Synthesis and Characterization of 4-[(1-Hydroxy 2-Methoxybenzylidene)] – 4amino Antipyrine Schiff Base Coated With Silver Nanoparticle for Removal of Heavy Metal Ion from Industrial Waste Water

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Abstract- *The Schiff base 4-[(1-hydroxy, 2-methoxybenzylidene)]-4amino antipyrine [HBAA] formed from condensation of equimolar quantity (1:1) of vanillin and 4-amino antipyrine in alcoholic medium. Synthesis of silver nanoparticles and coating of silver nanoparticles with above mention Schiff base. The structural features of Schiff base was determined from elemental analysis, FTIR, UV-VIS, and NMR spectral studies. The Schiff base coated silver nanoparticles were characterized by UV-VIS Spectra. Analysis of metal ion done by AAS analysis as well as spectrophotometric analysis. Pea nut shell was used as a solid phase for the removal of heavy metal ion from industrial waste water. The Schiff base 4-[(1-hydroxy, 2-methoxybenzylidene)]-4amino antipyrine coated silver nanoparticles is adsorbed on peanut shell. The solid phase is treated with acid as well as base to remove all impurities and to activate its surface for removal of metal ion. Various parameters such as pH, contact time, effect of initial metal ion concentration and Schiff base weight which influenced the adsorption capacity were investigated.*

Keywords- AAS, Adsorption, Schiff Base, Silver NanoParticle,Waste Water.

I. INTRODUCTION

Toxic heavy metal contamination of industrial wastewater is an important environmental problem. Many industries such as electroplating, pigments, metallurgical processes, and mining and leather industries release various concentrations of heavy metals. Metal ions such as cadmium, chromium, copper, lead, zinc, manganese, nickel and iron are commonly detected in both natural and industrial effluents [1]. In spite of strict regulations restricting their careless disposal, these metal cations may still emerge in a variety of wastewaters stemming from catalysts, electrical apparatus, painting and coating, extractive metallurgy, antibacterial, insecticides and fungicides, photography, pyrotechnics, smelting, metal electroplating, fertilizer, mining, pigments, stabilizers, alloy industries, electrical wiring, plumbing, heating, roofing and construction piping, water purification, gasoline additives, cable covering, ammunition and battery industries and sewage sludge [2-4].

In the past few years, special attention has been given to the environmental contamination with heavy metal ions because of their high toxicity and non-biodegradability. The commonly used procedures for removing metal ions from effluents include filtration [5], chemical precipitation [6], chemical coagulation [7], flocculation [8], ion exchange [9], reverse osmosis [10], membrane technologies [11-13] and solvent extraction [14]. However, these methods are limited by high operational cost and/or may also be inefficient in the removal of some toxic metal ions, mainly at trace level concentration [15, 16].

Schiff base have a chelating structure and are in demand because they are straight for word to prepare and are moderate electron donor with easily-tunable electronic and steric effect. The synthesis and application of Schiff base and their co-ordination compounds have been highly considered in inorganic and bioinorganic fields, since their structural properties similar to some of the biological system (17-20). Many Schiff base and their complexes have been widely studied because of their industrial, antifungal antibacterial, anticancer and herbicidal applications (21-24).Schiff base compounds (-CH=N-) are usually formed by the condensation of a primary amines with ketones or aldehydes. The crosslinking agents can also be derived from metal complexes with N, S or O ligands.

A nanoparticle is the most fundamental component in the fabrication of a nanostructure. A nanoparticle is bigger than an atom or a simple molecule that is governed by quantum mechanics [25]. Nanoparticle shaves unique properties, especially optical, electronic and biological properties [26]-[29]. Due to their high surface-to-volume ratio, nanoparticles can be used in heterogeneous catalysis [30]-[31]. In addition, they are applied in many fields, including photonics, micro-electronics, lithography and surface-enhanced Raman spectroscopy [32] [33]. As noble metal nanoparticles, silver nanoparticles show unique chemical and physical properties. They have excellent conductivity, chemical stability and catalytic activity. These properties are directly dependent on their size, size distribution and shape [34]-[36].

In present work, Schiff base coated silver nano particle was prepared to adsorb Zn (II) metal ion from industrial waste water. The effect of parameter such as initial metal ion concentration, pH, contact time and adsorbent dosage.

II. EXPERIMENTAL

2.1. Material and Reagents

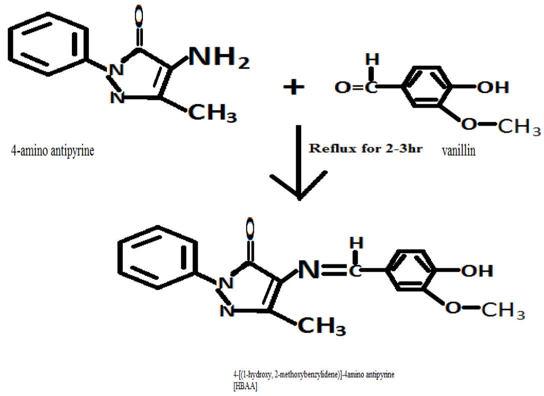
All other chemicals used of were analytical grade.Vanillin and 4-amino antipyrine were purchased from Sigma –Aldrich.During the course of present investigation, special precautions were taken to exclude even traces of moisture and other impurities from the chemical used for the practical work. Standard methods were used to purify solvents viz ethanol, ether, n-hexane,DMF, DMSO.

2.2. Apparatus.

In the characterization of Schiff base and Schiff base coated silver nps. , the melting points were determined by open capillary method on Melting point apparatus.^{1}HNMR spectra was conducted at MNIT Jaipur.Electronic spectra were recorded on UV-VIS Spectrophotometer 118. IR spectra were recorded on FTIR ABB horizon MB 03000 series instrument.

2.3. Synthesis of Schiff base:-

A Schiff base 4-[(1-hydroxy, 2-methoxybenzylidene)]-4amino antipyrine [HBAA] was prepared from equimolar quantity (1:1) of vanillin and 4-amino antipyrine and then refluxed in absolute ethanol for 2 to 3 hours. The Schiff base was isolated by crystallization after volume reduction by evaporation. Recrystallized from ethanol to ligand.Reaction is given below in scheme (I).



Scheme (I):- Synthesis of Schiff base [HBAA]

2.4.Synthesis of Silver NanoParticles:-

Synthesis of silver nps by chemical reduction method using $AgNO_3$ and $NaBH_4$. Trisodium citrate dihydrate (HOC(COONa)(CH2COONa) using as stabilising agent. Trisodium citrate dihydrate was mixed with AgNO3 solution under magnetic stirring for 10 min at room temperature before ice-cold NaBH4 was added. The colour of the mixture quickly changed to yellow, indicating the formation of AgNPs.

2.5. Coating of silver nps on Schiff base:-

To the silver nano colloid add 10 ml vanillin and 10 ml 4-amino antipyrine (1:1) in ethanol and stir on magnetic stirrer for 10 min. obtained ppt was collected.

2.6. Synthesis of Solid Phase:-

Peanut shells were crushed, and treated with acid, dried in an oven for overnight and carbonized in a tabular furnace for 2 carbonized material was further treated with base.

2.7. Extraction of heavy metal ion: -

Extraction of Zn (II) metal ion by AAS using columnmethod.

III. RESULT AND DISCUSSION

3.1. Characterization of Schiff base and Schiff base coated silver nano particle

Table (a):- Physical properties of [HBAA] and [HBAA@Agnps]:-

Compounds	Colour	M.P. °C	M.W.	Yield (%)
[HBAA]	Yellow	202	337.39	73.77
[HBAA@Ag nps]	Dull green	190	445.39	71

3.2. Spectral studies:-

FTIR spectral data of the ligand [HBAA] and [HBAA@Ag nps] shown in figure (1) and figure (2).

In FTIR spectra the peaks at 1744, 1589, and 3055cm-1 were due to the C=O, C=N, and Ar-OH bonds respectively .the present of C=N group confirmed that a Schiff base was formed. In FTIR spectra of Schiff base coated silver nano complex a peak at 555 cm-1 due to the presence of Ag nps and the other peaks same as a Schiff base mentioned in above which confirms the formation of Schiff base coated silver nano complex.

The ^{1}HNMR spectra of ligand [HBAA] in $CDCL_3$ shown in figure (3).In the spectrum the signal at 9.65, 7.40-7.46, 3.10 and 2.46 were due to (N=CH), (Ar-H), ($N-CH_3$) and ($-CH_3$) which confirms the formation of Schiff base.

In the UV-VIS spectra of ligand [HBAA] peaks at 240 and 330 were due to C=C and C=N confirms the formation of Schiff base.

The UV-VIS spectra of silver nano particles and Schiff base coated silver nano complex shown in figure (4).The absorbance at 400 nm indicated the formation of silver nanoparticles in starch matrix. The absorbance value was in agreement to literature reports [37]. In UV-VIS spectra of Schiff base coated silver nano complex the absorbance shifted at 400 to 450 nm which confirmed the formation of Schiff base coated silver nano complex.The SEM images of Ag nps and [HBAA@Agnps] in (figure 5) shows that Ag nano particle synthesized in this study with an average diameter of around 40 nm.

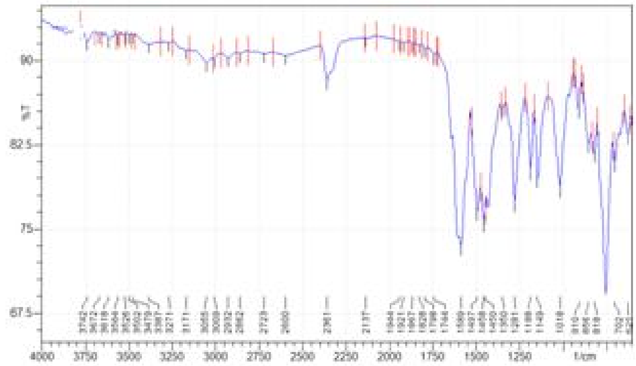


Figure (1):- FTIR spectra of Schiff base

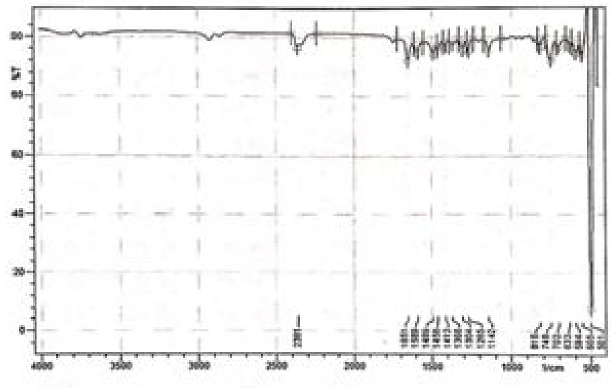


Figure (2) :- FTIR spectra of schiff base coated silver nano particle

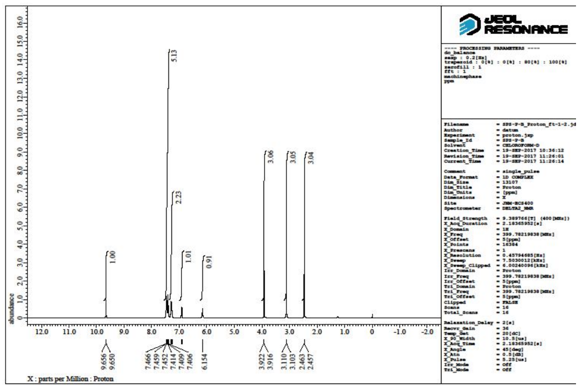


Figure (3):- ^{1}HNMR spectra of Schiff base

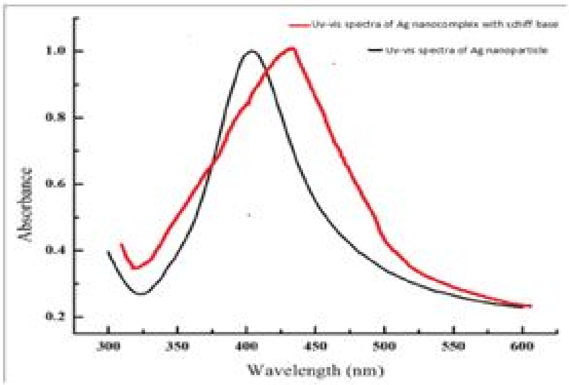


Figure (4):- UV-VIS spectra Silver nps andSchiff base Coated with silver nano complex

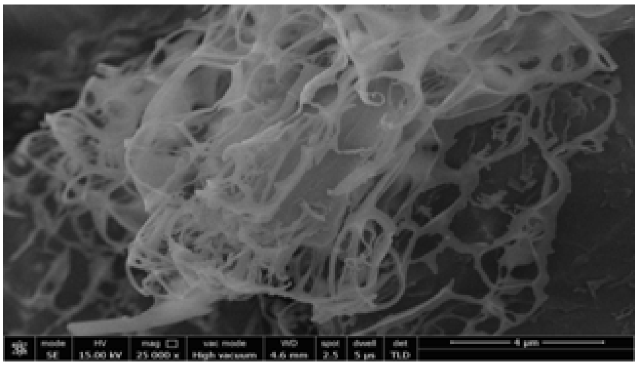


Figure (6):- SEM Images ofSchiff Base coated silver nps

3.3.Adsorption Studies:

1.Effect of pH: - The effect of P^H of metal ion test solution is an important parameter for adsorption of metal ions because it affects the solubilityof metal ions, concentration of counter ions, on the functional groups of the adsorbent and the dgree of ionization of the adsorbent [38]. The effect of p^H on metal ion % removal , the p^H was varied from 2.0 to 8.0 Zn (II) ion.the % removal was calculated and results were shown in figure (7) which indicates that the maximum % removal (94.2 %) take place at p^H 2.0 .

2. Effect of contact time: -The % removal of Zn (II) ions onto Schiff base coated silver nps on solid phase was examined as it represented the time of adsorption becomes constant and equi- librium was reached. As shown in Figure (8), for the first 10 min, the uptake rate was high and it decreased gradu- ally until it reached equilibrium at 60 min with an ad- sorption percentage of 93%.

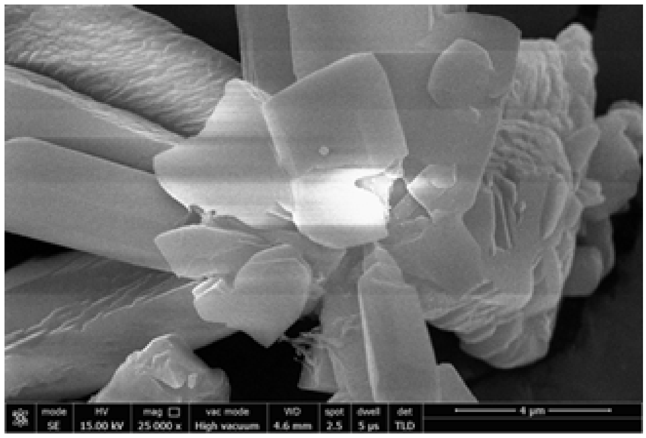


Figure (5):- SEM Image of Silver nano particles

3. Effect of Initial ion concentration:-

The % removal of Zn (II) ion onto Schiff base coated silver nps on solid phase was shown in figure (9) which indicates that % removal of Zn (II) ion was gradually increased when when increased initial ion concentration of metal with an adsorption percentage 91.62 %.

4. Effect of adsorbent weight:-

Schiff base coated silver nps on Zn (II) ion was examined at different weight (.001- .005 gm.)were shown in figure (10) which indicates that maximum % removal (92.5 %) of metal ion was obtained at .002 gm. Schiff base coated silver nps and then decreased when increased weight of Schiff base. The reduction in uptake is probably due to the excess of sorbent quantity inhibiting the approach of adsorbed ions to the active sites of the sorbent. Generally with increasing resin weight, there is a little decrease in metal ion removal which can be attributed to the presence of sorption sites of different affinities [39].

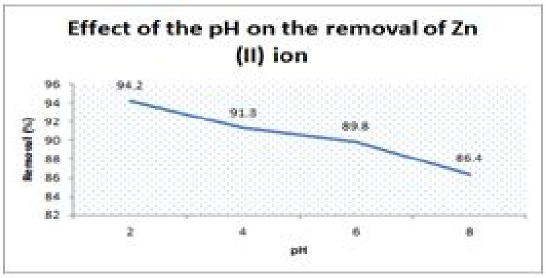


Figure (7):- Effect of p^H on the removal of Zn (II) ion

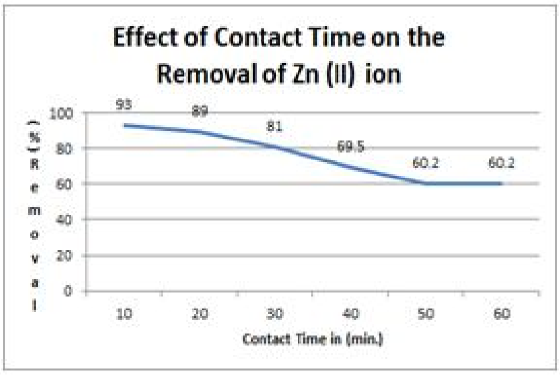


Figure (8):- Effect of Contact time on the removal of Zn (II) ion

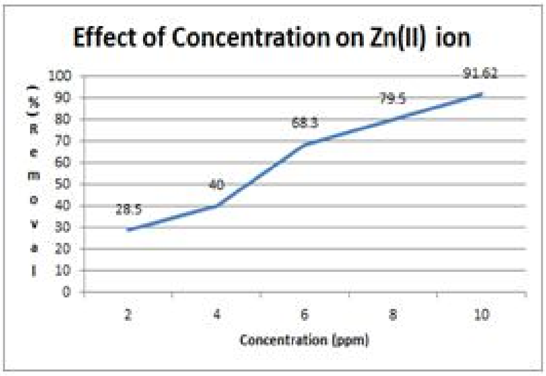


Figure (9):- Effect of Concentration on the removal of Zn (II) ion.

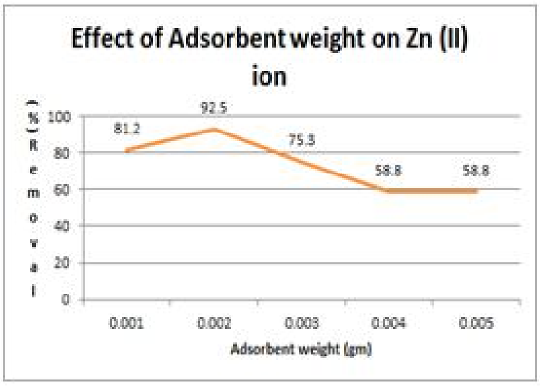


Figure (10):- Effect of Adsorbent weight on the removal of Zn (II) ion.

IV. CONCLUSION

In conclusion, a Schiff base [HBAA] and Schiff base coated silver nano particles were synthesized and characterized by (FTIR, 1HNMR, UV-VIS and SEM images.) and using in the removal of Zn (II) ion from industrial waste water. The results include studying the various factors such as pH, contact time, initial ion concentration and adsorbent for the removal of Zn (II) ion. We find that the maximum % removal of Zn (II) ion on various factor such as pH is 94.2 %, contact time is 93%, initial ion concentration is 91.62 and adsorbent weight is 92.5% obtained.

V. ACKNOWLEDGEMENT

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