ORIGINAL RESEARCH PAPER

Chemical Science

SYNTHESIS, CHARACTERIZATION AND ENVIRONMENTAL APPLICATIONS OF ZINC COMPLEXES USING AMINO ACID AS A LIGAND

KEY WORDS: Schiff base, metal complexes, FT-IR spectroscopy, elemental analysis, nanoparticles, SEM, TGA.

Dr. Preeti R. Dwivedi* Vikas College of Arts, Science and Commerce, Kannamwar nagar, Vikhroli East, Mumbai-83. *Corresponding Author

Sachin D. Yadav Vikas College of Arts, Science and Commerce, Kannamwar nagar, Vikhroli East, Mumbai-83

ABSTRACT

Amino acid derivative Schiff base was synthesized by reaction of glycine with salicyldehyde in basic medium. The synthesis of the same was confirmed by TLC technique. The synthesized Schiff base was used as a ligand to form Zn (II) metals in order to form the stable complexes. The synthesized ligand and their metals complex were characterized by FTIR, Elemental analysis, TGA, SEM and magnetic susceptibility. The Zinc nanoparticles were prepared by precipitation method by using the same synthesized complex. The synthesized ZnO-NPs were found to be spherical in shape with an average size of 23 to 57 nm. These ZnO-NPs were evaluated for antibacterial and antifungal activity. Photocatalytic degradation of Rhodamine B dye was also carried out by using the same synthesized Zinc complex.

INTRODUCTION:

The amino acids, essential components of peptides and proteins, are known to be the building blocks for all living things on earth. As glycine only has a hydrogen atom as its substituent therefore, it has the ability to fit into tight spaces of molecules where no other amino acid could possibly fit.

Schiff base ligands constitute an important class of organic building blocks for coordination and supramolecular chemistry[1] as they use for designing functional supramolecular complexes, medicinal molecules and catalysts. Schiff base ligands containing multiple coordinating sites, because of their ability in creating polynuclear metal complexes upon coordination, using in the observation of new magnetic materials and as catalysts to carry out important organic reactions[2-6].

Zinc, the second most abundant trace element in human bodies, associated with protein synthesis, cell division and proliferation, and many other metabolic processes[7], antioxidant activities and immune competence through a series of indirect mechanisms. Some of these mechanisms can cause the reduction in reactive oxygen species (ROS)[8] production, harmful to organisms at high concentrations and causes a variety of diseases.

The introduction of nanotechnology[9] resulted in development of Nano particles that can be used for wide range of applications, because of their unique character differing from those in the bulk state. Zinc oxide because of its unique physical and chemical properties viz., high chemical and mechanical stability, broad range of radiation absorption, high catalysis activity and non- toxic nature, are widely used in the synthesis of nanoparticles.

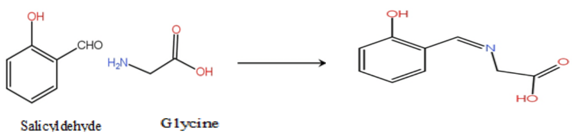
In the present paper, we report the synthesis, characterization and environmental applications of Zinc complexes and their nano particles, using amino acid as a ligand.

EXPERIMENTAL

Materials: All chemicals and reagents used were of the analytical grade (AR). Solvent like ethanol and methanol wherever used were distilled and purified according to standard procedures. Silica gel was purchased from Sigma Aldrich. Double distilled water was used throughout the experiment.

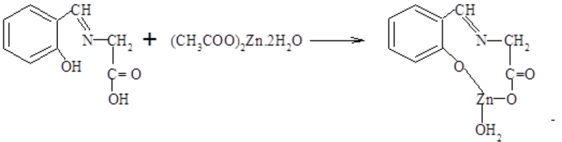
Methods:

Synthesis of Ligand: The ligand was synthesized by reacting equimolar quantities of glycine and salicyldehyde. By dissolving glycine (0.5g) in ethanol and salicyldehyde (1.0 g). 50% Sodium hydroxide solution was added drop wise to the above solution to make the reaction medium basic. This reaction mixture was refluxed for 7 hours at 50°C with continuous stirring. The success of the reaction was monitored by thin layer chromatographic (TLC) tests. The material was cooled and solvent was removed by rotary evaporator. The synthesized ligand was filtered, washed with ethanol and dried in desiccator.



Synthesis of complex:

The synthesized ligand was mixed with zinc acetates in 1:2 molar ratio in order to form the series of metal complexes. The zinc acetate were dissolved in toluene separately and ligand was dissolved in ethanol. Both the solutions were mixed in a 250 ml reaction flask. This mixture was than refluxed at 50-60°C for 6-7 hours with continuous stirring. The solid mass separated filtered through whatman filter paper no. 1 and washed several times with hot ethanol until the washing were free from the excess of ligand. These complexes were finally dried under vacuum desiccator over fused $CaCl_2$.The progress of the reaction was monitored by using TLC tests. The yield of the dark brown coloured product was 72.67 %.



Characterization of Synthesized Zinc metal Complexes:
The synthesized metal complex was characterized by following methods:

Elemental Analysis:

Table 1: Elemental analysis of Zinc complex

Elements	C	H	O	N	Zn	Empirical unit	%Yield complex	M.P.
Theoretical%	51.50	3.34	22.89	6.68	15.59	$C_{18}H_{13}O_6N_2Zn$	72.67%	290°C
Practical%	50.35	3.14	21.75	5.88	15.20			

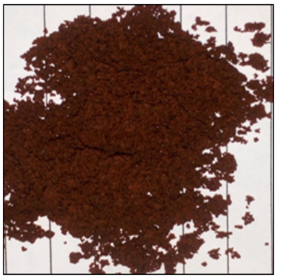


Fig.1: Zinc complex in powder form

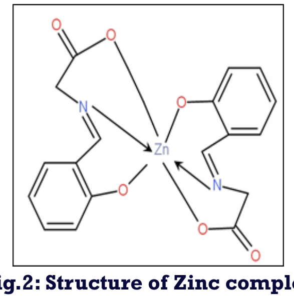


Fig.2: Structure of Zinc complex

FTIR SPECTRUM:

The IR spectra of the complex was recorded on a Perkin-Elmer instrument in KBr pallets in the range of 4000-400cm^{-1}. The analysis of the three functional groups (-NH, -OH and –C=O) were carried out as they act as donors in the dative bond for the formation of the complex. A broad signal at 3459 cm^{-1} indicates the presence of the –OH group in the formation of the coordination complex and suggest the presence of water in its structure (Figure 3). The medium intensity band at 1410-1579cm^{-1} is due to the aromatic (C=C) vibrations. The band around 1302 cm^{-1} to 1345 cm^{-1} indicating coordination through oxygen of (C-O) group. Two absorption bands at 755cm^{-1} and 848 cm^{-1} in the spectrum of the Zn(II) complex were observed which can be due to the stretching vibrations of zinc-oxygen bonds, namely C=O Zn and HO Zn. The (M-O) band was observed in the complexes around 651cm^{-1}.

Thermogravimetric Analysis (TGA): TGA analysis of metal complex was carried out in nitrogen atmosphere in the range of 10-350°C on Rigaku Thermo Plus-8120 TG-DTA instrument with a heating rate of 10°C min^{-1}. Thermogravimetric (TG) weight loss curves for the complex shows (Figure 4) two well-defined steps at 160°C (4.28%, Loss of water molecule) and 290°C (65.95%) together with another steps at 350°C (6.58%), totalling 72.53% weight loss.

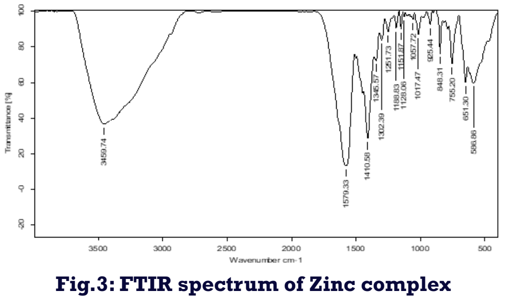


Fig.3: FTIR spectrum of Zinc complex

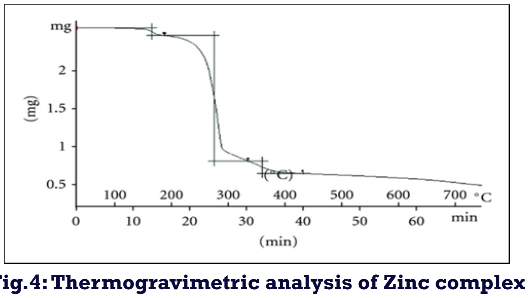


Fig.4: Thermogravimetric analysis of Zinc complex

Applications of Synthesized Zinc complex: Antimicrobial Activities

In vitro antimicrobial screening was performed by the agar cup method [10, 11]. Nutrient agar growth media was prepared according to the procedures in the laboratory only. The metal complexes shows significant effects on biological activities.

Antibacterial Screening: The Zinc metal complex was tested against gram-positive (Staphylococcus aureus), gram-negative (Escherichia coli) and Bacillus subtills pathogenic bacteria at a concentration of 100 μg disc $^{-1}$. In this method, bacterial culture suspensions are inoculated on the surface of assay agar medium (base layer). The holes were used as a reservoir for compound or antibiotics. The sample containing zinc complex solution in DMSO, to be tested present in the reservoir come into contact with inoculated medium and after overnight incubation at 37°C, the plates were observed for the zone of inhibition surrounding the reservoir. The zone of inhibition is the clear area around the reservoir, showing the inhibition of the microorganism by the diffused substances through the agar (Figure 5). The diameter of the clear zone around the reservoir (zone of inhibition) was measured. However, if the sample to be tested is ineffective, then no zone of inhibition will develop (Figure 6).

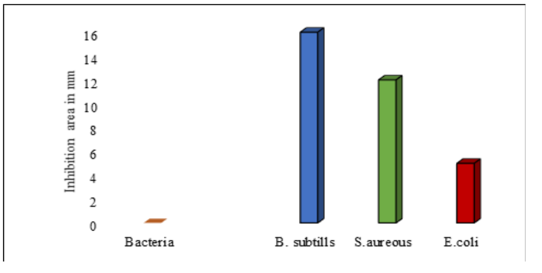


Fig.5: Antibacterial Screening

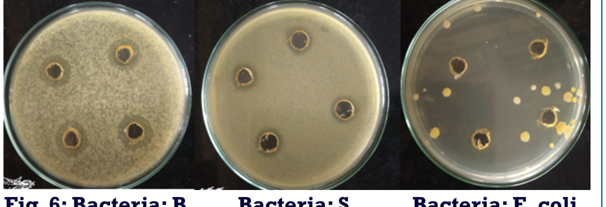


Fig. 6: Bacteria: B. subtills **Bacteria: S. aureous** **Bacteria: E. coli**

Antifungal Screening: The antifungal activity of the Zinc metal complexes was screened using Tube Dilution Method against pathogenic fungi Candida albicans and Aspergillus niger. The fungus was inoculated into sterilized Sabouraud broth to prepare fungus inoculums (Figure 7).

The 0.1 mL of 300 ppm Zinc metal complexes solution in DMSO was mixed with 5 mL of Sabouraud broth test tube, autoclaved it for 15 minutes, then kept on a rotary shaker and incubated at room temperature for 24 hours. The optical density (OD) of the solution was recorded using spectrophotometer at 530 nm with inoculated Sabouraud broth as a blank and on the basis of optical density the percentage growth of the fungus was calculated. The results are given in Figure 8 and 9.

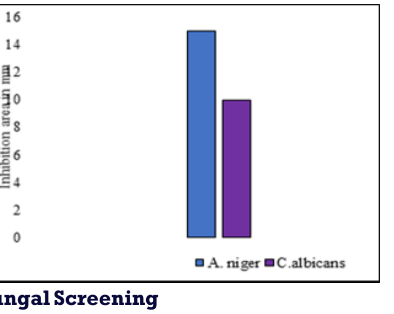


Fig.7: Antifungal Screening

Fig.8:Fungi: A. niger

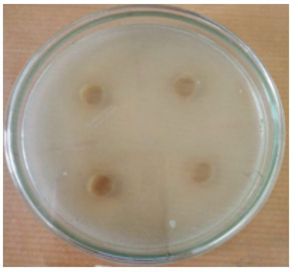


Fig.9: Fungi: C. lbicans

Synthesis of ZnO nanoparticles: The zinc oxide nanoparticles were synthesized by precipitation method according to the literature[12]. The surfactant Solution (5%PEG) was poured into a three-neck round bottom flask. A mixture of zinc acetate and ammonium carbonate were added drop wise into the flask by using dropping funnel with continuous stirring. After the completion of reaction, the suspension solution was kept under stirring for 2 hours at room temperature. The obtained precipitate was filtered and washed with ammonia solution and then with absolute ethanol several times, dried under vacuum for 12 hours, and then calcinated in an oven at 450°C for 3 hours. Then zinc oxide nanoparticles were obtained.

Characterization of Zinc nanoparticles: The synthesized Zinc nanoparticles was characterized by FTIR Spectroscopy and SEM techniques. The FTIR spectra of Zinc oxide nanoparticles were recorded on Perkin-Elmer spectrum on FT-IR spectrometer. The scans were recorded with the solid state as KBr pallets and over the wave number range of 4000–400 cm^{-1} at a scanning rate of 4 cm /min. The bands at around 533cm^{-1} and 721cm^{-1}, which can be assigned to the vibrations of Zn-O bonds. The broad absorption peak at around 3398cm^{-1} is caused by the adsorbed water molecules since the nano crystalline materials exhibit a high surface to volume ratio and thus absorbs moisture. This analysis confirmed the presence of metal-oxygen bonding in these nanoparticles (Figure 10).

Scanning Electron Microscopy (SEM): Scanning electron microscope is used to study the surface morphology of the Zinc oxide nanoparticles. These images demonstrated that zinc oxide

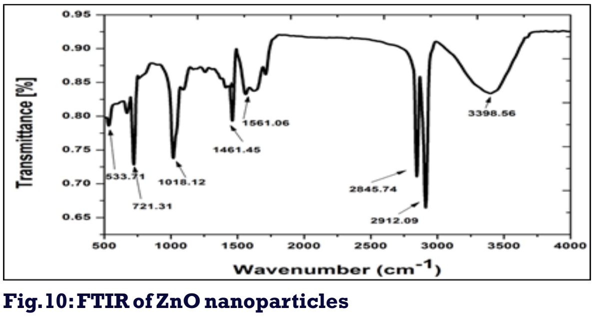


Fig.10: FTIR of ZnO nanoparticles

nanoparticles are spherical in shape. The SEM images of ZnO nanoparticles are shown in figure. 10 and 11. The ZnO nanoparticles sample was then analysed for their size determination on JEOL-JSM-6360 Scanning Electron Microscope (SEM) in the SAIF, IIT, Bombay.

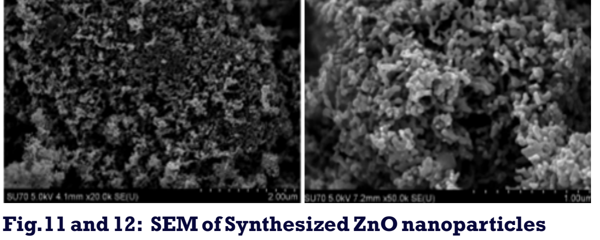


Fig.11 and 12: SEM of Synthesized ZnO nanoparticles

Application of Synthesized ZnO nanoparticles in the degradation of Rhodamine B Dye:

Rhodamine B stock solution was prepared by dissolving 0.0048g of dye in 100 mL of double distilled water (1.0X 10^{-5} M). Now 1.0 mL from the same prepared Rhodamine B solution was taken in a beaker and 24.0 mL of double distilled water was added. Now 0.1 g of ZnO (0.01 M) nanoparticle was added in the same beaker. The mixture thus obtained was stirred for two hours at acidic pH using digital pH meter Equip Tronics (EQ-614 A). Now the reaction mixture was exposed to light by using 150 W tungsten lamp (Philips) for irradiation at regular time intervals (i.e. 0 min to 150 min). The λ_{max} was found to be 560 nm. The results for typical run are given in Figure 13.

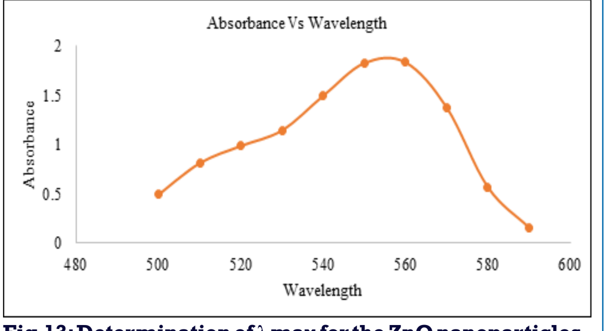


Fig. 13: Determination of λ max for the ZnO nanoparticles

Effect of Time: The time required for the degradation of the Rhodamine B was studied from 0 to 150 minutes. It was found that, the time required for optimum percentage of degradation %D of the dye was two and half hours. As the time increases, the absorbance of solution decreases with the increase in % degradation, which indicates that dye is photocatalytically degraded on irradiation. The observations obtained are tabulated in the Table 2.

Table 2.0: Effect of Time on Rhodamine B Degradation with ZnO Nanoparticles

Time(min)	Absorbance(A_0)	%X	%D
00	1.982	100.00	0.00
10	1.901	95.91	4.08
20	1.862	94.04	6.05
30	1.703	85.92	14.08
40	1.618	81.63	15.19
50	1.476	74.47	25.52
60	1.282	64.68	35.31
70	1.008	50.85	49.14
80	0.962	48.53	51.46
90	0.801	40.41	59.59
100	0.699	36.40	64.73
110	0.585	29.51	70.38
120	0.404	20.38	79.62
130	0.299	15.08	84.92
140	0.121	6.10	93.89
150	0.121	6.10	93.89

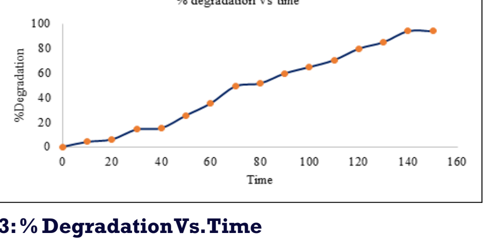


Fig. 13: % Degradation Vs. Time

CONCLUSIONS:

The studies viz., FTIR, Elemental analysis and TGA confirms the successful synthesis of Zinc complex by using a Schiff base. The antimicrobial activity of the synthesized Zinc complex shows that the complex is useful as an antibacterial and antifungal agent. The synthesis of Zinc oxide nanoparticles is confirmed by FTIR and SEM techniques. The ZnO nanoparticles are successfully used as Rhodamine B dye degradating agent.

REFERENCES:

1. J.L. Atwood, G. W. Gokel, L.J. Barbour, ed. Comprehensive Supramolecular Chemistry II, 2017, Elsevier.
2. P.G. Cozzi, Chem. Soc. Rev. 33 (2004) 410.
3. K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420.
4. E.C. Constable, G. Zhang, C.E. Housecroft, M. Neuburger, S. Schaffner, W.-D. Woggon, J.A. Zampese, New J. Chem. 33 (2009) 2166.
5. G. Zhang, C. Ta, S.-Y. Cheng, J.A. Golen, A.L. Rheingold, Inorg. Chem. Commun. 48 (2014) 127.
6. H. Xiong, L. Li, E. Liu, J. Cheng, G. Zhang, Inorg. Chem. Commun. 84 (2017) 24.
7. J. Dong, H. Li, W. Min, PII: S0141-8130(17)34013-8 DOI: doi:10.1016/j.ijbiomac.2018.01.223 Reference: BIOMAC 9133 To appear in: Received date: 16 October 2017 Revised date: 1 January 2018 Accepted date: 26 January 2018.
8. N. Xu, Z. Ren, J. Zhang, X. Song, Z. Gao, H. Jing, S. Li, S. Wang, L. Jia, International Journal of Biological Macromolecules. 95 (2017) 204-214.
9. B. Divya, C. Karthikeyan and M. Rajasimman , Department of Chemical Engineering, Faculty of Engineering and Technology, Annamalai University, P. O. Box 608002, Cuddalore, India.
10. A.W. Bauer, W. M. Kirby, J. C. Sherris, and M. Turck, American Journal of Clinical Pathology, vol. 45, no. 4, pp. 493–496, 1966.
11. C. Sheikh, M. S. Hossain, M. S. Easmin, M. S. Islam, and M. Rashid, Biological & Pharmaceutical Bulletin, vol. 27, no. 5, pp. 710–713, 2004.
12. R. F. Mulligan, A. A. Iliadis and P. Kofinas, Journal of Applied Polymer Science, 1, 1058 (2003).

Highlights

1. This paper includes the syntheses of zinc containing metal complexes using Schiff base.
2. The Schiff base was prepared by using salicyldehyde and glycine.
3. The synthesized complex was than characterized by elemental analysis, IR spectra and TGA.
4. Applications of the synthesized zinc metal complex have been carried out as an antibacterial and antifungal agents.
5. Then ZnO nanoparticles were synthesized using Zinc metal complex by precipitation method.
6. The synthesized ZnO nanoparticles were characterized by FTIR and SEM techniques.
7. Then these nanoparticles were used for the degradation of Rhodamine B dye in acidic medium.