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Review IJCSCR

Synthesis, Characterization and Catalytic Study of Chitosan-Schiff Base Manganese Complex

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Abstract

Schiff base is the condensation product formed when a primary amine reacts with a carbonyl compound. The term Schiff base is normally applied to those compounds when they are being used as ligands to form coordination complexes with metal ions. Its formation takes place under acid or base catalysis or with heat. Vanillin Schiff base and Aspartic acid-Salicylaldehyde Schiff bases have been synthesised by condensation reaction. The synthesized ligands were mixed together to improve the ligand efficiency. The mixed ligand was successfully complexed with metal ion manganese to study its catalytic activity. The structure and properties of the complex have been characterized by spectral and thermal techniques. The catalytic activity and recyclability of the complex has been proved by the efficient synthesis of Benzimidazole.

Keywords: Schiff base, Chitosan, metal complex, Benzimidazole, Mixed ligand

INTRODUCTION

Schiff base is the condensation product which forms when a primary amine reacts with a carbonyl compound [1]. These are flexible compounds which have a general formula R2C=NR (Figure 1). They can be considered as a subclass of imines being either secondary ketimines or secondary aldimines depending on their structure. They are neutral molecules with an electron pair [2]. Schiff base is an important ligand due to their synthetic flexibility, selectiveness and reactivity. They are highly selective towards the central metal atom attached to it and resembles in structure with naturally occurring biological molecules [3]. Schiff bases can be employed as ligands to construct coordination complexes with metal ions. Its formation takes place under acid or base catalysis or with heat.

Applications of Schiff base

Schiff bases and their complexes are versatile compounds which exhibit a broad range of biological activities including antifungal, anti-inflammatory, anti- bacterial, anti-viral properties [4]. Schiff base complexes exhibit very good catalytic activity in many reactions and is evident from the high yield and selectivity of the products [5]. Schiff base ligands have significant applications in catalysis and which is supported by the efficient route of synthesis and thermal stability of Schiff base ligands. There have been numerous reports on their applications in homogenous and heterogenous catalysis. The thermal and moisture stabilities of various Schiff base complexes played a significant role in their applications as catalysts in reactions involving at high temperatures. Their activities are usually increased by complexation which leads to the synthesis of highly active compounds [6]. One

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of the possible ways to enhance Chitosan's biological properties is its chemical modification via reactive functional groups present in Chitosan macrochain [7].

The presence of amino groups in the polymeric chain of Chitosan leads to the possibility of many chemical changes, comprising the preparation of Schiff bases [8]. The fabrication of reactive groups in the Chitosan matrix improves its capacity for complexation with metallic ions [9]. Thus the reaction of Chitosan with aldehydes to generate Schiff bases which can form complexes with metals. These metal complexes formed have found applications in analytical and environmental filelds [10].

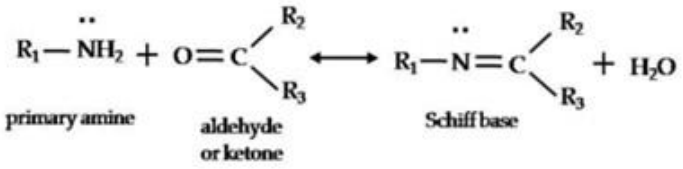

Figure 1. Formation of Schiff Base.

Structure of Chitosan

Chitosan is a linear polysaccharide (Figure 2) composed of randomly distributed β-(1→4)- linked D-glucosamine and N-acetyl-D-glucosamine [11].

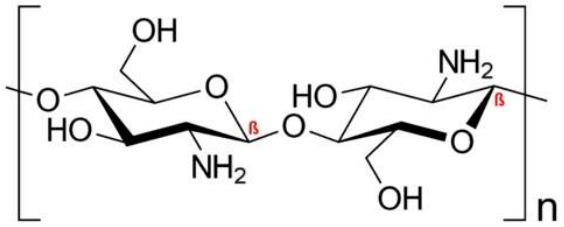

Figure 2. Structure of Chitosan.

Formation of Chitosan-Schiff base

Chitosan on condensation with salicylaldehyde is converted to Schiff Base (CSB) after eliminating water molecules. They can be easily prepared and it acts as an excellent chelating agent. In the present work chitosan -vanillin Schiff base and aspartic acid-salicylaldehyde Schiff base were prepared and this was complexed with Manganese. This mixed ligand Manganese complex was employed for the efficient synthesis of Benzimidazole.

Benzimidazole Synthesis

Benzimidazole derivatives have several medicinal, biological activities such as antivirus, anticancer, antifungal, antibacterial properties [12]. Benzimidazole derivatives are mainly used in textile industry in various applications like softening agents, dispersants and in dyeing process. It is also used in the treatment of fibers to improve whiteness of the undyed material or as an optical bleach. Benzimidazole derivetives have further applications in medical field as antimicrobial agents and employed as therapeutic agents. Also used in the treatment of cardiovascular disease, nerve disorders, endocrinology and ophthalmology. The ring structure of Benzimidazole derivatives finds applications in drug development. Several Benzimidazole derivatives have found use in the preparation of sunburn preventatives [13]. These compounds protect the skin by absorbing ultraviolet rays. 2-mercaptobenzimidazole can be used as an antioxidant for rubber. This compound is used for the detection of various metals also [14].

EXPERIMENTAL

Synthesis of chitosan-vanillin Schiff base: It is synthesized according to the following procedure. Chitosan was suspended in ethanol and it was stirred magnetically after adding vanillin (10 mmol). The

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resulting mixture was refluxed for 24 hrs. After cooling, the yellow colour solid was separated by filtration, washed with ethanol and ether and then dried at 50 C̊ under vacuum for 12 hrs.

Synthesis of aspartic acid-salicylaldehyde Schiff base: A mixture of salicylaldehyde (0.1 mol), aspartic acid (0.1mol) and ethanol was refluxed for the synthesis of Schiff base. The resultant mixture was cooled, filtered off washed with hot water and dried in vacuum.

Preparation of chitosan-Schiff base- manganese complex: The Ethanolic solution of Chitosan-Vanillin Schiff base and aspartic acid- salicylaldehyde Schiff base is mixed with manganese monohydrate sulphate and refluxed for12 hours with magnetic stirring. Then it is filtered, washed with ethanol and ether and dried. Chitosan-Schiff base -Manganese complex is thus obtained.

Benzimidazole synthesis: Benzimidazole synthesis is carried out using following procedure, 1mmol ortho phenylenediamine and 2mmol salicylaldehyde is mixed with different amount of catalyst (0.01g, 0.02g, 0.03g, 0.04g, 0.05g) using ethanol as solvent. The above mixture is kept for stirring for about half an hour. Filtered, washed with ethanol, dried and weighed. The amount of product formed is noted. Yield percentage of the product is calculated. The recrystallization of catalyst is done by dissolving the product obtained in ethyl acetate. The mixture is then filtered, washed with ethyl acetate and dried. The above procedure is repeated for different amounts of catalyst.

RESULTS AND DISCUSSION

TGA analysis of chitosan-Schiff base-manganese complex: The TGA graph of Chitosan-Schiff base-Manganese complex is represented in Figure 3. The catalyst is stable up to 300°C and this proved the efficient activity of the catalyst in higher temperature.

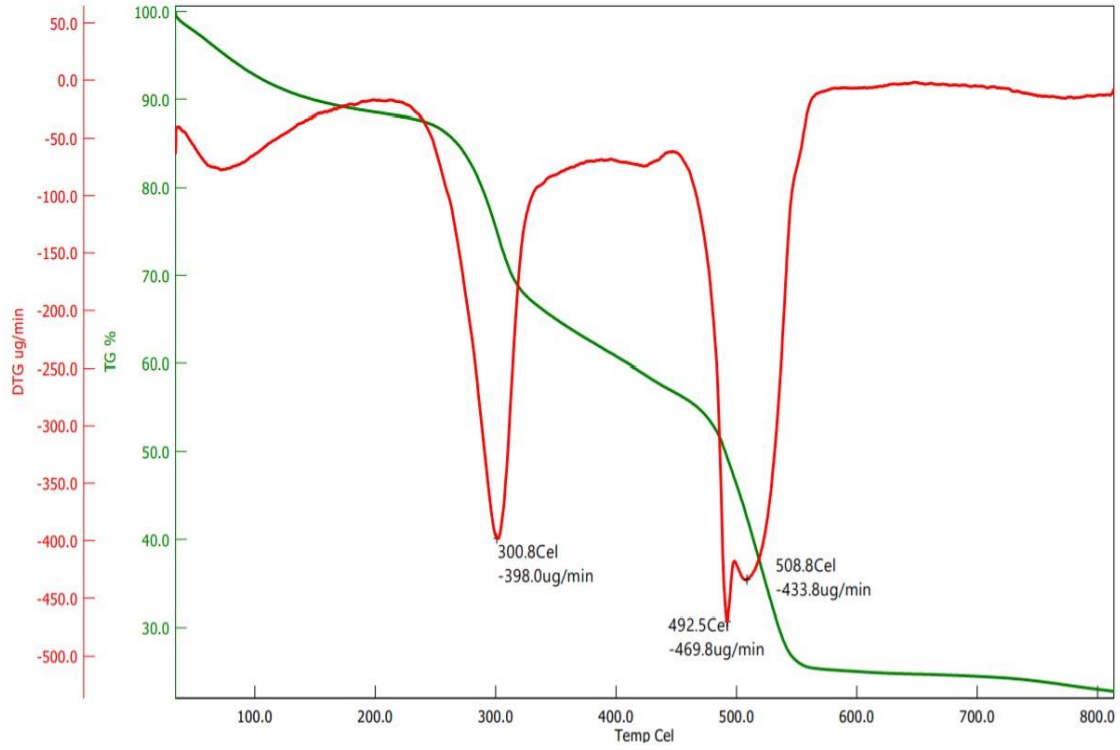

Figure 3. TGA spectrum of CSB-Manganese complex.

FTIR analysis of chitosan-Schiff base-manganese complex: The FT-IR spectrum was taken in order to illustrate the intramolecular interactions between the various components of synthesised CSB-Manganese complex shows in Figure 4 and Table 1.

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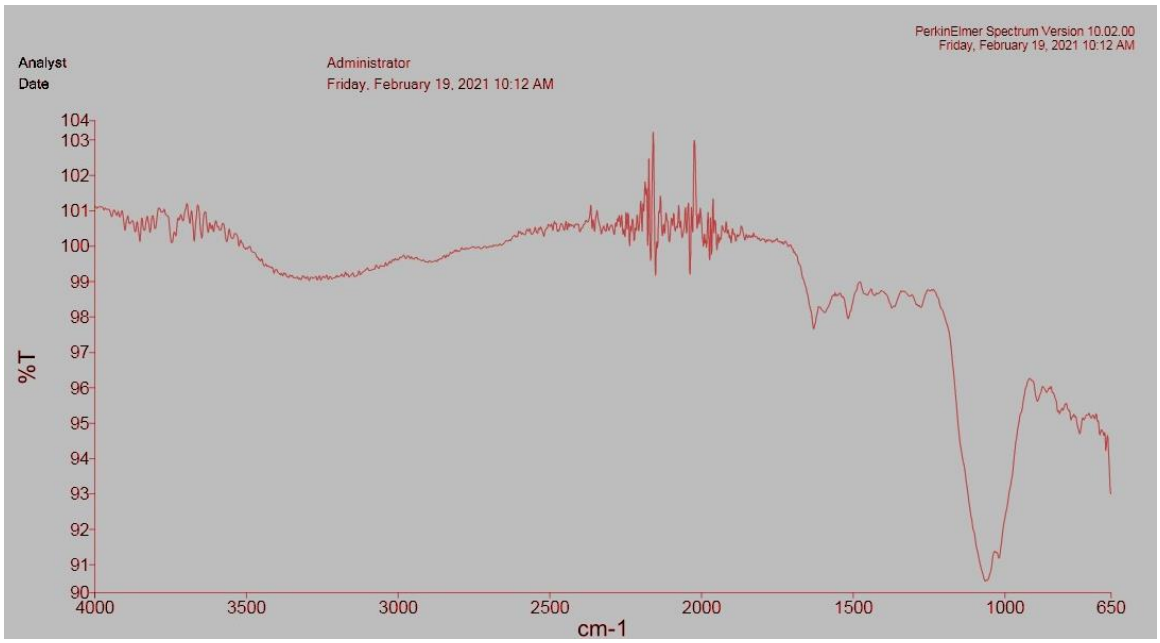

Figure 4. FT-IR spectrum of CSB-Manganese complex.

The IR spectrum showed a band at a region of 3300cm^{-1} which indicated the presence of -OH hydroxyl and -NH stretching vibration. The band at 1630 cm^{-1} concluded the presence of C=N stretching formed due to chitosan salicylaldehyde interactions. In addition, the presence of functional groups such as C-O stretching in alcohol, C-O-C linkage were confirmed from the peaks at 1154.02 cm^{-1} and 1062.02 cm^{-1} respectively. The band at 650cm^{-1} indicated the metal-oxide stretching frequency shows in Figure 5.

Scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX)

Optimization of amount of catalyst: As the amount of catalyst increases the yield percentage increases. 0.03 g of the catalyst is required to drive the reaction to completion within a short period of time shows in Table 2.

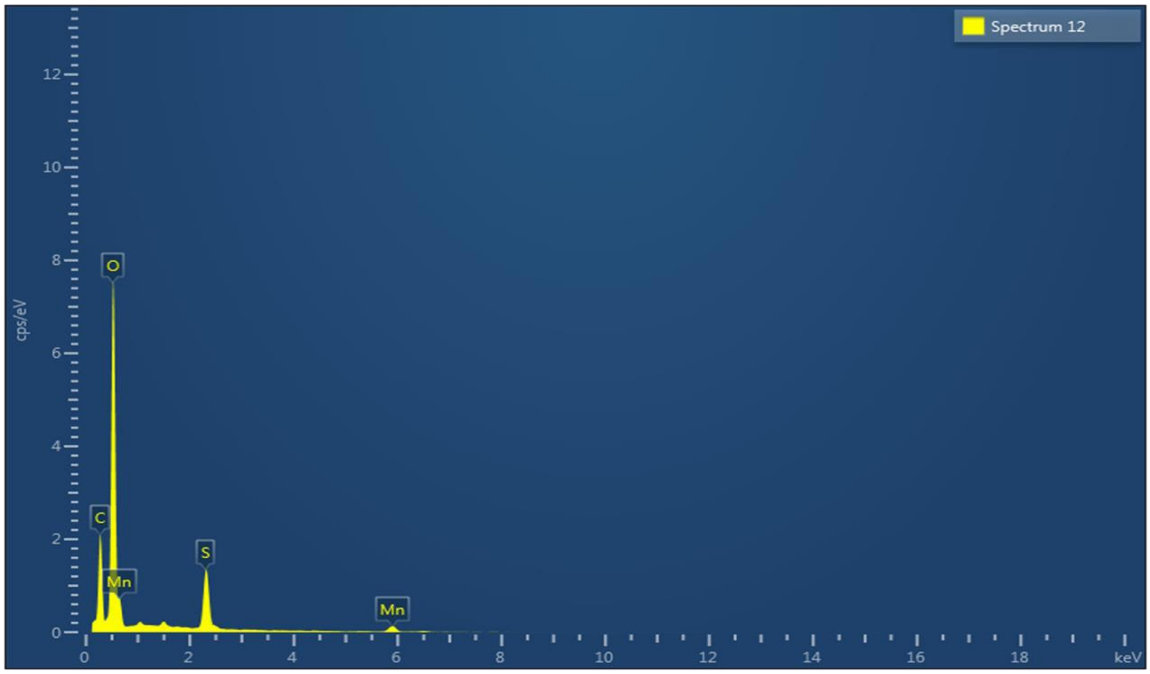

Figure 5. SEM EDX image of CSB-Manganese complex.

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Table 1. Data of SEM-EDX of CSB-Manganese complex.

Element	Line type	Wt%	Atomic %
C	K series	5.24	37.28
O	K series	11.29	60.3
S	K series	0.74	1.97
Mn	K series	0.29	0.45
Total		17.56	100

Table 2. Optimization of catalyst.

S.N.	Amount of catalyst (g)	Yield (%)
1	0.01	83.14
2	0.02	92.05
3	0.03	100
4	0.04	100
5	0.05	100

Recyclability of the catalyst: Product was dissolved in ethyl acetate and the catalyst was removed by simple filtration. The catalyst was washed with ethyl acetate, dried and can be used for further reaction cycles. It can be used for five times without appreciable loss of reactivity shows in Table 3.

Table 3. Recyclability of the catalyst.

S.N.	Number of cycles	Yield (%)
1	1	100
2	2	96
3	3	88
4	4	77
5	5	64

The above result confirms that as the number of experiment cycles increases the yield percentage decreases shows in Table 4.

Optimization of solvent

The results proved that ethanol is a better solvent than water and THF.

Table 4. Optimization of solvent.

S.N.	Solvent	Yield (%)
1	Ethanol	100
2	Water	88
3	THF	51

Optimization of aldehyde

Better yield is obtained with salicylaldehyde than benzaldehyde and anisaldehyde show in Table 5.

Table 5. Optimization of aldehydes.

S.N.	Aldehyde	Yield (%)
1	Salicylaldehyde	100
2	Benzaldehyde	78
3	Anisaldehyde	32

CONCLUSION

Synthesis of Schiff bases from Chitosan and Vanillin and using salicylaldehyde and aspartic acid were carried out. The synthesized ligands were mixed together to improve the ligand efficiency. The mixed ligand was successfully complexed with metal ion manganese to study its catalytic activity. Characterization of mixed metal ligand complexes were carried out by FTIR and TGA. Spectroscopic analysis had indicated the successful formation of chitosan supported Schiff bases and its complex. Thermal analysis proved that the catalyst is stable up to 300°C.

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In order to establish the efficacy of this mixed ligand complex in heterogeneous catalysis a pharmacologically important compound Benzimidazole was synthesised. The synthesis was carried out with different aldehydes (salicylaldehyde, benzaldehyde, anisaldehyde) and different solvents (ethanol. water, THF) using the mixed metal ligand complex. In order to optimize the catalyst, amount the synthesis was conducted using different weight percentages of the catalyst. All the methods gave a good yield of Benzimidazole. The recyclability of the catalyst was also carried out and proved its efficient recyclability. Thus, a novel mixed ligand complex prepared from Chitosan was introduced as an efficient catalyst system in organic synthesis by successfully synthesizing Benzimidazole in good yield.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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