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Research Article

CHITOSAN-SCHIFF BASE METAL COMPLEXES: SYNTHESIS AND APPLICATION STUDIES

Jaya T Varkey[1]*, Ashitha Mary N J[1], Mercian Gloria Vivera[1], Sandra Maria C X[2] and Anitta Antony[1]

[1]Department of Chemistry, St Teresa's College (Autonomous), Ernakulam-682011, Kochi, Kerala
[2]Department of Chemistry, St Paul's College, Kalamassery, Ernakulam-683503, Kerala

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ABSTRACT

An efficient procedure for the synthesis of chitosan based schiff base and their metal complexes were carried out. Chitosan has both reactive amino and hydroxyl groups. The presence of amino group leads to the synthesis of schiff base (-RC=N) by reaction with aldehydes and ketones. The insertion of functional groups in the chitosan matrix can improve its interaction with metal ions. This work involved the condensation reaction of salicylaldehyde with chitosan and the schiff base formed were complexed with transition metals like Mn, Zn, Ni, and Ag. The synthesized schiff base and their metal complexes were characterized by FTIR and SEM EDX. The metal complexes of chitosan based schiff base were found to act as a heterogeneous catalyst in Knoevenagel reaction. The antibacterial activity of schiff base and its metal complexes against E.coli were compared and the metal complexes were found to have greater antibacterial activity than the schiff base.

INTRODUCTION

Chitin is a natural polysaccharide obtained from shells of crustaceans such as crab, shrimp[1]. Chitosan is a partially deacetylated form of chitin. As a natural renewable resource, chitosan possesses unique properties such as biocompatibility, biodegradability, non-toxicity, and has important applications in the biomedical, agriculture, environmental protection, biotechnology and cosmetics domains[2-4] chitosan has both reactive amino and hydroxyl groups[5]. The presence of amino group in chitosan lead to the preparation of schiff base (-RC=N) by reaction with aldehydes or ketones. The insertion of functional group in the chitosan matrix may improve its capacity of interaction with metal ions by complexation. In this sense the modification of chitosan with aldehydes to produce schiff base may result in a potential analytical and environmental applications. Schiff base are compounds containing azomethine group (-HC=N-). They are condensation products of aldehydes or ketones with primary amines and were first reported by Hugo Schiff in 1864[6]. Chitosan schiff base derivatives are considered one of thebest choices for increasing antibacterial activity of chitosan, since carbonyl groups of aldehyde or ketone can efficiently couple with NH_2 groups of chitosan to form the corresponding chitosan schiff base with imine characteristic group(-RC=N-)[7]. This leads directly to altering chitosan molecular structure, enhancement its hydrophilicity as well as increasing the positively charged ions, which results in better antibacterial activity compared to the unmodified chitosan[8]. By making the use of the chelating ability of chitosan with metal ion, researchers have studied a new catalyst with more catalytic activity and reusable features[9].

The Knoevenagel reactionis a nucleophilic addition for an active hydrogen compound to a carbonyl group followed by a dehydration reaction in which a molecule of water is eliminated. It is a key step in the commercial production of the antimalarial drug. It is employed in the synthesis of therapeutic drugs, natural products, herbicides, insecticides, fine chemicals.

In this study, we report the synthesis of chitosan based schiff base compound and their corresponding metal complexes which were characterized by various methods such as FTIR spectroscopy and SEM-EDAX and also their catalytic in Knoevenagel reaction and antibacterial activity against E.coli.

MATERIALS AND METHODS

Materials*:*Chitosan, salicylaldehyde, ethanol, aqueous acetic acid, metal chloride (Mn, Ni, Zn), silver nitrate, NaOH pellets, Malononitrile, methanol.

METHODS

Synthesis of Schiff bases*:* 1g chitosan was dissolved in 200ml of an aqueous acetic acid solution (1%) at ambient temperature. Then predetermined amount of salicylaldehyde dissolved in ethanol was added to the chitosan solution. The schiff base formed was filtered, washed with ethanol and

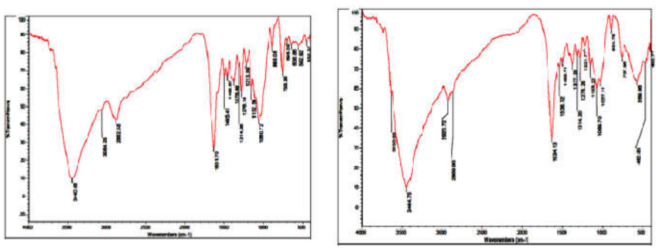
Corresponding author:* **Jaya T Varkey
Department of Chemistry, St Teresa's College (Autonomous), Ernakulam-682011, Kochi, Kerala

dried. Synthesis of Schiff base metal complex: 0.161g of chitosan was dissolved in 1% acetic acid solution.1.2g of salicylaldehyde was dissolved in ethanol and was added to the solution of chitosan. Then corresponding metal salt (Mn, Zn, Ni, Ag) dissolved in ethanol was added to chitosan in separate beakers. Then each reaction mixture was stirred for 6hrs at room temperature, boiled in water bath and finally left over night and then filtered and washed with ethanol.

Knoevenagel reaction using Schiff base metal complex: 5 millimoles of Salicylaldehyde and 5millimoles of Malononitrile are mixed together along with 5ml methanol and the corresponding amount of schiff base metal complex is added. It was kept in magnetic stirrer and the time for product formation is noted. The product is dissolved in methanol and filtered, the heterogeneous catalyst is recovered and the methanol is evaporated and yield is noted.

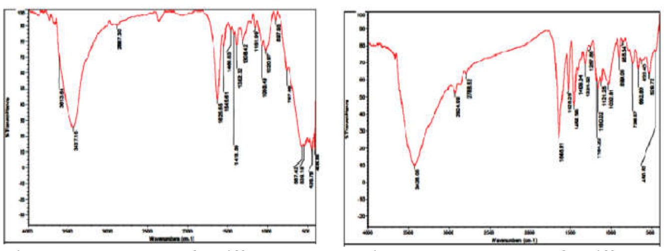
Antibacterial assay using microtiter plate method*:* Microtiter plates were prepared under aspecticth65wells, 100 µl of nutrient broth was added to each well, and finally 100µl of microbial suspension was added to each well (test). Control dilutions of test material were also kept (extract control). A column with all solutions except the test compound was prepared as organism controls (nutrient broth and microbial suspension). Plate was wrapped loosely with cling film to ensure that organism did not become dehydrated. The plates were incubated at 37◦ C for 24 hours and OD reading was taken (OD_{600}) after sufficient incubation. Optical density of final test was obtained from subtracting the extract control OD from the test OD. The % of inhibition was calculated from the following equation: % inhibition = (control-final test)/control x 100

RESULTS AND DISCUSSION



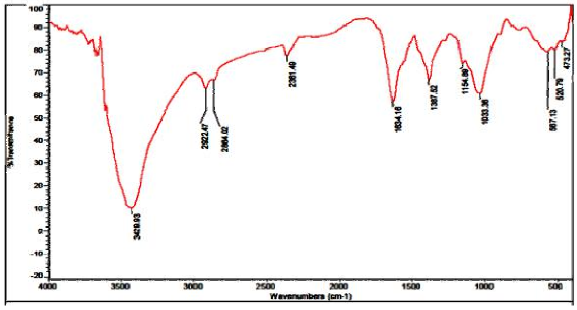
Schiff base

Manganese metal complex of schiff base



Zinc metal complexes of schiff base

Nickel metal complexes of schiff base



Silver metal complexes of schiff base

Fig 1 IR Spectral studies of Schiff base and its metal complexes

Table 1 comparison of IR spectra of schiff base and its metal complexes

Compound	υ(C=N) cm^{-1}	υ (O-H) cm^{-1}	υ(M-O) cm^{-1}	υ(M-N) cm^{-1}
Chitosan-salicylaldehyde Schiff base	1631.70	3440.08		
Mn-Schiff base complex	1634.13	3444.75	569.96	462.83
Zn-schiff base complex	1625.65	3437.15	567.42	436.78
Ni-schiff base complex	1646.91	3426.05	529.72	450.52
Ag-schiff base complex	1634.16	3429.93	567.13	473.27

The IR spectral data of ligand showed a band at a region of 1580-1680 cm^{-1} which is assigned to C=N stretching frequency, a feature of schiff base. This band was also observable in complexes, suggesting the ligand is coordinated to the metal.In the case of complexes, the band in the region 540-620 cm^{-1} and 440-495cm^{-1} are attributed to υ (M-O) and υ (M-N) stretching vibrations respectively, conforming coordination of schiff base to metal ions.

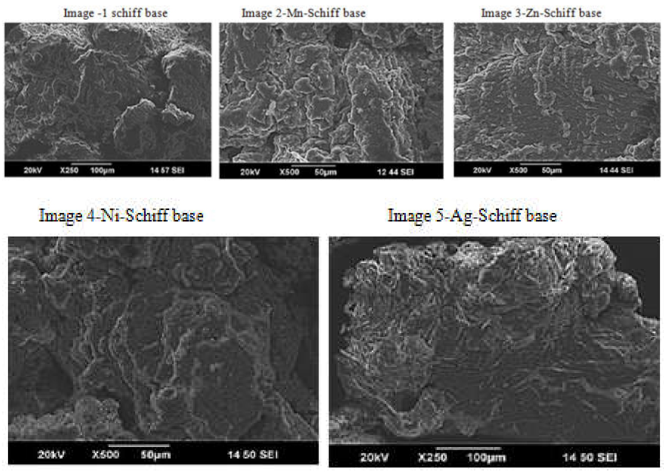
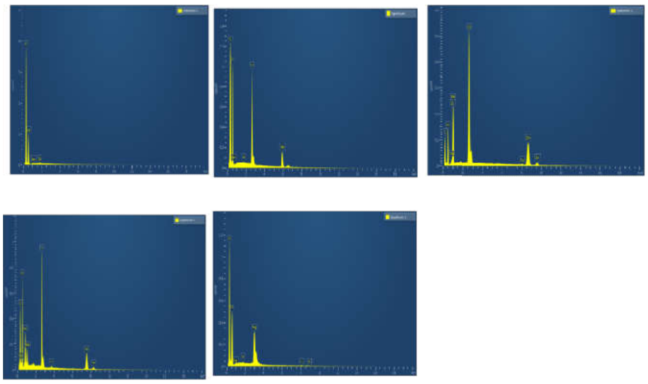


Fig 2 SEM of Schiff base and its metal complexes

SEM of metal complexes showed roughened compared to the parent ligand which is due to the contraction of the voids by the cooperative contribution of ligand for complexation with metal ions. This gave a further evidence for complexation.

Graph 1-SCHIFF base Graph-2 Mn-Schiff base Graph 3- Zn-Schiff base



Graph 4 Ni-Schiff base Graph 5- Ag-Schiff base

Fig 3 SEM-EDAX of Schiff base and its metal complexes

Table 2 SEM-EDAX of Schiff base and its metal complexes

	Element	Line type	Wt.%	Atomic %
Mn-Schiff base complex	Mn	K series	4.61	1.21
Zn-Schiff base complex	Zn	K series	24.81	7.16
Ni-Schiff base complex	Ni	K series	9.1	2.46
Ag-Schiff base complex	Ag	L series	15.48	2.27

SEM-EDAX spectra have indicated that there were Mn, Zn, Ni and Ag peakswhich showed the attachment of respective metal to the schiff base ligand.

Bacteria			50 mg
E.coli	CH01Mn	Control OD	0.485
		Test OD	0.009
		% of inhibition	98.14
	CHOINi	Control OD	0.485
		Test OD	0.022
		% of inhibition	95.46
	CHOIAg	Control OD	0.485
		Test OD	0.01
		% of inhibition	97.94
	CHOIZn	Control OD	0.485
		Test OD	0.008
		% of inhibition	98.35

It was observed that metal complexes of Chitosan-Salicylaldehyde polymer showed inhibition against E.coli and all of them showed more than 95% inhibition. The bulky polymer on chelation to the metal cation reduces the polarity of the metal due to the ligand orbital overlap with the metal orbitals, resulting in delocalization of positive charge. This increases the lipophilic character of the metal chelate and favours its permeation through the lipid layer of the bacterial membranes.

Table 4 Study of catalytic activity of chitosan based Schiff base metal complexes

Metal complex of Schiff base	Reaction condition	Time	Yield %
Mnschiff base complex	Rt,	30 min	94.84
Zn schiff base complex	Rt,	9 min	69.92
Ni schiff base complex	Rt,	1 min	93.9
Ag schiff base complex	Rt,	3 min	94.72

The catalytic activity of Schiff base and its metal complex were analyzed based on Knoevenagel reaction and the Manganese based complex gave higher yield indicating more complexation.

CONCLUSION

Synthesis of Schiff base from Salicylaldehyde with Chitosan was carried out. The synthesized Schiff base ligands and their complexes were characterized by IR, SEM and SEM-EDAX. Surface morphology of the Schiff base and the metal complexes have been examined using SEM. Metal complexes showed porous region compared to the parent ligand which may arise from the contraction of the voids by the cooperative contribution of ligand for complexation with metal ions. This gave a further evidence for complexation. Based on antibacterial study of Schiff base and their complexes against E.coli, it was found that metal complexes of Schiff bases are more efficient antibacterial agents than the Schiff base. The catalytic activity of these metal complexes were tested in Knoevenagel reaction and it was found that the reaction was very fast and the product is obtained in good yield. Schiff base complexes of Manganese was found to give good yield when compared to other metal complexes indicating more complexation. Chitosan based Schiff base metal complex acts as a good catalyst with antibacterial activities.

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