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Synthesis and Characterization of Transition Metal Complexes with Amino-Acid Derived Schiff Bases for Heavy Metal Immobilization

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Abstract
The research investigates the methods to synthesize and analyze the binding properties of heavy metals through the use of transition metal complexes which are formed by L-alanine Schiff base ligand. We conducted a study of Cu^{2+} and Ni^{2+} and Zn^{2+} complexes through the application of FTIR and UV–Vis spectroscopic techniques. The results demonstrated that three coordination maintained its stability through the utilization of oxygen and nitrogen atom sources. The complexes underwent testing to determine their efficiency in removing Pb^{2+} and Cd^{2+} ions from aquatic environments. The adsorption experiments demonstrated that the process followed pseudo-second-order kinetics while the Langmuir isotherm model was used to describe the results with correlation values exceeding 0.995. The Copper (II) complex exhibited the highest capacity to bind Pb^{2+} with an ability to bind 284.5 mg/g. The evidence demonstrates its high degree of sensitivity. The research work results indicate here that these materials possess potential applications for heavy metal elimination herein.
Keywords: L-alanine Schiff base, Cu^{2+} and Ni^{2+} and Zn^{2+}, FTIR and UV–Vis, Pb^{2+} and Cd^{2+} ions, Langmuir isotherm model.

I. Introduction

The world has experienced rapid industrial development during the past thirty years. Uncontrolled city expansion has created an environmental emergency because it introduces hazardous heavy metals which contaminate water bodies and terrestrial ecosystems. The microorganisms and chemical substances within wastewater treatment systems operate to decompose organic waste materials. The environment suffers permanent contamination from heavy metals which include Pb^{2+}, Cd^{2+}, Hg^{2+}, and As^{3+} [1]. The substances in question pose a human health threat because they remain in the environment for extended periods and through biomagnification they accumulate in organisms across different trophic levels. The metals in their minimal concentrations produce health issues which include kidney failure and brain damage and cancer. The primary objective of current environmental chemistry research focuses on developing permanent methods for hazardous metal removal from water sources and industrial wastewater treatment. The methods create permanent solutions which effectively resolve pollution issues.

Environmental Threat and Heavy Metal Toxicity

Heavy metals become toxic substances because their strong attraction to sulphur-containing proteins enables them to disrupt the natural balance of metal ions within biological coordination centers. Lead acts as a calcium (Ca^{2+}) substitute which disrupts bone chemistry and makes the blood-brain barrier more vulnerable [2]. The association between cadmium and kidney damage leads to severe bone mineral density loss which results in major health issues. The traditional cleanup methods which include chemical precipitation and ion exchange and reverse osmosis face major difficulties because these approaches require high operational costs and fail to perform well when handling small quantities while they produce additional hazardous sludge. The existing issues drive researchers to search for advanced materials which particularly include multifunctional chelating agents that can extract and eliminate heavy metal ions from complex natural environments.

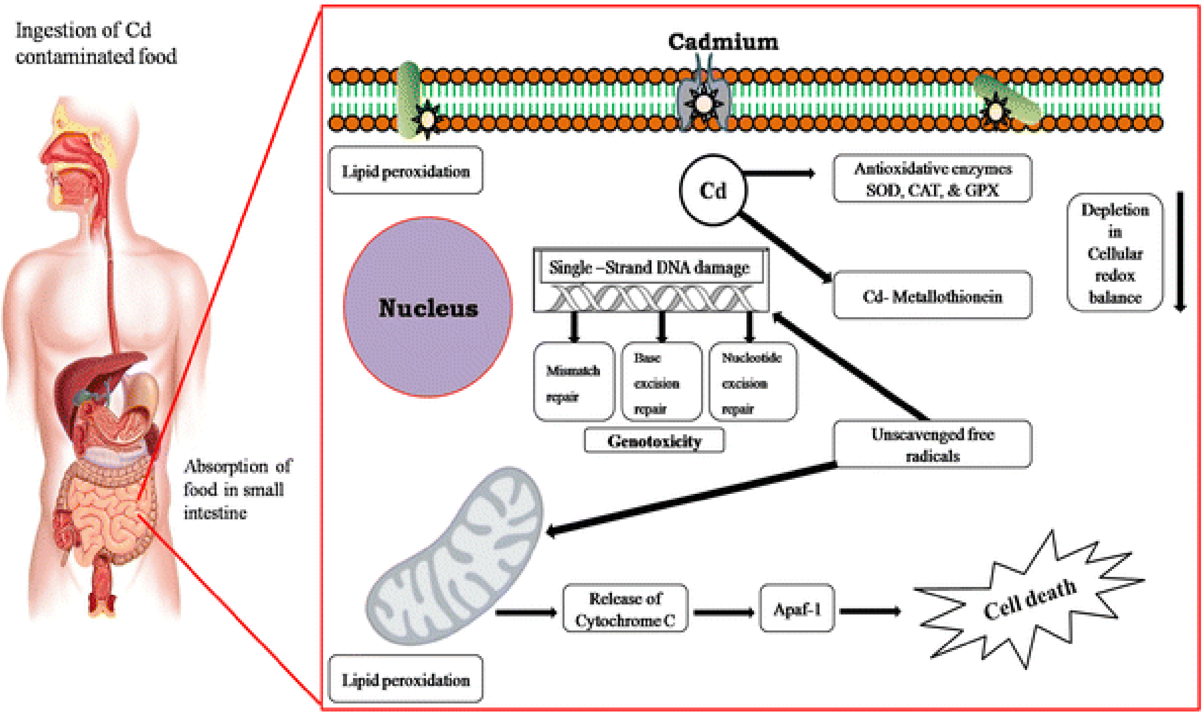

Figure 1: Environmental Problem (Heavy Metal Pollution), Source: Author Generated

Versatility of Schiff Base Ligands

The process of preparation of Schiff bases requires the combination of primary amines with carbonyl compounds to produce compounds that contain the azomethine functional group (>C=N–) [3]. The structural flexibility of these materials enables precise control over their electronic and steric properties. The properties of these materials make them suitable for use as ligands in coordination chemistry. The use of amino acid-derived Schiff bases is preferred because they demonstrate natural biocompatibility and provide multiple source atoms, including oxygen and nitrogen. The combination of these characteristics enables transition metals to form five or six membered stable chelate rings. These complexes work together as host systems, effectively capturing and holding onto secondary heavy metal ions. This prevents the ions from being released into the environment.

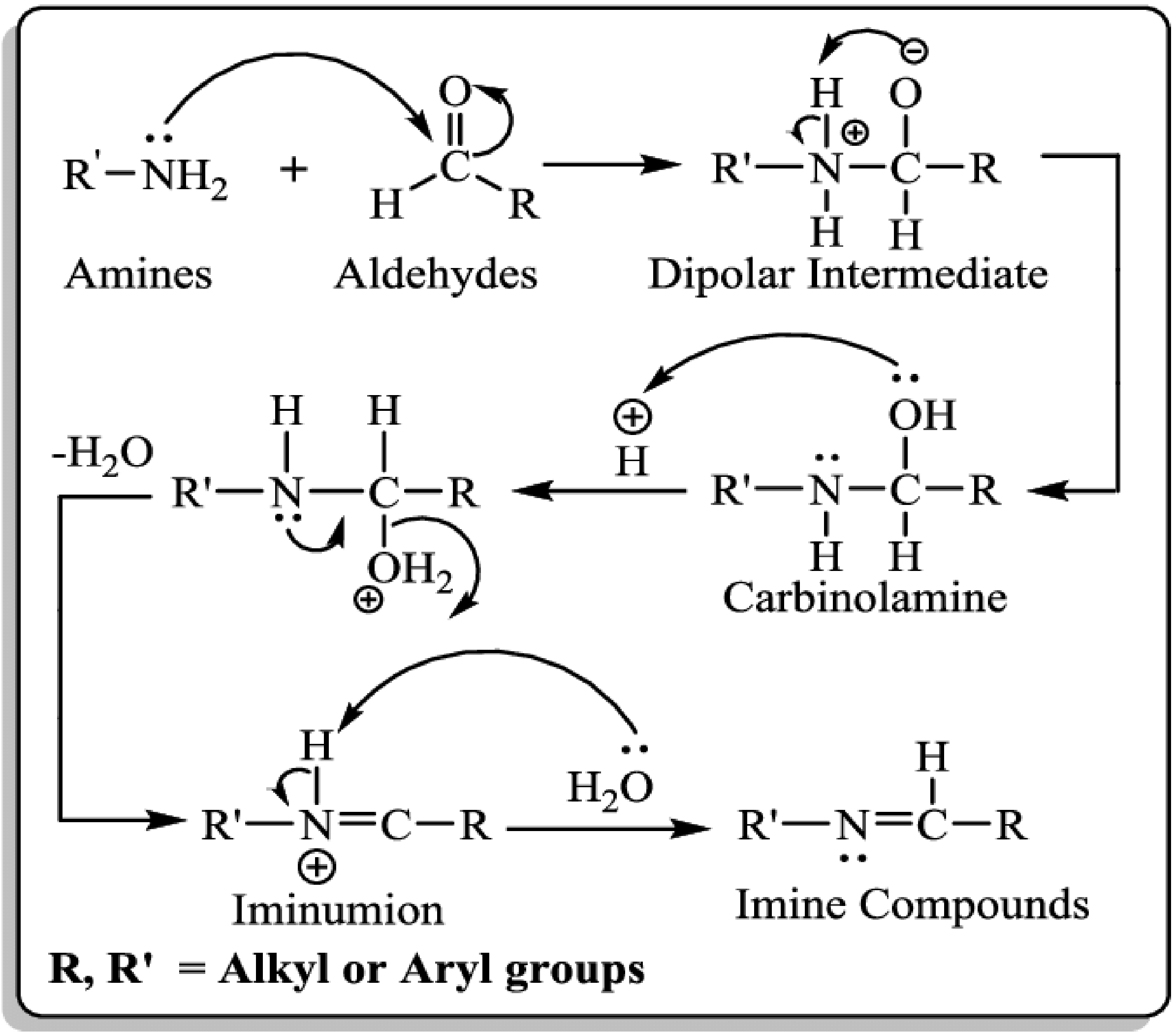

Figure 2: Ligand Formation (Schiff Base Synthesis), Source: Author Generated

Rationale for the Present Study

The present study aims to synthesize and enhance more understanding of transition metal complexes of Schiff bases derived from amino acids. The coordination complexesof transition metals, such as Cu and Ni metal complexes, remain intact despite exposure to chemicals and extreme temperatures [4]. The study demonstrates that these compounds can establish bonds with lead and cadmium ions through fundamental principles of coordination chemistry. The study's here based on results show that the materials can be easily used as long-term solutions to waste problems based on spectroscopic and thermodynamic analysis.

Experimental Section

The researchers designed their experiments to ensure that the amino acid-derived Schiff bases and their accompanying transition metal complexes would be produced with high purity standards. The selection of reagents and the enhancement of reaction conditions were driven by the requirement to produce complexes that maintained thermodynamic stability for environmental application purposes. The researchers conducted all chemical reactions using standard Schlenk methods in an inert nitrogen environment to prevent metal salts and coordination compounds from undergoing oxidation or decomposition. The researchers obtained analytical grade reagents from Sigma-Aldrich as well as Merck and used these materials here without any additional purification processes for such. The laboratory procedures involved standard methods for cleaning and drying solvents.

Synthesis of Amino Acid Derived Schiff Base Ligand

The Schiff base ligand, Salicylidene-L-alanine, was here to form through a green condensation reaction, which almost combined salicylaldehyde and L-alanine in this manner. The potassium salt wasprepared directly by mixing 0.01 mol of L-alanine (0.89 g) with 0.01 mol of potassium hydroxide (0.56 g) in 15 mL of distilled ethanol by this process [5]. After this, a solution of salicylaldehyde in distilled ethanol, containing 0.01 mol of the compound, was added to the mixture. This was done in a 1:1 molar ratio, with the addition occurring dropwise over a period of about 15 minutes. The solution mixture was refluxed with stirring for five hours. After cooling the content to room temperature, it was kept in the ice bath for three hours.The solution produced yellow crystals after the complete process. After washing thecrystals of Schiff base with cold ethanol and diethyl ether, were dried under vacuum in desiccator over P_4O_{10} [6].The researchers monitored the mixture through thin-layer chromatography in which a mixture of ethyl acetate and hexane (3:1) was used.

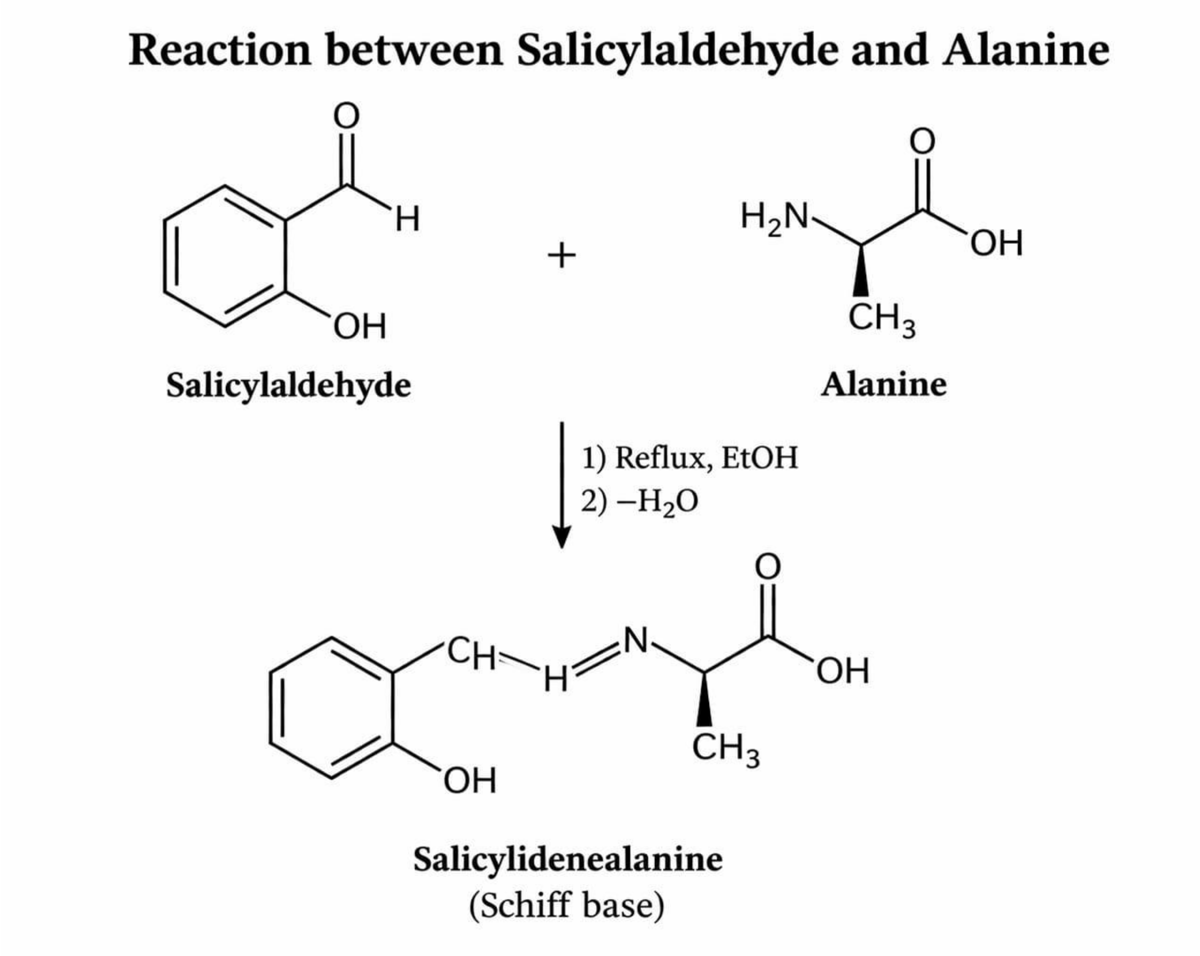

Figure 3: Reaction between Salicylaldehyde and Alanine, Source: Author Generated

Synthesis of Transition Metal Complexes

The experiments yielded metal complexes, resulting from the interaction of Cu(II), Ni(II), and Zn(II)salts with the Schiff base ligand. In order to form the metal complexes, the Schiff base ligand (0.01 mol, 1.93 g) was dissolved in 25 mL of distilled alcohol. Subsequently, the ethanolic solution of metal acetate (0.01mol), were introduced gradually to the ethanolic solution of Schiff base under continuous stirring and then the whole content was refluxed for two hours [7].

The coloured precipitates,dark green for copper, light green for nickel, and pale yellow for zinc,were produced which was indicative of the complex formation. After that, the precipitate was filtered, which was then cooled and washed with water and ethanol and diethyl ether. The complexes underwent a 24-hour drying process at 60°C, which resulted in the removal of more than 80% of the water content.

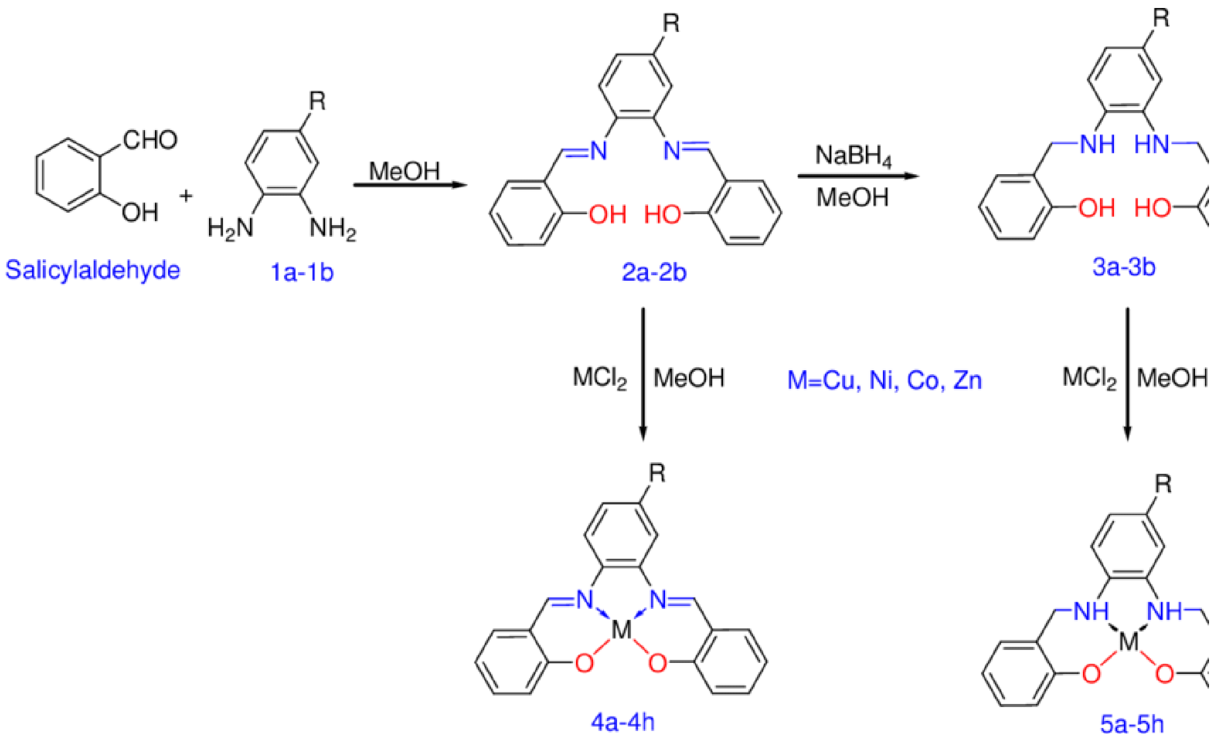

Figure 4: Metal Complex Formation & Heavy Metal Immobilization, Source: Author Generated

Instrumentation and Analytical Techniques

The researchers employed KBr pellets and Fourier transform more infrared spectroscopy to identify functional groups, such as C=N, C=O, M–N bonds, and M–O bonds, within the 4000–400 cm^{-3} range here in. The researchers conducted ultraviolet–visible spectroscopy by using 10^{-3} M solutions of dimethyl sulfoxide and dimethylformamide to study electronic transitions between π–π* and n–π* and d–d states within the 200–800 nm range [8]. The researchers determined magnetic susceptibility through Gouy balance measurements which generated essential data to determine the sample's magnetic moment and coordination geometry. The researchers examined thermal stability through thermogravimetric and differential thermal studies which measured the sample's thermal stability until 800°C in a nitrogen environment.

Reagents / Compounds	**Chemical Formula**	**Molar Mass (g/mol)**	**Amount (mmol)**	**Mass / Volume Used**
Salicylaldehyde	$C_7H_6O_2$	122.12	10.0	1.221 g
L-Alanine	$C_3H_7NO_2$	89.09	10.0	0.891 g
Ligand (H_2L)	$C_{10}H_{11}NO_3$	193.20	10.0	1.932 g
Copper(II) acetate monohydrate	$Cu(CH_3COO)_2 \cdot H_2O$	199.65	10.0	1.997 g
Nickel(II) acetate tetrahydrate	$Ni(CH_3COO)_2 \cdot 4H_2O$	248.84	10.0	2.489 g
Zinc(II) acetate dihydrate	$Zn(CH_3COO)_2 \cdot 2H_2O$	219.51	10.0	2.195 g

Table 1: Stoichiometric Amounts used in the Synthesis of Schiff Base and Complexes

Compound	Colour	M.P. (°C)	Yield (%)	μeff (BM)	Conductance (Ω^{-1} cm^2 mol^{-1})
Ligand	Yellow	215–218	88	----	12
[Cu(L)]	Dark Green	>300	82	1.85	18
[Ni(L)]	Light Green	>300	85	3.10	15
[Zn(L)]	Pale Yellow	>300	80	Diamagnetic	22

Table 2: Physical and Analytical Properties of Synthesized Compounds

II. Results and Discussion

Spectroscopic Characterization and Coordination Behaviour

The experiments here synthesized the Schiff base ligand from amino acids and characterized its transition metal complexes containingCu(II) and Ni(II) and Zn(II) metals. The investigation used three techniques which included spectroscopic measurements, thermal and magnetic testing. The free ligand showed a strong FTIR spectrum which produced a band at 1628 cm^{-1} which was assignable to the azomethine (C=N) stretching vibrations.This band confirmed the formation of Schiff base [9]. The absence of the aldehydic C=O band made it more probable that condensation would occur. The phenolic hydroxyl group produced a wide band which extended from 3420 cm^{-1}. The carboxylate group showed two different stretching patterns at 1580 cm^{-1} and 1410 cm^{-1}. The spectra underwent major changes after the complexation process. The C=N band reached lower frequencies which ranged from 1603 $cm^{-1}$to 1618 cm^{-1}. This demonstrates that nitrogen serves as a coordinating element. The molecule appeared to undergo deprotonation while it established a bond with phenolic oxygen through its phenolic hydroxyl group. The metal formed bonds with nitrogen and oxygen because more bands appeared in the 510–550 $cm^{-1}$and 420–460 cm^{-1}ranges [10].

The UV-visible spectral analysis contributed additional evidence which supported these discoveries. The free ligand exhibited spectral changes at 270 nm and 335 nm which displayed transitions from π to π^* and n to π^* states. The copper complex exhibited a broad spectral range which extended from 630 nm to 645 nm, and this range matched its distorted square planar structure, which the 1.85 BM magnetic moment confirmed [11]. The nickel metal complex displayed two bands at 415 nm and 680 nm, which suggested an appearance octahedral stereochemistry for the complex. The complex displayed a magnetic moment of 3.10 BM, which indicated the presence of water molecules that formed clusters. The zinc complex lacked the ability to d–d transitions. The complex maintained its tetrahedral shape through the presence of ligand-centered and charge transfer bands which made up most of its composition.

Heavy Metal Immobilization Studies

The researchers assessed the lead and cadmium removal capabilities of various complex substances through their testing procedures. The immobilization process achieved its maximum efficiency after 120 minutes because contact time together with concentration and temperature had a crucial impact on the procedure [12]. The pseudo-second-order model provided the best match because its correlation values exceeded 0.995. The process is controlled through chemisorption according to this information. The chemical interactions between ion exchange and chelation processes hold more significance than the physical adsorption mechanisms [13].

The Langmuir model explained both Pb^{2+} and Cd^{2+} ions through adsorption isotherm studies because the model provided a good match which resulted in correlation values above 0.992. The complexes demonstrate monolayer adsorption on their active sites because all active sites remain identical. The highest adsorption capacities reached extremely high levels. The [CuL] complex worked best, with capacities of 284.5 mg/g for lead and 195.2 mg/g for cadmium. The copper complex functions better because its stable coordination environment enables its metal center to interact with the tridentate ligand structure which enhances the complex's performance [14].

The preference for Pb^{2+} over Cd^{2+} supports the Hard–Soft Acid–Base theory according to our expectations. The bonding strength of Pb^{2+} with nitrogen and oxygen donor atoms exceeds that of Cd^{2+} because Pb^{2+} exists in a state that approaches acids. The copper complex shows high removal efficiency for Pb^{2+} because the Schiff base complexes demonstrate potential as effective long-lasting materials which immobilize heavy metals.

Adsorbent (Complex)	Heavy Metal	qmax (mg/g)	KL (L/mg)	R^2 (Langmuir)	R^2 (Freundlich)
[Cu(L)]	Lead (Pb^{2+})	284.5	0.095	0.998	0.965
[Cu(L)]	Cadmium (Cd^{2+})	195.2	0.072	0.995	0.971
[Ni(L)]	Lead (Pb^{2+})	245.1	0.088	0.996	0.958
[Ni(L)]	Cadmium (Cd^{2+})	180.4	0.065	0.992	0.962
[Zn(L)]	Lead (Pb^{2+})	220.8	0.075	0.994	0.949
[Zn(L)]	Cadmium (Cd^{2+})	165.7	0.058	0.993	0.955

Table 3: Langmuir Isotherm Constants and Correlation Coefficients for Pb^{2+} and Cd^{2+} Immobilization

A mechanical look at immobilizing heavy metal

Transition metal–Schiff base complexes secure heavy metal ions through their ability to bind with Pb^{2+} and Cd^{2+} ions. The system depends on two factors which include the coordination geometry and the Hard and Soft Acids and Bases (HSAB) theory. The process of sequestration works well because the metal–ligand structure that was already there works well with the toxic ions that come in. The Schiff base ligand made from amino acids coordinates in a tridentate way which creates stable chelate rings that contain five and six members to stabilize the structure. The [Cu(L)] complex shows maximum adsorption ability because its distorted square planar shape creates axial spaces that allow for simple interaction with other substances [15]. The [Ni(L)] and [Zn(L)] complexes use coordinated water molecules to create octahedral and tetrahedral shapes which become easily transported by incoming heavy metal ions. The chelate effect drives this replacement process which makes the complex matrix more thermodynamically stable and makes it easier for Pb^{2+} and Cd^{2+} to stick together strongly.

HSAB theory explains the preference for Pb^{2+} over Cd^{2+} which demonstrates its superior value. Lead exists as a nearly acidic metal while cadmium exhibits stronger acid characteristics. The Schiff base ligand presents two types of donor atoms which include borderline nitrogen atoms from azomethine and hard oxygen atoms from phenolic and carboxylate structures. According to HSAB rules borderline acids form stronger connections with borderline bases than they do with other acids. The ligand structure creates an easier pathway for Pb^{2+} to bond with the metal. Due to this characteristic, Pb^{2+} ions show greater stability and can hold a charge longer than Cd^{2+} ions. These complexes act as molecular systems, allowing for the permanent trapping of harmful metal ions, which helps protect the environment over time.

III. Conclusion

The study produced a series of transition metal complexes by combining a Schiff base ligand derived from L-alanine with Cu^{2+}, Ni^{2+}, and Zn^{2+} metal ions. These complexes showed good abilities to capture heavy metals. The spectroscopic tests through FTIR and UV–Vis confirmed the successful synthesis of the ligand which formed stable chelate structures through its tridentate coordination via nitrogen and oxygen atoms. The immobilization process of lead and Cadmium followed two separate second-order kinetic mechanisms which matched the Langmuir isotherm model. The correlation values exceeded 0.99 which confirmed that the adsorption process involved chemisorption to form a single layer of adsorbate on the surface. The synthesized complex [Cu(L)] achieved maximum adsorption capacity with 284.5 mg/g for lead which made it the most effective complex. In accordance with HSAB theory, lead ions (Pb^{2+}) exhibit greater selectivity compared to cadmium ions (Cd^{2+}), a characteristic attributable to their capacity to establish more robust interactions with ligand donor sites. These complexes offer a potent and enduring approach to heavy metal remediation, owing to their inherent stability and persistence.

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