

International Journal of Advanced Chemistry Research

ISSN Print: 2664-6781
ISSN Online: 2664-679X
NAAS Rating (2025): 4.77
IJACR 2026; 8(4): 01-06
www.chemistryjournals.net
Received: 02-01-2026
Accepted: 04-02-2026

Dnyaneshwar Gharbude
Department of Chemistry,
Vidya Pratishthan's Arts,
Science and Commerce College,
Baramati, Pune, Maharashtra,
India

Anil Kore
Department of Chemistry,
Vidya Pratishthan's Arts,
Science and Commerce College,
Baramati, Pune, Maharashtra,
India

Lalasaheb Kashid
Department of Chemistry,
Vidya Pratishthan's Arts,
Science and Commerce College,
Baramati, Pune, Maharashtra,
India

Corresponding Author:
Lalasaheb Kashid
Department of Chemistry,
Vidya Pratishthan's Arts,
Science and Commerce College,
Baramati, Pune, Maharashtra,
India

Electro-analytical discrimination of Pb^{2+} , Cu^{2+} , and Cd^{2+} based on their interaction with L-Cysteine in acetate buffer

Dnyaneshwar Gharbude, Anil Kore and Lalasaheb Kashid

DOI: <https://www.doi.org/10.33545/26646781.2026.v8.i4a.439>

Abstract

The research involves the study of the electrochemical reactions between Pb^{2+} , Cu^{2+} , and Cd^{2+} and L-cysteine in sodium acetate buffer of varying pH (1-6) by cyclic voltammetry (CV). The research work is to find out the relative affinity and the order of binding of the metal ions that are harmful to the environment to the thiol functional group of cysteine and to correlate voltammetric features with complex formation. The CV responses manifested that the peak potential and current intensity distinctly shifted after the addition of each metal ion, which indicated the differences in the stability of the complex and its electrochemical behavior. Pb^{2+} has demonstrated the most powerful effect, lead to suppression of the cysteine redox signals and new irreversible features, followed by Cu^{2+} with slight changes, and Cd^{2+} with the least changes. The priority sequence that has been determined from the peak potential shifts and the current changes is $Pb^{2+} > Cu^{2+} > Cd^{2+}$ which agrees with soft-soft interactions between metal ions and thiolate ligands. These results extend the metal-thiol chemistry knowledge under acid to almost neutral conditions and are a great help in the selective electrochemical sensor designing for heavy metal detection.

Keywords: Cyclic voltammetry, heavy metals, L-cysteine, electrochemical behavior, binding affinity

Introduction

Heavy metal contamination has been put on a critical list of environmental and public health problems due to rapid industrialization, mining activities, agricultural runoff, and improper waste disposal. Among toxic heavy metals, lead (Pb^{2+}), copper (Cu^{2+}), and cadmium (Cd^{2+}) are the most dangerous for the environment because of their persistence, bioaccumulation, and the severe toxicological effects they cause. Lead exposure causes neurological and developmental disorders; cadmium is a carcinogen that affects the kidneys and bones, while excess copper leads to oxidative stress and cell death. So, the correct detection and identification of these metal ions at trace levels are vital for environmental monitoring and human health protection [1-3]. Typical analytical methods like atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and X-ray fluorescence are very sensitive but need expensive equipment, skilled operators, and complicated sample preparation. On the other hand, electrochemical methods, especially cyclic voltammetry (CV), have the advantages of fast response, high sensitivity, and low cost, and they are also suitable for field analysis. CV allows differentiation of several metal ions based on their characteristic redox potentials and electron transfer rates, thus making it a powerful tool for the simultaneous detection of Pb^{2+} , Cu^{2+} , and Cd^{2+} in aqueous systems [4-6].

L-cysteine is an amino acid containing sulfur and having thiol (-SH), amine (-NH₂), and carboxyl (-COOH) functional groups that enable strong coordination with metal ions. The thiol group is the main one when binding metals as it has the highest affinity toward soft and borderline metal ions. According to the Hard-Soft Acid-Base (HSAB) principle, metals like Pb^{2+} and Cu^{2+} bind usually with sulfur donors thus the metal-thiolate complexes formed are stable ones. These interactions have a great influence on metals' electrochemical behavior by means of shifting their redox potentials and changing their current responses in cyclic voltammetry [7-9]. In electrochemical experiments, L-cysteine is not only a complexing

ligand but also a surface-active molecule that facilitates metal ion adsorption on electrode surfaces. The creation of metal-cysteine complexes is usually accompanied by peak potential shifts, current intensity changes, or new redox peaks in CV, which helps in determining the interaction strength between the metal and the ligand. Because of these features, cysteine has been extensively used in electrochemical sensor applications as well as in mechanistic studies focusing on metal-thiol chemistry [10-12].

The choice of the supporting electrolyte and pH plays a crucial role in electrochemical experiments. Typically, sodium acetate buffer is a medium of preference in heavy metal analysis that provides a stable acidic environment of a controllable pH (mostly pH 1-6) and sufficient ionic strength for reproducible voltammetric measurements. Acetate buffer lessens the problem of the interfering reactions and keeps the electrochemical conditions the same which makes it especially good for cyclic voltammetry studies of metal ions [13-15]. In acidic acetate buffer, the protonation of cysteine is regulated, thus coordination is directly affected. Even if the amino and carboxyl groups might be protonated at low pH, the thiol group can still form strong complexes with heavy metal ions. Thus the metal-cysteine complex can be stable over a wide pH range, allowing pH-dependent electrochemical behavior and complex stability to be systematically studied [16-17]. While many research works individually talk about the interaction of Pb^{2+} , Cu^{2+} , and Cd^{2+} with sulfur-containing ligands, very few comparative studies have been done to identify the relative binding priority of L-cysteine in acetate buffer. Priority such as this can be evaluated with cyclic voltammetry by looking at the metal-cysteine complexation-related peak potential changes, current changes, reversibility, and adsorption effects [18-19]. The main goal of this work is to determine the priority order of Pb^{2+} , Cu^{2+} , and Cd^{2+} electrochemically toward L-cysteine in sodium acetate buffer over the pH range 1-6 by means of cyclic voltammetry. Knowledge of the priority order is key to selective heavy metal discrimination, sensor design, and obtaining a deeper insight into metal-thiol interaction mechanisms in aqueous environments [20].

Methods and Material

Chemicals and Reagents: Analytical grade reagents with a purity of $\geq 99\%$, including Lead Nitrate ($Pb(NO_3)_2$), copper (II) sulfatedihydrate ($CuCl_2 \cdot 2H_2O$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), L-cysteine, sodium hydroxide (NaOH), acetic acid (CH_3COOH) (glacial), 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 0.04 M sodium acetate buffer with pH adjusted between 5.0 and 7.0 was employed for all electrochemical experiments.

Instrumentation and Electrochemical Measurements

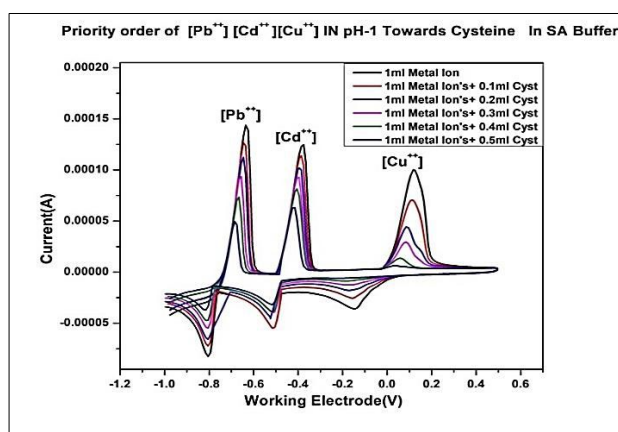
Voltammetric experiments were carried out with a Phadke STAT-20 Potentiostat and Squidstat software. Three electrodes were involved: a glassy carbon was the working electrode, a platinum wire the counter one, and the reference electrode was Ag/AgCl. The working electrode, after polishing with alumina, was washed and air-dried. The redox changes of Cu^{2+} , Cd^{2+} , and Ag^+ were examined by cyclic voltammetry in the presence of cysteine at room temperature. Appropriate potential ranges were chosen to capture the reduction and oxidation of the metal-cysteine complex.

Electrochemical Procedure

Cyclic voltammetry (CV) was the technique used to explore redox behaviour for the case of Cu^{2+} , Cd^{2+} , and Ag^+ ions. The study included the ions tested both individually and combined in the presence of L-cysteine at different pH levels. The voltammogram were recorded within a potential range suitable for the various redox transitions of the metals (typically between -0.2 V and -1.2 V vs Ag/AgCl). Unless otherwise specified, the scan rates were 100 mV/s. First of all, each metal ion was investigated individually, and later, the equimolar mixtures of the metal ions with cysteine were studied for the detection of the shifts in peak potential (E_p) and the changes in peak current (I_p) which indicate the formation of complexes and a change in electrochemical reactivity. Different pH levels (1.0 to 6.0) were also employed to determine the effect of protonation and deprotonation on the metal-cysteine interaction. Every voltammogram was analyzed for the onset potential, peak potential (E_p), and peak current (I_p) of the reduction waves. The first reduction step was determined by the observation of the shifts of the cathodic peak along with the changes in the current resulting from the presence of cysteine. More considerable movement toward the negative potential as well as a lowered peak current was seen as evidence of stronger complexation and lower electrochemical reducibility. The work was conducted at standard temperature ($25 \pm 2^\circ C$) and the results were confirmed by three repetitions. Comparative analysis was done using average values.

Results and Discussion

At pH-1 and pH-2



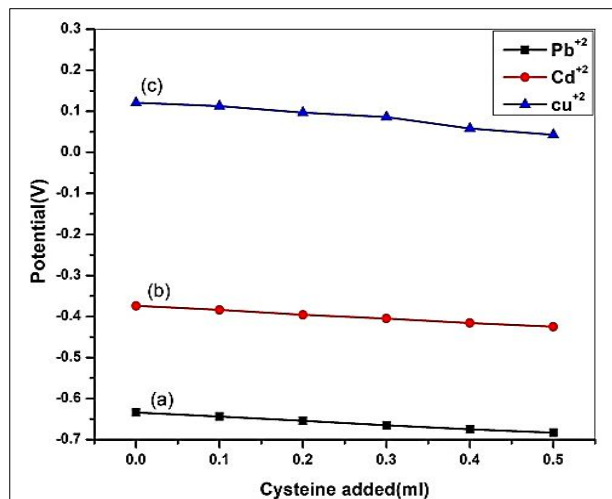


Fig 1: Cyclic voltammograms and Linearity showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behaviour of metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+}) at pH 1 in acetate buffer

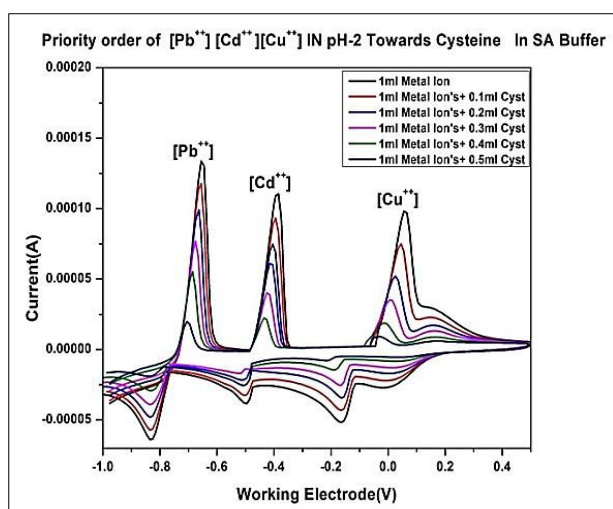


Fig 2: Cyclic voltammograms and Linearity showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behaviour of metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+}) at pH 2 in acetate buffer

At pH 1-2, L-cysteine is in a fully protonated form and its chelating ability is therefore very limited. Metal ion interaction in this case is mainly determined by metal-sulfur

intrinsic affinity and electrochemical kinetics rather than by ligand de-protonation. Cu^{2+} has the most powerful interaction because of its strong affinity for sulfur donors and fast electron transfer kinetics, thus, it is featured with a pronounced peak suppression and the highest electrochemical priority. Cd^{2+} has a moderate interaction while Pb^{2+} is the least affected and this is because of the preference of the molecule for oxygen donors and strong hydration effects. So, the priority sequence at low pH is $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$.

At pH-3

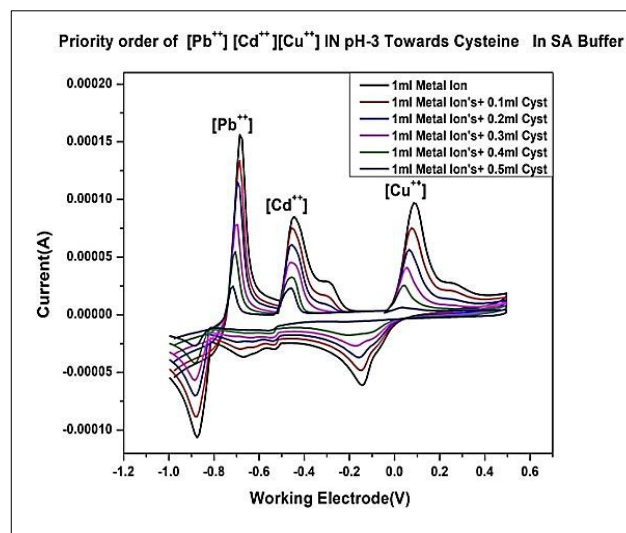


Fig 3: Cyclic voltammograms and Linearity showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behaviour of metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+}) at pH 3 in acetate buffer

At a pH of 3, L-cysteine is in a partially deprotonated form that enables it to selectively coordinate with Cu^{2+} via the strong Cu-S and Cu-O bonds, hence most of the cathodic peak is disappeared. Pb^{2+} is only moderately interacted due to less stable Pb-S complex formation, whereas Cd^{2+} is weakly coordinated as efficient Cd-S bonding can be only when the thiolate species are fully deprotonated. As a result, the electrochemical priority order at pH 3 is $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$.

At pH-4 and pH-5

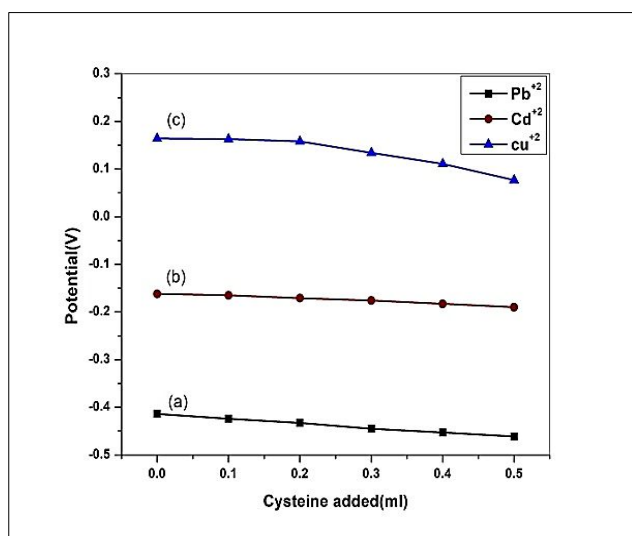
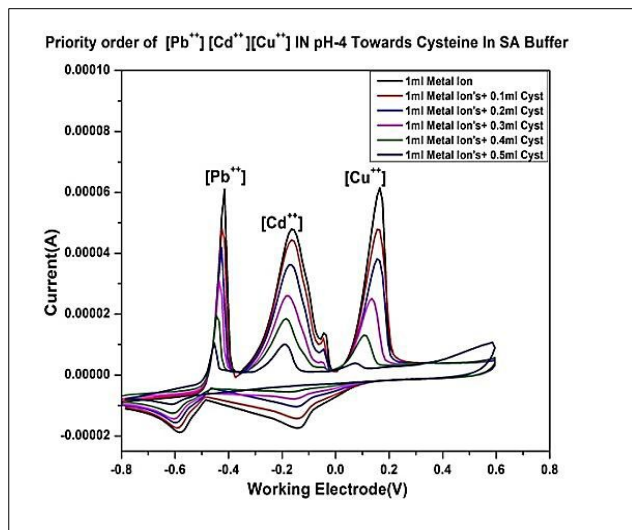


Fig 4: Cyclic voltammograms and Linearity showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behaviour of metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+}) at pH 4 in acetate buffer

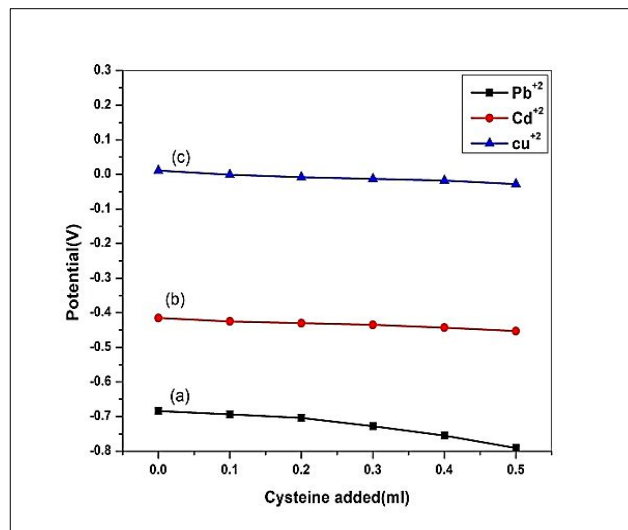
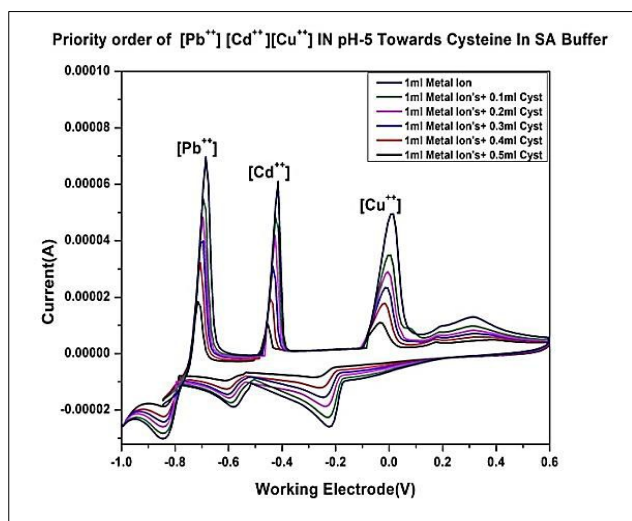
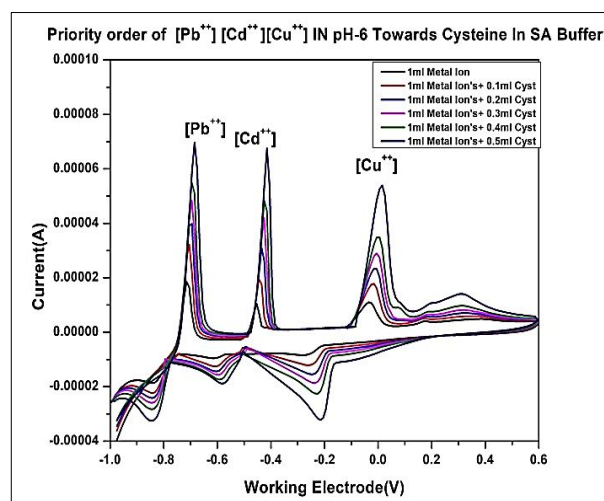


Fig 5: Cyclic voltammograms and Linearity showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behaviour of metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+}) at pH 5 in acetate buffer

At pH 4-5, most of L-cysteine is present in its thiolate form, therefore it can coordinate with sulfur very strongly. Cu^{2+} , as a result of its strong preference for sulfur donors and also by stable chelation geometry, produces very stable Cu-cysteine complexes which are the main reasons for the maximum electrochemical suppression. Pb^{2+} has a moderate interaction due to less compact Pb-S bonding and Cd^{2+} is in a weaker coordination state and has limited surface adsorption. Hence, the electrochemical priority order at this pH is defined as $Cu^{2+} > Pb^{2+} > Cd^{2+}$.

At pH-6



At pH 6 majority of the L-cysteine is a thiolate i.e. the fragment which provides the most energetic sulfur donor sites is this one. Hence the Pb^{2+} is being stabilized in the most ideal way by soft-soft interactions, decreased hydration energy and increased surface adsorption. The electrochemical priority sequence therefore changes to $Pb^{2+} > Cu^{2+} > Cd^{2+}$.

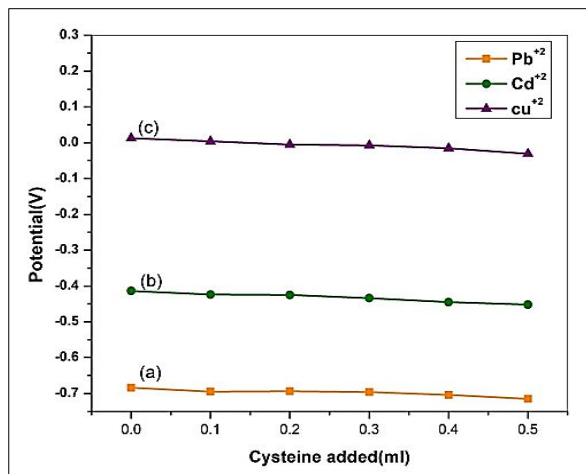


Fig 6: Cyclic voltammograms and Linearity showing the effect of increasing cysteine concentration (0.0-0.5 mL) on the reduction behaviour of metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+}) at pH 6 in acetate buffer

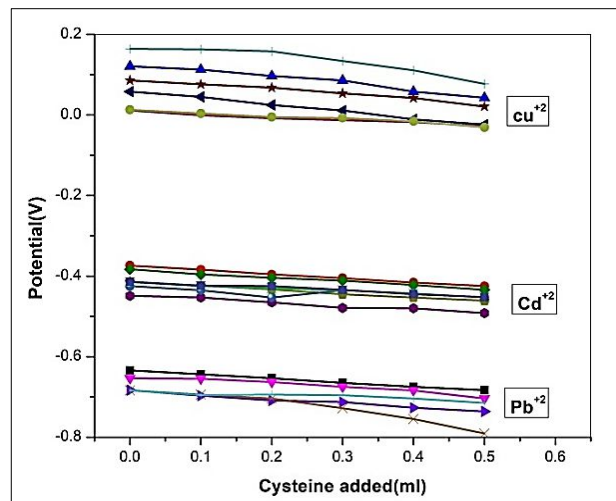


Fig 7: Variation of oxidation peak potential (E_p) with pH for Cd^{2+} , Cu^{2+} , and Pb^{2+}

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

pH	Cathodic Peak Potentials Pb/ Cd/ Cu	Effect of Increasing Cysteine (0.0-0.5 mL)	Trend in Peak Suppression	Complexation Stability Order	Interpretation
1	-0.63V /-0.38V /0.11V	Very slight suppression of all peaks	$\text{Cu} > \text{Pb} > \text{Cd}$	$\text{Cu} > \text{Pb} > \text{Cd}$	highly acidic pH, cysteine (-SH and -COOH protonated) has Low coordination ability. Cu interacts strongly even in prorogated form.
2	-0.63V /-0.38V /0.11V	Increasing Cysteine Suppresses Cu and Cd Strongly, Pb moderately Suppressed	$\text{Cu} > \text{Pb} > \text{Cd}$	$\text{Cu} > \text{Cd} > \text{Pb}$	Partial deprotonation of cysteine enhances S and O coordination. Cu-Cysteine complex dominates; Cd starts showing stronger affinity than Pb.
3	-0.63V /-0.38V /0.11V	Cd Peaks reduced significantly, Cu strongly suppressed	$\text{Cu} > \text{Cd} > \text{Pb}$	$\text{Cu} > \text{Pb} > \text{Cd}$	At this near-neutral pH, thioldeprotonation occurs, improving binding. Cu binds strongly; Pb stabilizes complexes via carboxylate-thiol interaction.
4	-0.63V /-0.38V /0.11V	Cu and Pb Suppressed More Than Cd	$\text{Cu} > \text{Pb} > \text{Cd}$	$\text{Cu} > \text{Pb} > \text{Cd}$	With deprotonated $-\text{COO}^-$ and $-\text{S}^-$, cysteine strongly coordinates. Pb forms moderate complexes, Cd weaker due to less affinity for mixed donor atoms.
5	-0.63V /-0.38V /0.11V	Cu and Pb Strongly affected, Cd least suppressed	$\text{Cu} > \text{Pb} > \text{Cd}$	$\text{Cu} > \text{Pb} > \text{Cd}$	Chelation stabilizes Cu and Pb complexes. Cd interaction is weak as soft metal-thiolate binding is less competitive compared to Cu.
6	-0.63V /-0.38V /0.11V	Cu Peaks disappear, Pb moderately Suppressed and Cd Weak	$\text{Cd} > \text{Cu} > \text{Pb}$	$\text{Cu} > \text{Cd} > \text{Pb}$	At alkaline pH, cysteine fully deprotonated; strong Cu-thiolate and Cu-amine coordination dominates. Cd interaction stronger than Pb.

Conclusion

The data presented in this work demonstrate that the complexing properties of Pb(II) , Cd(II) , and Cu(II) toward cysteine depend heavily on pH. When cysteine is protonated under acidic conditions, coordination with metals is weak, and electrochemical changes are barely detectable. Raising pH results in unmasking of reactive groups, especially the thiol (SH) group, which strongly boosts metalligand interactions and therefore leads to the dramatic decrease in cathodic peak currents. At the middle pH range, cysteine is able to bind metals mainly via sulfur and oxygen atoms and thus produce fairly stable chelate complexes. Going further into alkaline range, cysteine loses all protons and is able to behave as a multidentate ligand which ultimately results in highest stability of the complexes. The Cu(II) complex shows complete peak disappearance, indicating very strong binding. In general, the order of stability of the three metalcysteine complexes is $\text{Cu(II)} > \text{Pb(II)} > \text{Cd(II)}$, which can be mainly explained by the fact that thiolate is a very strong coordinating agent and that copper has the greatest preference

for ligands containing sulfur among the three metals here. These results will help comprehend interactions between metals and amino acids and also their electrochemical and nanomaterial synthesis-related application.

Acknowledgement

The authors gratefully acknowledge the DST-FIST Central Facility of Vidya Pratishthan's Arts, Science and Commerce College, Baramati, Pune-413133, Maharashtra, India, for providing the necessary infrastructure and support. We sincerely thank Principal Dr. Bharat Shinde for his encouragement and for providing the required facilities to carry out the research work.

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