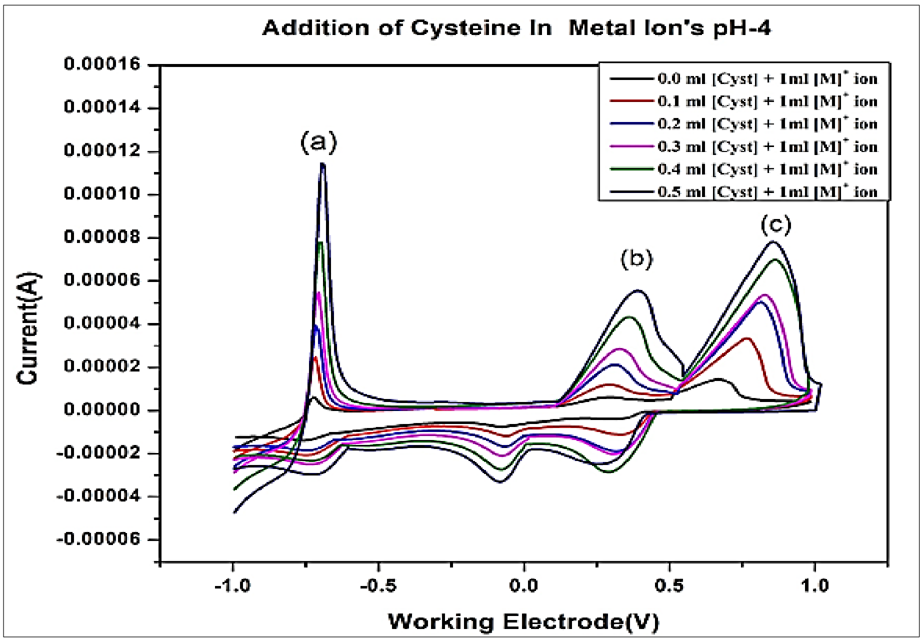
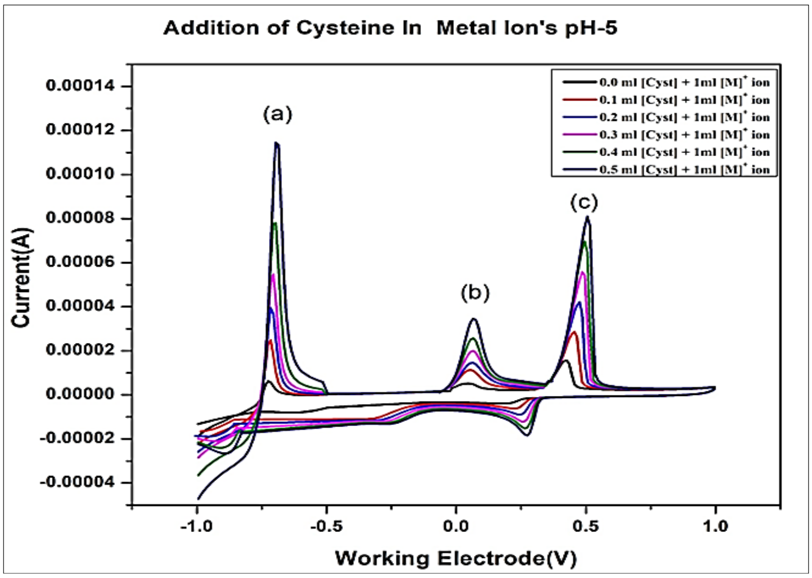


Fig 2: Cyclic voltammograms showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behavior of metal ions (Ag^+, Cu^{2+}, Cd^{2+}) at pH 3 and pH 4 in acetate buffer.

At pH 4, a similar trend was observed, with increasing cysteine concentration resulting in further suppression of the cathodic peak currents. The peak potentials remained distinct, while current intensities declined sharply, especially for Cd^{2+}. This reinforces the trend of stronger complexation at higher pH, with the same order of affinity retained. The data confirm that both pH and ligand concentration play critical roles in modulating redox behavior through complex formation, and at pH 4, metal-ligand interactions are notably enhanced due to increased ligand nucleophilicity.

At pH 5 and pH 6: At pH 5, the cyclic voltammograms recorded in acetate buffer displayed three well-resolved cathodic peaks, corresponding to the reduction of Ag^+ (approximately -0.55 V), Cu^{2+} (around +0.25 V), and Cd^{2+} (near +0.75 V). As the concentration of L-cysteine increased from 0.0 to 0.5 mL, the peak currents for all metal ions decreased steadily, indicating effective formation of metal-cysteine complexes. This complexation reduces the concentration of free metal ions available at the electrode surface for reduction. Among the three, Cd^{2+} exhibited the most significant current suppression, followed by Cu^{2+} and Ag^+, suggesting that Cd^{2+} forms the most stable complexes with cysteine at this pH. The trend observed $Cd^{2+} > Cu^{2+} > Ag^+$ reflects the increased reactivity of cysteine's thiol and amino groups under moderately acidic conditions.

At pH 6, this behavior becomes even more pronounced. The cathodic peaks for Ag^+ (0.6 V), Cu^{2+} (+0.1 V), and Cd^{2+} (~+0.6 V) continued to show decreasing peak currents with rising cysteine concentration. The suppression of current was again strongest for Cd^{2+}, indicating formation of highly stable Cd-cysteine complexes due to enhanced nucleophilicity of fully deprotonated thiol and amine groups. Cu^{2+} also showed strong complexation, while Ag^+ remained the least affected. These observations confirm that metal-ligand complexation increases with pH, and cysteine becomes a more efficient chelator in slightly basic environments, maintaining the order $Cd^{2+} > Cu^{2+} > Ag^+$ across both pH levels.



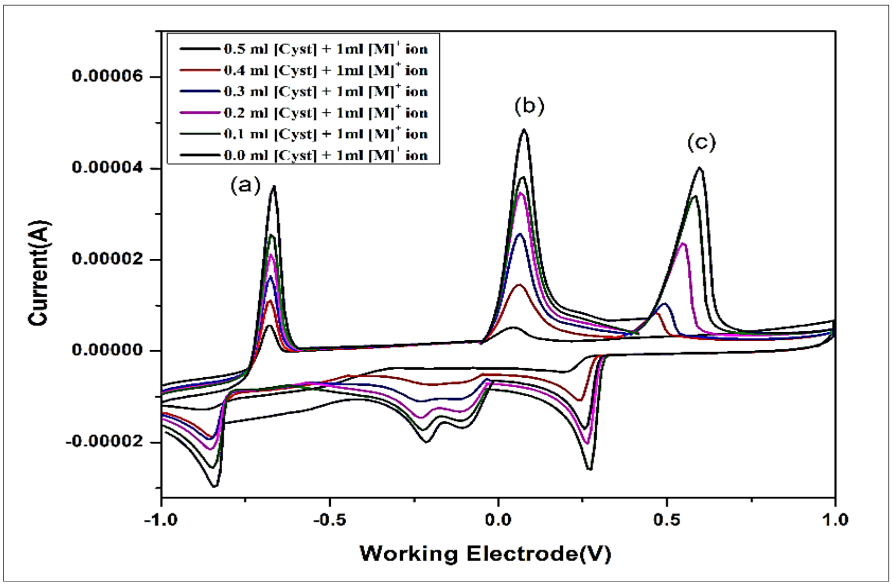


Fig 3: Cyclic voltammograms showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behavior of metal ions (Ag^+, Cu^{2+}, Cd^{2+}) at pH5 in acetate buffer

Table 1: Priority of Metal-Cysteine Complexation Based on Suppression of Reduction Peaks

pH	Cathodic Peak Potentials (Ag^+ / Cu^{2+} / Cd^{2+})	Effect of Increasing Cysteine (0.0–0.5 mL)	Trend in Peak Suppression	Complexation Stability Order	Interpretation
1	–0.55 V / +0.25 V / +0.75 V	Initial current decreases (partial complexation); re-increase beyond 0.3 mL for some metals	$Cu^{2+} > Ag^+ > Cd^{2+}$	$Cu^{2+} > Ag^+ > Cd^{2+}$	Cu^{2+} forms stable complexes even at low pH; partial binding of Ag^+ and Cd^{2+} observed
2	–0.55 V / +0.15 V / +0.55 V	Progressive current decrease for all; no re-increase at higher cysteine	$Cu^{2+} > Cd^{2+} > Ag^+$	$Cu^{2+} > Cd^{2+} > Ag^+$	Functional groups of cysteine more reactive; Cu^{2+} binds strongly, Ag^+ least affected
3	–0.55 V / +0.25 V / +0.75 V	Significant current suppression with increasing cysteine	$Cd^{2+} > Cu^{2+} > Ag^+$	$Cd^{2+} > Cu^{2+} > Ag^+$	Complexation efficiency increases; Cd^{2+} peak most reduced
4	–0.55 V / +0.25 V / +0.75 V	Sharper decrease in peak current, especially for Cd^{2+} and Cu^{2+}	$Cd^{2+} > Cu^{2+} > Ag^+$	$Cd^{2+} > Cu^{2+} > Ag^+$	Deprotonation improves cysteine binding; Ag^+ remains weakly complexed
5	–0.55 V / +0.25 V / +0.75 V	Clear peak suppression trend with strong Cu^{2+} and Cd^{2+} interaction	$Cd^{2+} > Cu^{2+} > Ag^+$	$Cd^{2+} > Cu^{2+} > Ag^+$	Stable complex formation; Ag^+ less reactive
6	–0.60 V / +0.10 V / +0.60 V	Peak suppression highest for Cd^{2+}; Cu^{2+} follows; Ag^+ least	$Cd^{2+} > Cu^{2+} > Ag^+$	$Cd^{2+} > Cu^{2+} > Ag^+$	Thiol & amine groups most active at this pH; Cd–cysteine complex dominates

The figure 4 illustrates the variation of oxidation peak potential (E_p) for Cd^{2+}, Cu^{2+}, and Ag^+ ions as a function of pH in the presence of L-cysteine. For Cd^{2+}, the peak potential shows a slight negative shift with increasing pH (slope: -0.0074), indicating that as pH increases, the reduction of Cd^{2+} becomes easier. This is attributed to enhanced complexation due to deprotonation of cysteine's thiol and amine groups, which increases their nucleophilicity and strengthens metal-ligand interactions. A similar but more pronounced trend is observed for Cu^{2+}, which exhibits a steeper negative slope (-0.0188), suggesting that Cu^{2+} experiences stronger pH-dependent complexation with cysteine, thereby lowering its oxidation potential more significantly. In contrast, Ag^+ shows an opposite trend with a positive slope (+0.0092) for pH ≥ 2, suggesting that its oxidation potential increases slightly as pH rises. This behavior indicates weaker complexation with cysteine, likely due to the relatively lower affinity of Ag^+ for thiol groups compared to Cd^{2+} and Cu^{2+}. The lesser dependence of Ag^+ peak potential on pH highlights its reduced electrochemical reactivity in the presence of cysteine under mildly acidic to near-neutral conditions. Overall, the figure supports the conclusion that Cu^{2+} and Cd^{2+} form stronger pH-dependent complexes with cysteine, leading to significant modulation of their redox behavior, whereas Ag^+ remains relatively less affected by pH, indicating weaker coordination. This reinforces the complexation affinity trend of $Cd^{2+} > Cu^{2+} > Ag^+$.

Conclusion

The cyclic voltammetric investigation revealed a clear pH-dependent pattern in the complexation behavior of Cu^{2+}, Cd^{2+}, and Ag^+ with L-cysteine. At lower pH values (1-2), Cu^{2+} exhibited the strongest interaction with cysteine, indicated by significant suppression of its cathodic peak current, while Ag^+ and Cd^{2+} showed comparatively weaker responses. As the pH increased from 3 to 6, Cd^{2+} emerged as the dominant ion forming the most stable complexes, as evidenced by the highest degree of peak current suppression, followed by Cu^{2+}. This trend corresponds with the increasing deprotonation of cysteine's thiol and amino groups, which enhances its nucleophilic character and coordination efficiency. In contrast, Ag^+ consistently showed the weakest and least pH-sensitive complexation behavior. The observed shifts in oxidation peak potentials (E_p) further supported these findings: Cu^{2+} and Cd^{2+} showed decreasing E_p values with rising pH, while Ag^+ displayed a slight increase. This indicates stronger pH-dependent complex formation for Cd^{2+} and Cu^{2+}, whereas Ag^+ remains relatively inert in the presence of cysteine under the tested conditions. Overall, the complexation affinity followed the order $Cd^{2+} > Cu^{2+} > Ag^+$, emphasizing the critical role of pH in modulating electrochemical metal-ligand interactions.

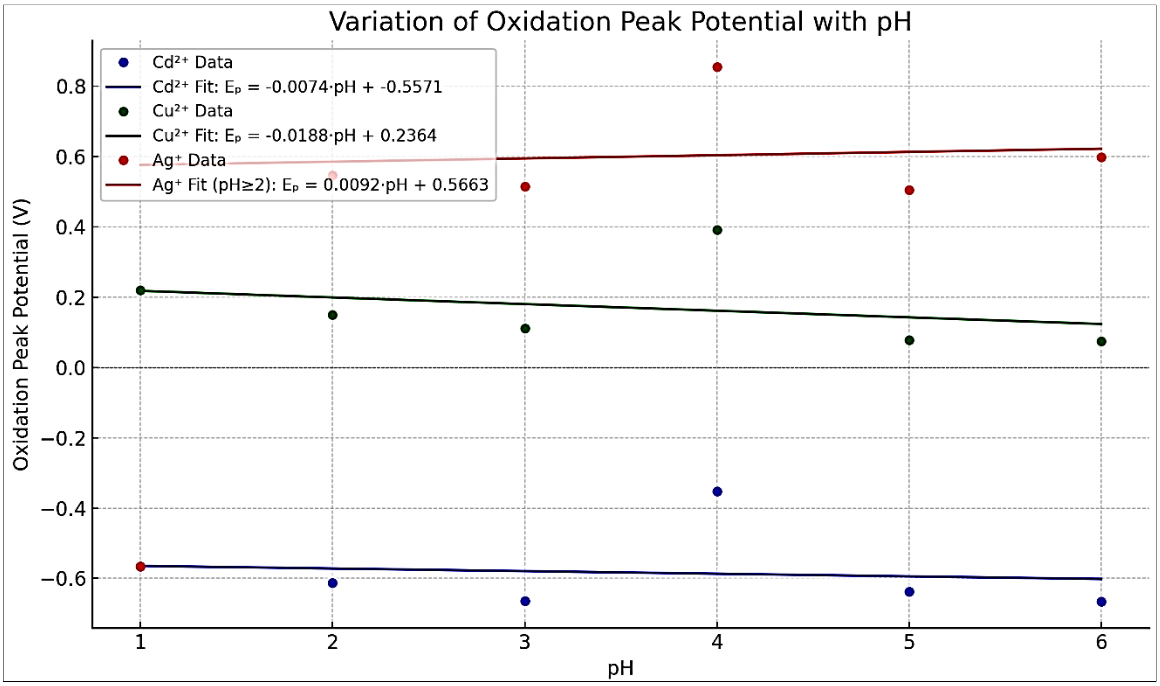


Fig. 4: Variation of oxidation peak potential (E_p) with pH for Cd^{2+}, Cu^{2+}, and Ag^+

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