

Schiff Bases, Syntheses, Characterisation and their Application to Heavy Metal Removal: A Review

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ABSTRACT

Schiff bases are compounds resulting from the condensation reaction between an aldehyde or ketone with primary amines. The confirmation of the formation of these compounds involves the use of characterisation techniques which encompasses spectroscopic and thermoanalytical techniques. Recently, Schiff bases have garnered attention because of their wide applications which range from industrial uses to use in remediation of metal ions. Their use in extraction of heavy metal is of particular interest due to rising levels of metal pollution globally. The ability of Schiff bases to form coordination complexes with metal ions makes them suitable for these purposes. This review article outlines the synthesis, characterisation and application of Schiff bases to metal extraction.

Keywords: Schiff bases, synthesis, characterisation, extraction, metal, heavy metals

INTRODUCTION

In recent years, there have been a growing number of researches involving the syntheses and characterisation of Schiff bases (Ali *et al.*, 2022; Aranha *et al.*, 2007). This increase is attributed to the various applications of Schiff bases in pharmacy, coordination chemistry, catalysis, materials science, and metal extraction.

Schiff bases application in the extraction of metals from aqueous phase is of particular interest due to the alarming level of metal pollution, which poses significant health to both humans and the ecosystem (Nyamoto, 2023). Metals, such as cadmium, chromium, copper, mercury and nickel, etc., are abundant in industrial processes, mining activities, urban runoff, contaminating water bodies, soil, and air (Olaka *et al.*, 2019). Their persistence and toxicity have prompted rigorous efforts to develop effective remediation strategies aimed at controlling their adverse impacts on human populations and also the ecosystem.

Despite the significant advancements in heavy metal remediation strategies, challenges persist in achieving efficient and selective removal of pollutants (heavy metals) from complex environments (Al Zoubi, 2013). Several conventional methods such as adsorption, precipitation, ion exchange, and membrane filtration often suffer from limitations such as low selectivity, high energy consumption, and generation of secondary waste streams (Krishnan *et al.*, 2021). In contrast, the use of Schiff bases as chelating agents suggests an alternative characterized by high selectivity, rapid kinetics, and slight environmental impact.

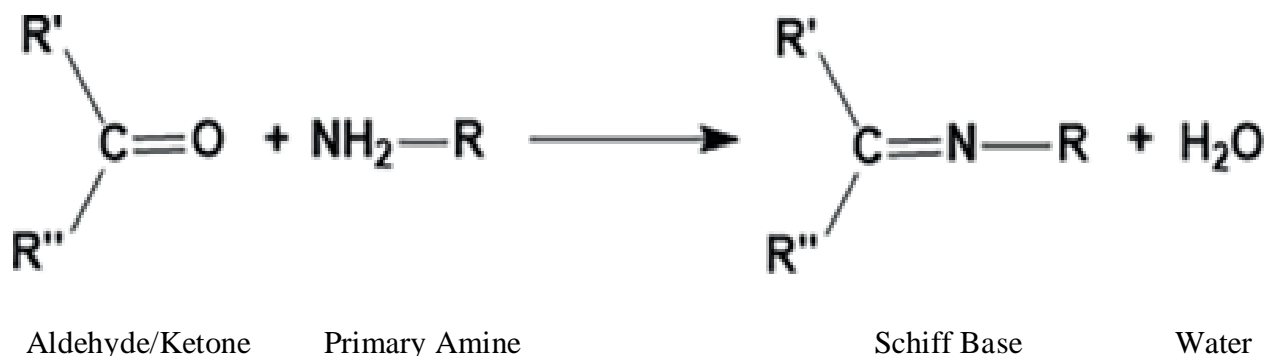
The unique chemical structure of Schiff bases, containing azomethine ($-C=N-$) linkages and donor atoms

(Nitrogen and Oxygen), facilitates the formation of stable complexes with heavy metal ions through coordination bonds (Meena *et al.*, 2023; Al Zoubi, 2013; Abdallah *et al.*, 2009). This chelation process results in the immobilization and subsequent removal of heavy metals from solution, effectively reducing their concentrations to environmentally acceptable levels. Furthermore, the reversible nature of metal-chelate interactions allows for the regeneration and reuse of Schiff base ligands, enhancing the economic feasibility and sustainability of remediation processes. Therefore, in this review, we will discuss the synthesis synthetic routes, characterisation techniques and highlight the efficiency of Schiff bases as heavy metal extraction agents.

SYNTHESIS OF SCHIFF BASES

Schiff base was first synthesized in 1864 by German Scientist Hugo Schiff (Schiff, 1864) while investigating the reaction between anilines and aldehyde, which led to the formation of imine compounds presently known as Schiff bases. Schiff bases are condensation products of the reaction between an aldehyde or ketone and a primary amine (Al Zoubi, 2013). Schiff bases are considered as the nitrogen equivalents of an aldehyde or ketone, where the C=O group is substituted with a C=N-R group with the R representing either an alkyl or aryl group. Those with aryl substituents are more stable and easier to synthesize compared to those with alkyl substituents (Hussain *et al.*, 2014, Meena *et al.*, 2023). In addition, the aliphatic aldehyde derivatives tend to undergo polymerization, while those originating from aromatic aldehydes with effective conjugation exhibit greater stability. Schiff bases act as excellent ligands for metal ions in various chemical reactions as the nitrogen atom of the imine group (C=N-R) is electron rich and can readily donate lone pair of electrons to a metal ion, forming a coordination bond (Abdallah *et al.*, 2009).

The formation of a Schiff base from an aldehyde or ketone involves a reversible reaction that commonly occurs under acid or base catalysis, or with the application of heat (Meena *et al.*, 2023). To drive this reaction to completion, the products are separated or the water is removed by a combination of both methods, as hydrolysis of the obtained Schiff bases would occur in an aqueous acidic or basic media resulting in their reactants (amines and aldehydes).

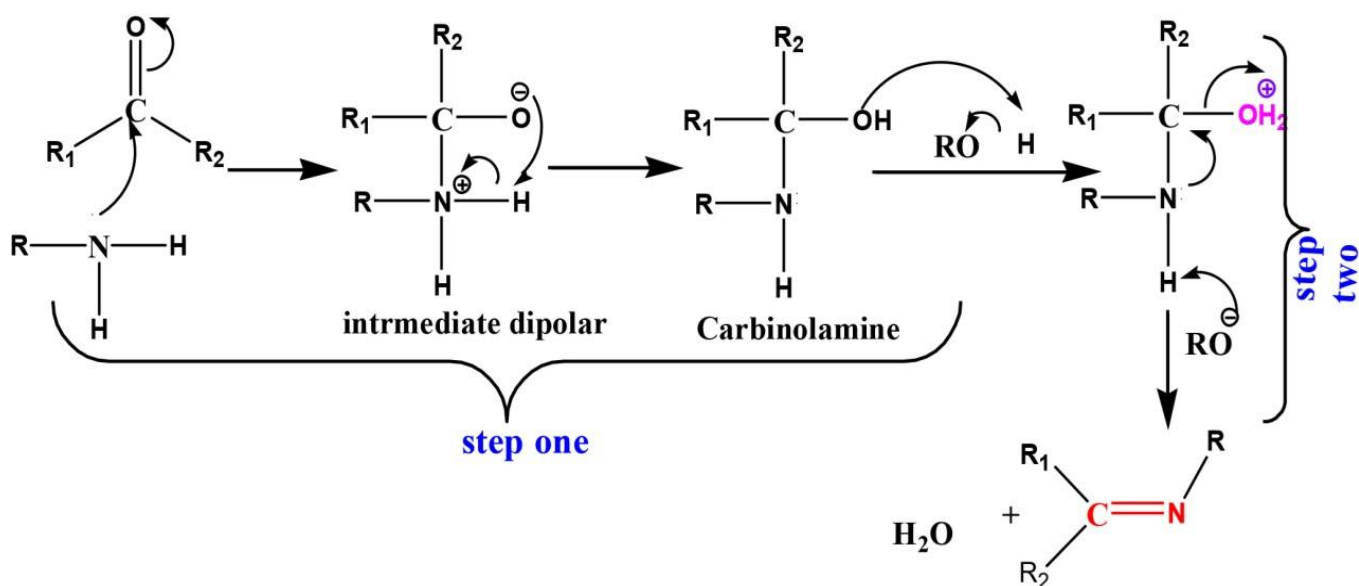


Scheme 1: General preparation of Schiff bases from aldehydes or ketones (Mandel and Pratiher, 2023)

The mechanism for the reaction involves a variation of nucleophilic addition to the carbonyl group, with the amine acting as the nucleophile. This reaction proceeds with the nucleophilic amine reacting with an aldehyde or ketone to create an unstable compound known as a carbinolamine. The carbinolamine then undergoes dehydration, either through an acidic or basic catalyzed pathway, to yield the Schiff base.

The carbinolamine is notably an alcohol, thus acid-catalyzed dehydration is generally favoured. Acid catalysis in the Schiff base formation reaction is preferred because the dehydration of the carbinolamine represents the rate-determining step of the reaction. However, an equilibrium shift to the left may occur if the acid concentration is excessively high. This is due to the protonation of the amine compounds, rendering them non-nucleophilic and causing the shift in equilibrium. Therefore, the synthesis of several Schiff bases

is typically conducted under mild acidic pH conditions.



Scheme 2: Reaction Mechanism of Schiff base formation (Anthony et al., 2019)

From the reaction mechanism illustrated in **Scheme 2**, the conversion of the aldehyde or ketone and the amine into a Schiff base involves a two-step mechanism. In step one, the nucleophilic nitrogen atom of the amine attacks the carbonyl group, resulting in the formation of an intermediate carbinolamine which rearranges to a stable intermediate. Step two involves the formation of the Schiff base, which is largely dependent on the rate of water dehydration from the reaction mixture. This second step includes formation of a -C=N- bond, ultimately leading to the final formation of an imine (a Schiff base).

SYNTHETIC ROUTES OF SCHIFF BASES

Numerous investigations have focused on the synthesis of Schiff bases. The interest in these compounds is due to their physiological and pharmacological properties and most recently their use in the extraction of heavy metals from aqueous media. The synthesis however, is obtained through two major routes namely; conventional and green synthetic routes (Nagar *et al.*, 2023, Meena *et al.*, 2023).

Conventional Synthetic Route

The conventional method requires refluxing and or stirring different aldehydes or ketones with the appropriate primary amines at elevated temperatures to form the Schiff bases (Gogoi *et al.*, 2023; Patan & Patel, 2023).

The magnetic stirring synthetic route for Schiff bases, involves the use of a magnetic stirrer to facilitate mixing and homogenization of the reaction mixture (Gupta *et al.*, 2005). The stirring is to ensure uniform distribution of reactants and enhance the kinetics of the reaction. The reaction typically proceeds in acidic conditions to promote the formation of the Schiff base. Acid catalysis helps in the activation of the carbonyl group of the aldehyde, making it more prone to nucleophilic attack by the amine. Magnetic stirring also enhances the contact between the reactants and consequently boosts the progress of the reaction. This is particularly useful for reactions involving solid reactants or where thorough mixing is essential for achieving high yields. While magnetic stirring itself does not alter the chemical reaction, it plays a vital role in optimizing the synthetic conditions and enhancing reaction kinetics, leading to improved efficiency in the

synthesis of Schiff bases.

The reflux synthetic route for Schiff bases syntheses involves heating the reaction mixture to boiling point under a reflux condenser to ensure continuous evaporation of volatile components, while the condensed vapours are returned to the reaction vessel, in order to facilitate the condensation reaction between an aldehyde and an amine (Patan & Patel, 2023). The refluxing process ensures thorough mixing of reactants and continuous removal of water, driving the reaction towards completion (Gupta *et al.*, 2023). Refluxing is advantageous for reactions that require long heating and for the removal of water, which is a common by-product in condensation reactions. By maintaining a constant temperature and ensuring efficient removal of volatile components, refluxing helps in achieving higher yields and improving the purity of the desired product.

Green Synthetic Routes

Using green chemistry tools and methodologies in the syntheses of Schiff bases offer substantial environmental and economic advantages over conventional synthetic methods (Nagar *et al.*, 2023). The most common green synthetic route in Schiff base synthesis is the microwave-assisted synthesis, first proposed by Abirami and Nadaraj (2014). This route offers a solvent free synthesis or the use of minimal solvents. The microwave synthetic route of Schiff bases involves using microwave irradiation to fasten the condensation reaction between an aldehyde and an amine, resulting in the formation of the Schiff base. Microwave irradiation enables rapid and uniform heating of the reaction mixture, leading to enhanced molecular collisions and increased reaction rates. This acceleration results in significantly reduced reaction times as opposed to conventional heating methods. Additionally, the precise control over reaction conditions provided by microwave irradiation allows for improved selectivity and increase in yields of the desired Schiff base. These advantages have led to many researches on the synthesis of various Schiff bases and their derivatives.

Other green synthetic methods include ultrasonic synthetic route and grinding stone route. The grindstone technique involves use of a mortar and pestle which generates heat locally to grind the substrate crystal and reagents (Bedi *et al.*, 2020). The act of grinding initiates reactions by transferring a small amount of energy through friction. This route takes longer time but is more efficient and selective compared to other green methods. Ultrasonic Synthetic route involves the use of ultrasonic radiation to cause excitation of molecules for reaction. (Premalatha & Santhi, 2014). The apparatus used is an ultrasonic bath or probe called a sonicator. The ultrasonic probes normally employ frequencies greater than 20 Hz for reactive purposes.

Figure 1 illustrates the various synthetic routes to obtain Schiff bases.

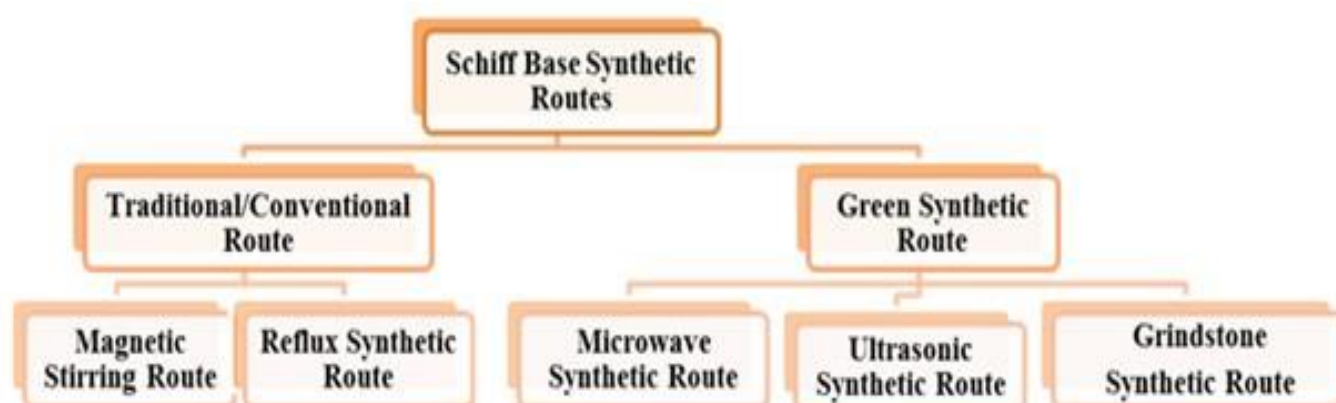


Figure 1: Various synthetic routes to obtaining Schiff bases

CHARACTERISATION

The characterisation of Schiff bases involves the use of spectroscopic techniques such as infrared (IR) spectrometry, UV-Visible spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry (MS). Other methods include magnetic susceptibility, X-ray diffraction (XRD), thermoanalytical techniques such as thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Each technique provides useful information on the composition, molecular structure, and thermal stability of the synthesized Schiff bases.

Infra-Red Spectroscopy

Infrared spectroscopy provides insight into the type of functional groups attached to the organic molecule. The underlying principle involves the absorption of radiation by an organic molecule which leads to vibrational transitions in the molecule. The vibrational transitions correspond to a frequency observed for a functional group with each functional group exhibiting a characteristic vibrational frequency.

In Schiff Bases, IR confirms the presence of the main C=N functional group that indicates the formation of a Schiff base. Other functional group like C=O, O-H, C-C are also identified from the IR spectrum (Al-Shboul *et al.*, 2022). The C=N bond is typically observed as resonance bands within the region of 1600-1700 cm^{-1} . Complexation of Schiff base with metal atoms or ions results in a shift of C=N frequency, typically to a lower wave number, indicating the binding mode of the Schiff base (ligand) to the metal centre. New bands are also observed for metals coordinated with other atoms e.g M-O and M-N. A broad resonance band shown at 3300 – 3600 cm^{-1} is attributed to the O-H stretching of phenolic or hydroxyl groups present in the Schiff Bases.

UV-Visible Spectroscopy

UV-Vis technique is employed to study the conjugation system in organic molecules, evaluate the electronic environment within metal complexes, and quantify concentrations through Beer's Law (Vogt *et al.*, 2023). The principle involves absorption of ultraviolet and visible radiation by organic molecules which leads to electronic transitions in those molecules.

The UV measurement of Schiff bases and their metal complexes are done in solvents like dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or chloroform (CHCl_3) producing spectra which exhibits characteristic UV absorption bands (Al Zoubi *et al.*, 2017). Typical electronic transitions include $\pi \rightarrow \pi^*$ transitions and $n \rightarrow \pi^*$ (Hussain *et al.*, 2014). Upon coordination with metal ions, new band are shown on the UV spectra which are associated with d-d transitions or metal-to-ligand charge transfer (Aranha *et al.*, 2007). Where these new bands are found, their intensity and nature, provide insight into the electronic transition around the central metal atom

A study on the UV-Visible absorption of a Schiff base (4-(((5-mercapto-4H-1,2,4-triazol-3-yl)imino)methyl)-2-methoxyphenol) and its complexes in DMSO solutions was carried out at room temperature, scanning from 200 to 700 nm (Vinusha *et al.*, 2019). Two absorption bands were observed at 310 nm and 316 nm for the free ligand. The authors attributed the band at 310 nm to the $\pi \rightarrow \pi^*$ transition of the heterocyclic moieties while that at 316 nm was for the $n \rightarrow \pi^*$ transition of the ligand's azomethine group. Upon coordination with the metals Co, Cu, Mn, Ni and Zn all in the +2 oxidation states, a shift to longer wavelengths was observed in the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. For example, a shift from 310 nm to 312 nm was observed for the $\pi \rightarrow \pi^*$ and from 316 nm to 334 nm for the $n \rightarrow \pi^*$ in the transition bands for the Co(II) Schiff base complex. The researchers also specifically assigned the bands at 318 nm and 329 nm in the Cu(II), 310 nm and 316 nm in the Ni(II), 316 nm and 326 nm in the Mn(II), and 315 nm and 337 nm in the Zn(II) metal complexes, to the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ transitions respectively. These transitions to longer

wavelengths in these complexes suggest the formation of coordinate bonds between metals and the Schiff bases.

NMR spectroscopy

NMR is a well-established characterisation technique used to determine the molecular structure of compounds and substances (). This works by using studying the magnetic properties of certain nuclei (^1H , ^{13}C) when placed in an external magnetic field.

The utilization of HNMR and CNMR for characterisation of Schiff bases provides information on the different proton environments and carbon environments respectively. The spectral data show characteristic peaks corresponding to various organic groups present in different proton or carbon environments. These groups often identified include $\text{CH}=\text{N}$, Aryl-H, $-\text{OCH}_3$, and $-\text{PhOH}$ (Hassan *et al.*, 2013). Upon complexation with a metal ion or atom, the peak of the azomethine group $\text{CH}=\text{N}$, moves further downfield, indicating the deshielding of the azomethine proton due to coordination of the nitrogen atom of the azomethine to the ligand.

In the earlier cited study by Vinusha *et al.*, (2019), the HNMR spectra of the **ligand [4-(((5-mercapto-4H-1,2,4-triazol-3-yl) imino) methyl)-2-methoxyphenol]** revealed a peak at 7.50 ppm which is attributed to $\text{CH}=\text{N}$ proton. The peak of aryl-H is observed at 7.0 – 7.40 ppm. The peak at 3.86 ppm represents the proton from the $-\text{OCH}_3$. Analyses using ^{13}C NMR revealed that carbon atoms for the methoxy group ($-\text{OCH}_3$) were observed at $\delta = 54.79$ ppm for the ligand while other aromatic ring carbons were observed at $\delta = 112$ -130 ppm. The peak at $\delta = 152$ ppm corresponded to the carbon in the C-OH group which confirmed formation of Schiff base ligand.

X-ray Diffraction

X-ray diffraction, a technique employed to deduce the molecular structure of crystalline materials involves the collimation of X-rays to a sample, which are then deflected by the crystal lattice of the sample, producing a diffraction pattern. By examining the diffraction pattern, information about the location of atoms within the crystal is provided. From the information, the molecular structure of the sample is obtained.

Using XRD to characterize Schiff bases metal complexes provides information on the bond lengths, bond angles, intermolecular interactions and the presence or absence of additional ligands or molecules within the complexes (Meena *et al.*, 2023). XRD also reveals the geometry surrounding the central metal atom or ion, and whether a Schiff base binds as a chelate, forming rings with the metal centre as it can help in classifying the ligand as monodentate, bidentate and polydentate.

Mass Spectrometry

Mass Spectrometry is an analytical tool used to determine the molecular formula, molecular weight, and structure of substances. The underlying principle involves measuring the mass-to-charge ratio of ions resulting from an ionized sample.

Mass spectrometry is an important method for characterizing Schiff bases and their metal complexes, providing information on molecular weight, elemental composition, and structural details by measuring the mass-to-charge ratios. The molecular ion peak corresponds to the molecular mass of the Schiff base (Refat *et al.*, 2013). Structural information is obtained from the fragmentation pattern observed in the spectra as each fragmentation pattern corresponds to specific parts of the molecule. For example, the confirmation of the formation of both the ligand, 4-(((5-mercapto-4H-1,2,4-triazol-3-yl) imino) methyl)-2-methoxyphenol, and its metal complexes of Co(II), Cu(II), Mn(II), Zn(II), and Ni(II) was achieved using mass spectrometry (Vinusha *et al.*, 2019). Specifically, the molecular ion peak at $m/z = 251.08$, was identified as the molecular

weight of ligand. Similarly, the molecular ion peaks at m/z ranging from 555 to 561 were also assigned as evidence for the coordination of Cu, Co, Mn, Zn, and Ni ions with the ligand.

Magnetic Susceptibility

Magnetic susceptibility measures the extent to which a substance will become magnetized when placed in a magnetic field. Magnetic susceptibility measurements provide insight into the number of unpaired electrons (paramagnetism and diamagnetism), geometry and field strength of a material.

Schiff bases and their metal complexes are analysed for magnetic susceptibility to determine the electron pairing, stereochemistry, and metal-metal interactions in the complexes. Such analyses also provide insight on the geometry around specific metal centres, and determine if they are high spin or low spin complexes. A study reported by Kumar and John (2006), on a polystyrene anchored Schiff base, magnetic susceptibility measurements were done to indicate the geometry its complexes with selected metals. The value of the magnetic moment indicates the geometry around the metal centre of the complex. For instance, magnetic moments of 5.92 BM of the Fe(III) complex and 3.34 for the Ni(II) complex indicated an octahedral structure. The Co(II) complex showed a magnetic moment of 2.75 BM corresponding to a low spin square planar geometry. The value of 1.83 BM for the magnetic moment of the Cu(II) complex was reported to be magnetically dilute. The polystyrene based Schiff base complexes with Zn(II) and U(VI) were reported as diamagnetic as expected.

Thermogravimetric Analysis (TGA)

TGA measures the variation in mass when a sample is heated and cooled as a function of controlled temperature or time (Menczel & Prime, 2008). TGA provides insight into the thermal stability and composition of Schiff bases by identifying the temperature at which a Schiff base begins to decompose (Taha *et al.*, 2013; Calu *et al.*, 2018). Furthermore, TGA can help in the identification of coordinated and crystallized solvents within a Schiff base metal complex. The identification of these solvents is based on the temperature and weight loss associated with their removal. Additionally, the stoichiometry of a metal complex can be determined by TGA. The presence of two coordinated or crystallized water in a complex for instance may be determined by the decrease in weight corresponding to the amount equal to two molecules of water.

Differential Thermal Analysis

In differential thermal analysis, the temperature difference between a sample material and a reference material is measured (Devi *et al.*, 2021). The principle applied here is that a sample undergoes phase transitions when heated while the reference does not.

Similar to TGA, DTA can be used to determine when Schiff bases begin to decompose. As noted earlier, such decomposition provides insight into the thermal stability of the Schiff bases. The events of this decomposition are indicated as exothermic peaks on the DTA curve (Omar *et al.*, 2009). Additionally, DTA can be used to determine the melting point and phase transitions in a Schiff base, typically shown in the DTA curve as an endothermic peak. Most instruments now provide simultaneous TGA and DTA measurements. The simultaneous measurement of TGA and DTA gives complete information of the thermal events that occur from desolvation and loss of ligand due to decomposition.

EXTRACTION OF HEAVY METAL

Heavy metals are considered toxic metals that cause severe environmental and health problems (Etorki *et al.*,

2013). In wastewaters, toxic metals such as nickel, lead, copper, zinc, arsenic, chromium and mercury which pose severe health risk have been reportedly found in this media. Exposure of humans to these heavy metals can cause diseases such as cancers and organ damage. It is therefore pertinent to develop means of extraction of these metals. Extraction of metals includes procedures such as chemical precipitation, filtration, flocculation, ion-exchange, membrane technologies and solvent extraction (Yadav *et al.*, 2021; Krishnan *et al.*, 2021). These methods employ the use of different materials and reagent to achieve extraction purposes. However, some of these methods are quite expensive and may be rather inefficient in extraction of metal ions in trace concentrations; hence there is a need for more economic and safe methods of heavy metal extraction (Olaka *et al.*, 2019).

One safe and economic method is the solvent extraction technique. Solvent extraction over the years has been utilized for extracting and determining metal ions (Al Zoubi, 2013). This technique is cost-effective and exhibit high efficiency in the extraction of metals. The solvent extraction procedure involves introducing the aqueous metal solution to an organic solvent, such as chloroform, containing a metal-selective chelating agent. An advantage of this method is its application in determining low concentrations of metals in natural and wastewaters as very low metal concentrations require preconcentration and separation before analysis. However, solvent extraction also known as liquid-liquid extraction is able to do preconcentration and separation and this is done in one step.

Schiff bases are employed in this method as an organic phase for extraction of metals because they are very good chelating agents (Al Zoubi, 2013). As chelating agents, they are able to bind metal ions to form stable complexes. Schiff bases are good chelating agents for extraction of metals ions because they possess high distribution coefficients and are pH dependent in the system used. Reports have shown that Schiff bases extract heavy metals with quite good efficiency. To obtain optimum conditions for efficient extraction, parameters such as contact duration, solution pH, adsorbent quantity, and temperature are measured. Generally, the efficiency of the Schiff base extraction is affected by certain factors such as pH, addition of an extra ligand, type of metal ions, and type of donors in ligand (Chukwu & Jackson, 2013; Godwin *et al.*, 2014). For instance, at some pH levels, better extraction efficiency is obtained than other pH levels.

Commonly synthesized Schiff bases used for metal ion extraction include Pyrazole-based Schiff bases, Chitosan-based Schiff bases and SBA-15 modified Schiff bases.

Pyrazole Based Schiff Bases

Pyrazole based Schiff bases have been typically studied for their biological activities. However, there are reported uses of pyrazole derived Schiff bases to successfully remove heavy metal from solutions.

Chukwu and Godwin (2013) reported the extraction of uranium(VI) from aqueous phase using a chloroform solution of a pyrazole based Schiff base, N,N-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine), (H_2PrEtP) in Figure 2a, at pH values ranging between 3 to 9. The obtained results showed the ligand, H_2PrEtP , as a weak acid with pK_{a1} value of 6.1 ± 0.1 and pK_{a2} value of 7.6 ± 0.1 . The ligand exhibited optimal percentage efficiency at 96.9% with the extraction occurring between pH 6.0 to 8.5. In the presence of a co-ligand, 4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one, ($HPrP$), extraction occurred at lower pH values between 4.0 to 6.5 at an increased optimal percentage efficiency of 99.9%. The mixed ligands showing better extraction efficiency and increased optimal percentage efficiency at lower pH values suggest that the ligand mixture uranium complex $[UO_2(HPrEtP).HPrP.X]$ shown in Figure 2b, has better distribution than the single ligand uranium complex $[UO_2(HPrEtP)X]$ in Figure 2c, in the organic phase, resulting in more favourable extraction of uranium(VI) ion in aqueous media. The organic phase containing the mixed ligands proves to be a more effective extractant for uranium(VI) compared to using H_2PrEtP alone.

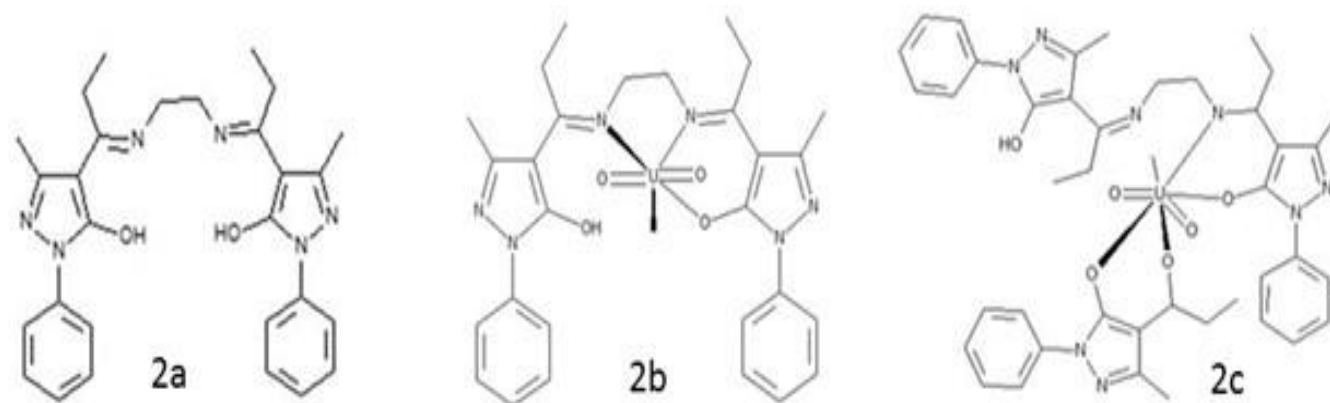


Figure 2: (2a) Structure of N,N-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine), (H₂PrEtP), (2b) Proposed structure of UO₂(HPrEtP).X: and (2c) Proposed structure of UO₂(HPrEtP). PrP.X. where X in 2b and 2c = Cl⁻, CH₃COO⁻, etc. from buffers.

A chloroform solution of the ligand N,N'-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine), (H₂BuEtP) and its mixture with 4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP) used to extract Pb(II) ions from aqueous media (Godwin & Uzochukwu, 2012). The findings on the distribution of Pb(II) ions from buffered aqueous solution into the chloroform solutions of only the Schiff base H₂BuEtP and its mixture with the co-ligand HBuP revealed a slight reduction in the pH_{1/2} when a combination of the two ligands was employed. Partition coefficients, (log k_{D1}) value of 1.92 ± 0.25 and (log k_{D2}) value of 1.82 ± 0.22 were observed for the complexes, indicating the tendency for more effective distribution of Pb(II) ions into the chloroform solution of H₂BuEtP alone instead of the mixed ligands H₂BuEtP and HBuP solution. This tendency was attributed to the extraction of Pb(II) tris complex species into the H₂BuEtP solution, suggesting the extraction of species featuring both strong Pb-O and weak Pb-N bonds into the organic phase. The influence of anions, mineral acids, and complexing agents on the extraction process was also studied. The results showed the extraction as quite poor in acidic solutions both in the single ligand and mixed ligands, except for sulphuric acid. Additionally, removal of Pb(II) ions from EDTA solution was found to be completely inhibited.

The effect of anions, common acids, and additional complexing agents on the extraction of Fe²⁺ from aqueous media into chloroform solutions of the Schiff base ligand, 4,4'-(1E,1E')-1,1'-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-ol) (H₂BuEtP) was investigated in its single form and also in mixture with 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) as a co-ligand (Godwin *et al.*, 2014). The concentration of Fe²⁺ in aqueous solutions post-extraction was determined using a colorimetric method with 1,10-phenanthroline, and the percentage extraction was calculated based on the differences. Separation factors (β_{XY}) were computed using the data from prior studies involving the same organic phases to ascertain the theoretical conditions for the separation of Fe²⁺ from Ni²⁺, Pb²⁺, and UO₂²⁺. All the acids tested yielded extraction efficiency > 90% for Fe²⁺ at most concentrations, with HNO₃ and H₃PO₄ exhibiting the highest percentage extraction of 99.93% at 0.01 M and 0.1 M respectively in the mixed ligands H₂BuEtP/HBuP organic system. H₃PO₄ also provided the highest extraction efficiency of 99.3% at 0.1 M in the H₂BuEtP system. Similarly, all the anions investigated also yielded > 90% extraction of Fe²⁺ at varying concentrations in both types of organic phases. Notably, CH₃COO⁻, PO₄³⁻, Br⁻, and tartrate ions exhibited the most effective extraction of Fe²⁺ with H₂BuEtP. The anions and acids acted like masking and salting out agents at various concentrations. Calculation of the separation factors (β_{XY}) showed that, it was theoretically possible to separate Fe²⁺ from Ni²⁺ using H₃PO₄ exclusively, and Fe²⁺ from Pb²⁺ using H₃PO₄, HCl, and EDTA with only H₂BuEtP. Calculated β_{XY} for the mixed ligands H₂BuEtP/HBuP, suggested the potential to separate Fe²⁺ from Ni²⁺ using HNO₃ and H₃PO₄, Fe²⁺ from Pb²⁺ using HCl and oxalate, and Fe²⁺ from U(VI) using CH₃COOH, PO₄³⁻, Br⁻, and oxalate.

Salicyclic Derived Schiff Bases

Salicyclic derived Schiff bases usually contain additional donor atoms such as nitrogen, oxygen, and sulphur making them suitable chelating ligands for coordination with metal ions to form Schiff base complexes (Maheer & Mohammed, 2015). Due to this phenomenon, studies have employed on the use of salicyclic Schiff bases for heavy metal extraction.

The Schiff base 2-[(E)-[(8-aminonaphthalen-1-yl)imino]methyl]phenol derived from salicyclic and suitable amino compounds, was synthesized and assessed for its potential for uptake of metal ions such as Cd(II), Pb(II) and Zn(II) ions (Etorki *et al.*, 2013). It was observed that, as the concentration of Cd(II) ions increased, the percentage extraction also increased up to a certain point. However, no further increase in the percentage removal of Cd(II) was observed beyond this point. Conversely, the ligand exhibited a reduction in removal percentage of Zn(II) ions as the concentration of Zn(II) ions increased. It did not perform effectively with Pb(II) ions.

SBA-15 Modified Schiff Bases

Some studies have investigated the modification of SBA-15 materials with Schiff bases for heavy metal removal. The modified heterogeneous SBA-15 Schiff bases have shown interesting selective extraction to various metal ions at various pH levels. Chelation also plays important roles in this selective adsorption of metal ions.

The possible role of chelation in the selective adsorption of Cd(II), Co(II), Cu(II), Cr(III), Mn(II), Ni(II), Pb(II) and Zn(II) ions at pH values ranging between 2-6 using modified SBA-15 Schiff Base from aqueous media was investigated (Surendan *et al.*). Two heterogeneous Schiff bases (2-HB-SBA-15 and 4-HB-SBA-15) derived from the modification of SBA-15 exhibited varying affinities for these metal ions in the same mixture under different pH conditions. At pH 2, 2-HB-SBA-15 showed 100% selectivity towards Pb(II) ions, while its selectivity shifted to Cu(II) at higher pH levels. On the other hand, 4-HB-SBA-15 exhibited an affinity towards Cr(III) and Pb(II) at pH 2, with a broader selectivity observed at higher pH, including significant portions for Cr(III), Pb(II), and Cu(II). The observed affinity for a specific metal ion was heightened when considering Cr(III), Pb(II), and Cu(II) ions individually and in combination at pH 5. Upon examining the structure of both organic molecules, it was found that 2-HB-SBA-15 has a potential for chelation, whereas 4-HB-SBA-15 exhibits less chelation capability. The disparity in molar adsorption selectivity between 2-HB-SBA-15 and 4-HB-SBA-15, clearly demonstrates the impact of chelation in ligands on the selective adsorption of metal ions from aqueous mixtures under same adsorption conditions (Parambadath *et al.*, 2020).

SBA-15 was modified with amine ($-NH_2$) and 3-methoxy salicylaldehyde (3-MS) to form a mesoporous silica surface modified with Schiff base (3-MS-SBA-15) (Abdul *et al.*, 2018). The investigation focused on the removal of Cu(II) and Cr(VI) metal ions from their aqueous solutions using 3-MS-SBA-15, aiming to understand and optimize the impact of contact duration, solution pH, adsorbent quantity, and temperature in a batch system. Equilibrium data were evaluated using the Tempkin, Dubinin-Radushkevich, Langmuir, and Freundlich isotherms. The Freundlich and Langmuir isotherms were found to be suitable fits for the adsorption process of Cu(II) and Cr(VI) respectively. Kinetic analysis revealed that the entire adsorption process aligned well with the pseudo-second-order kinetics model. The adsorption process was notably affected by temperature, where the adsorption capacity decreased for Cu(II) and increased for Cr(VI) with rising temperature. This suggested an exothermic and spontaneous nature for Cu(II) adsorption, while Cr(VI) exhibited an endothermic and spontaneous nature.

Chitosan Based Schiff Bases

Chitosan based Schiff bases are commonly synthesised by the condensation of the carbonyl groups of aldehydes or ketones with chitosan's amino groups through the removal of water molecules (Antony *et al.*, 2019). Their usefulness as removal of metal ions have been reported and shown to be very efficient.

Elhag *et al.*, (2020), synthesized two new chitosan Schiff bases, (chitosan phenyl-1H-pyrazolo[3,4-b]quinoxaline Schiff base designated as Ch-PQ2 and chitosan pyrazolo[3,4-b]quinoxaline Schiff base named Ch-PQ1), in order to enhance chitosan's capacity for removing heavy metals from wastewater. They were specifically evaluated for their effectiveness in removing hexavalent chromium from synthetic samples. The study investigated various factors, including pH levels, polymer dosage, initial metal concentration, and contact time, as crucial elements influencing the adsorption of Cr(VI) ions from aqueous media. Kinetic analyses of the removal process were conducted, and the experimental equilibrium data were fitted to Langmuir and Freundlich adsorption isotherms. Both chitosan Schiff bases exhibited excellent removal efficiency, with Ch-PQ1 and Ch-PQ2 achieving removal rates of 96.4% and 98.8% for Cr(VI) respectively.

Jasim *et al.*, (2018) synthesised CsSB@Fe/NiFe, a novel modified chitosan Schiff base@Fe₂O₃-NiFe₂O₄, as a sorbent for the adsorption of Pb(II) ions from aqueous solutions. The effect of key parameters namely solution pH, contact duration, adsorbent quantity, and initial Pb(II) ion concentration was investigated and optimized. The optimal conditions for removing Pb(II) were determined to be an adsorbent dosage of 0.05 g, an initial Pb(II) concentration of 75 ppm, and a contact time of 120 minutes at pH 5. At these conditions, the maximum removal percentage of Pb(II) reached 97%. Moreover, CsSB@Fe/NiFe demonstrated approximately 88% removal of Pb(II) after undergoing five adsorption-desorption cycles. These findings suggest that the sorption of Pb(II) onto CsSB@Fe/NiFe was both feasible and spontaneous.

CONCLUSION

This review examined the synthesis and characterisation of Schiff bases, and their application in heavy metal removal. Schiff bases represent an important class of coordination compounds with diverse applications in science, medicine, and industry. The characterisation of these Schiff bases by employing various spectroscopic and thermoanalytical techniques offers insights into the formation of the desired compounds, their structural properties, coordination, and stability. Moreover, Schiff bases have demonstrated their potential in heavy metal removal, exhibiting impressive extraction efficiency and selectivity. Their ability to form chelates with metal ions makes them particularly suitable for this purpose, which is crucial for addressing heavy metal pollution. Nonetheless, further investigation is recommended to deepen our understanding in this field.

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