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**Research Article**

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# Synthesis, characterization and biological activity of carboxymethyl chitosan/ p-dimethylamino benzaldehyde metal complexes

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**ABSTRACT**

*In the present study Schiff bases of Carboxymethyl Chitosan/p-dimethylamino benzaldehyde Schiff base (CMC-SB) and its copper complex (CMC-SB-Cu) were prepared and characterized by FTIR, XRD and SEM studies. The results show the formation of Schiff bases with the amine of carboxymethyl chitosan and aldehyde. The copper (II) metal complexes were prepared by sol gel method. The complexes were again characterized by FTIR, XRD and SEM studies. The antioxidant activities of the prepared CMC derivatives were studied by DPPH studies. From the results it can be concluded that the complexes are less toxic and have good antioxidant activity. The results are discussed.*

**Key words:** Carboxymethyl Chitosan, p-dimethylamino benzaldehyde Schiff base, Copper Schiff bases, antioxidant studies.

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## INTRODUCTION

Polymers are substances, made up of recurring structural units, each of which can be regarded as derived from a specific compound called a monomer. Polymers play an essential and ubiquitous role in human life. In fact, our body is made of lot of polymers, e.g. Proteins, enzymes, etc. Polymers are playing an important role in all branches of industry [1]. Especially the biopolymer chitosan derived from renewable resources are available for various applications[2-3].

Carboxymethyl chitosan is one of the derivatives of chitosan plays a vital role in many fields generally obtained from the reaction of Chitosan with monochloroacetic acid and in alkaline condition [4]. In comparison to chitosan, CMC has higher moisture absorption and retention and better biological, chelating and sorption properties [5-7]. Moreover, CMC exhibit low toxicity, biocompatibility, biodegradable, antibacterial property and apoptosis inhibitory activity [8-10]. So it could promote growth in skin keratinocytes and skin fibroblast, and wound healing to make CMC as a good wound dressing materials [11].

Hence in this present study O-Carboxymethyl Chitosan was used to prepare the Schiff bases which are often reported for the reason that they offer opportunities for inducing biological activity. Also the copper metal was complexed with the prepared Schiff bases to evaluate its physico-chemical and biological properties.

This study includes an efficient method to synthesize the Schiff base and Schiff base metal complexes by the reaction of Carboxymethyl Chitosan and p-Dimethylamino Benzaldehyde under sol gel method. Schiff bases and its complexes were characterized by FTIR, XRD and SEM studies. The antioxidant activity for CMC, CMC-SB and CMC-SB-Cu was investigated.

## EXPERIMENTAL SECTION

### Materials

Chitosan and carboxymethyl chitosan were purchased from India Sea Foods, Cochin, Kerala, India. The p-Dimethylamino Benzaldehyde was purchased from Sigma Aldrich, India. All the chemicals used were of analytical grade.

### Preparation of carboxymethyl chitosan Schiff base with p-Dimethylamino Benzaldehyde

### Synthesis of Carboxymethyl Chitosan Schiff Bases (CMC-SB)

Carboxymethyl chitosan was dissolved in a mixed solution of ethanol with a small amount of water and stirred at room temperature for 30 min. Then, p-Dimethylamino Benzaldehyde was added to the mixture. The mixture was stirred and heated at 60°C for 12 h under water bath heating. After cooling, the crude product was washed with ethanol to the point of colorless filtrate. The product was dried at 60°C in vacuum for 24 h [12].

### Synthesis of Carboxymethyl Chitosan Schiff Base of Copper (II) (CMC-SB-Cu) Complexes

0.5 mmol of the purified CMC-SB was taken in a flask and magnetically stirred for 5 h in ethanol. This pre-treated methanolic suspension was again stirred with 0.5 mol ethanolic solution of $CuSO_4$ for 15 h. The resulting product after the filtration of the solution was washed well with ether and dried at $50^oC$ in vacuum.

### Fourier transform infrared studies

Fourier transform infrared spectra of chitosan Schiff base derivatives using KBR pellet method were recorded in the frequency range of 400 – 4000 $cm^{-1}$ using Thermo Nicolet AVATAR 330 spectrophotometer.

### X – Ray diffraction studies

X – ray diffractograms of samples were obtained using an X – ray powder diffractometer (XRD – SHIMADZU XD – D1) with Ni – filter and Cu Kα radiation source. The relative intensity was recorded in the scattering range 2θ, varying from $10^o$ to $90^o$.

### Scanning Electron Microscopy (SEM)

The surface morphology and cross section morphology of chitosan Schiff base derivatives were observed with scanning electron microscopy to verify the compatibility of the mixtures of chitosan Schiff base derivatives. To analyze the samples, the films were cut into pieces of various sizes and wiped with a thin gold – palladium layer by a sputter coater unit (UG – microtech, UCK field, UK) and the cross section topography was analyzed with Cambridge Stereoscan 440 Scanning Electron Microscope (Leica, Cambridge UK).

### Antioxidant activity

Evaluation of antioxidant activity The DPPH (α,α-diphenyl- β-picryl-hydrazyl) scavenging activity of the samples was measured using the modified method of Sun et al., (2008). 0.1 mL of ethanol solution of DPPH (0.1 mmol/L) was incubated with varying concentrations of test samples (0.1 mL). The reaction mixture was shaken well and incubated for 20 min at 30◦C and the absorbance of the resulting solution was read at 517 nm against a blank. The radical scavenging activity was measured as a decrease in the absorbance of DPPH and was calculated using the following equation:

$$\text{Scavenging effect (\%)} = \frac{1 - A_{sample}}{A_{control}} \times 100\%$$

## RESULTS AND DISCUSSION

### FTIR studies

**Figure-1** shows the FTIR spectrum of the Carboxymethylchitosan. The broad peak appears at 3420 $cm^{-1}$, corresponds to intramolecular hydrogen bond O-H and N-H stretching. A peak at around 2918 $cm^{-1}$ is due to the

stretching of C-H bonds [13]. The band observed for C=O stretching and NH bending is observed at 1725 and 1630 $cm^{-1}$. An additional peak which was observed at 1430 $cm^{-1}$ corresponds to coupling of C-N axial stretching and N-H angular deformation.

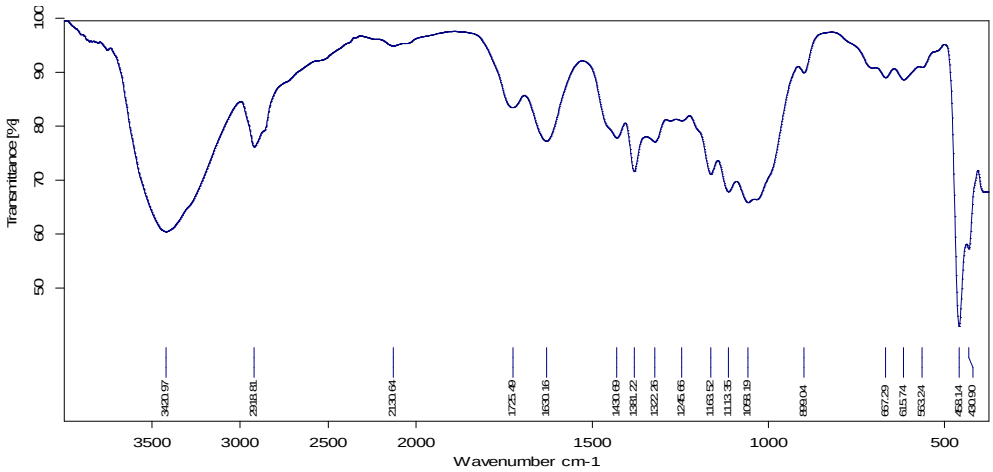



**Figure 1: FTIR spectrum of Carboxymethyl Chitosan**

**Figure-2** shows the FTIR spectrum of the Carboxymethyl chitosan/p-Dimethylamino Benzaldehyde Schiff bases. After the formation of Schiff base the broad peak at 3420 $cm^{-1}$ was shifted to 3393 $cm^{-1}$ which indicates that the polymer and the aldehyde involves in the hydrogen bond interaction. On comparing the spectrum of pure CMC and CMC-SB there was the peak shift and also the formation of new C=N imine peak (1642 $cm^{-1}$) was observed which confirms the formation of Schiff base.

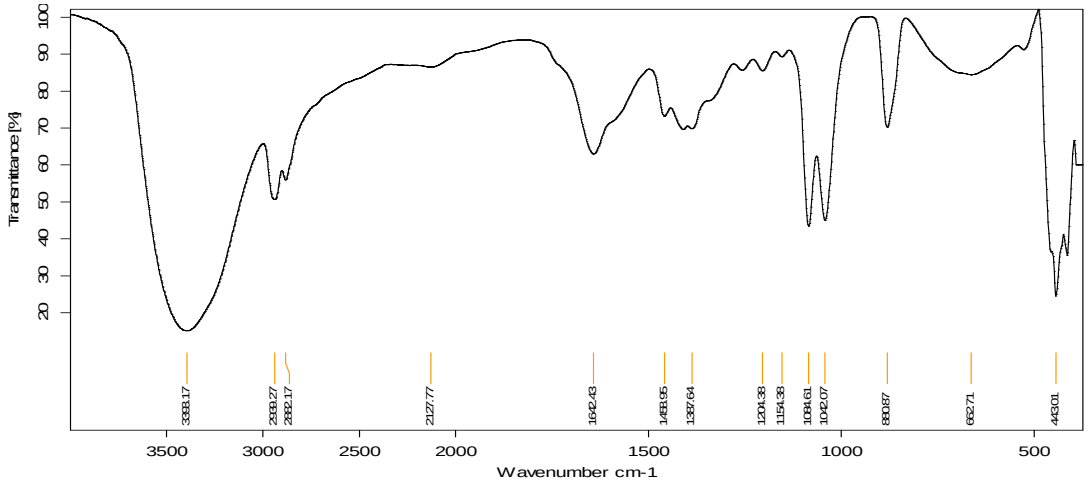



**Figure 2: FTIR spectrum Carboxymethyl Chitosan/p-Dimethylamino Benzaldehyde Schiff bases**

The FTIR spectrum of copper Schiff bases complex (**Figure 3**) showed the prominent peak at 3377 $cm^{-1}$ is due to the OH and NH stretching vibrations. This shift in peak represents that the metal ion was incorporated in the Schiff base ligand. Due to this the lone pair of electrons present in the heteroatom of the ligand coordinated with the metal ion. On comparing the spectrum the peak was shifted from 3393 to 3377 $cm^{-1}$ after the complexation.

Also during the formation of Schiff base and its metal complexes, the peak at around 2900 $cm^{-1}$ is due to CH stretching vibration mode shifted to the higher region confirming the presence of aromatic CH stretching vibration. The peak observed at around 1640 $cm^{-1}$ confirms the presence of the aromatic ring and C=N (Schiff base) stretching modes of vibration. The band observed at around 500 – 600 $cm^{-1}$ indicates the M-O and M-N stretch confirms the presence of metal in the prepared object. The peak shift and the increased intensity showed that the effective blending with the formation of new metal complexes.

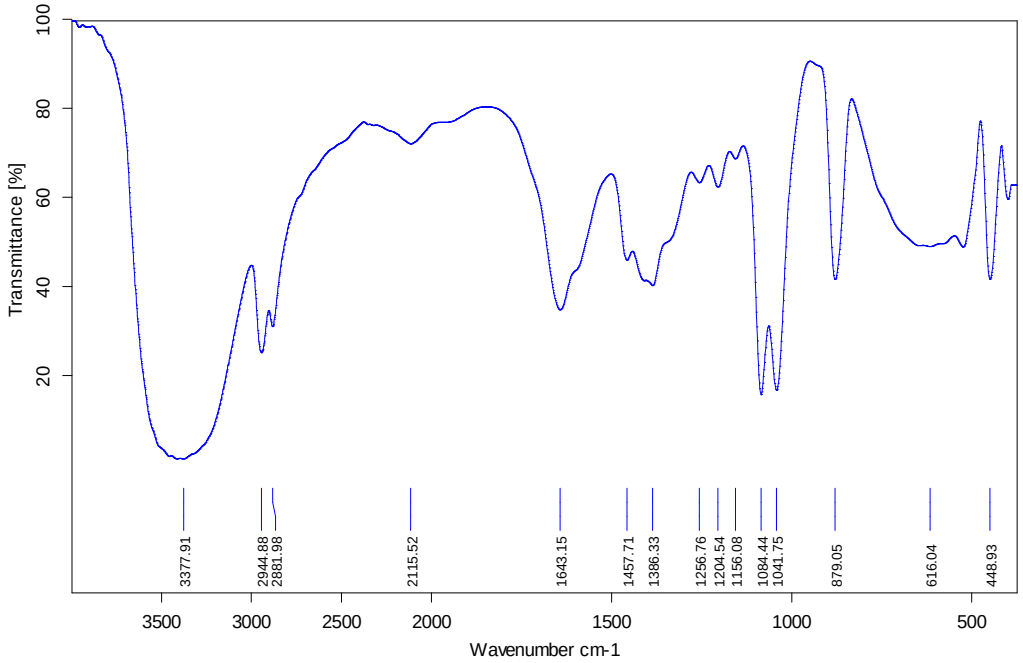
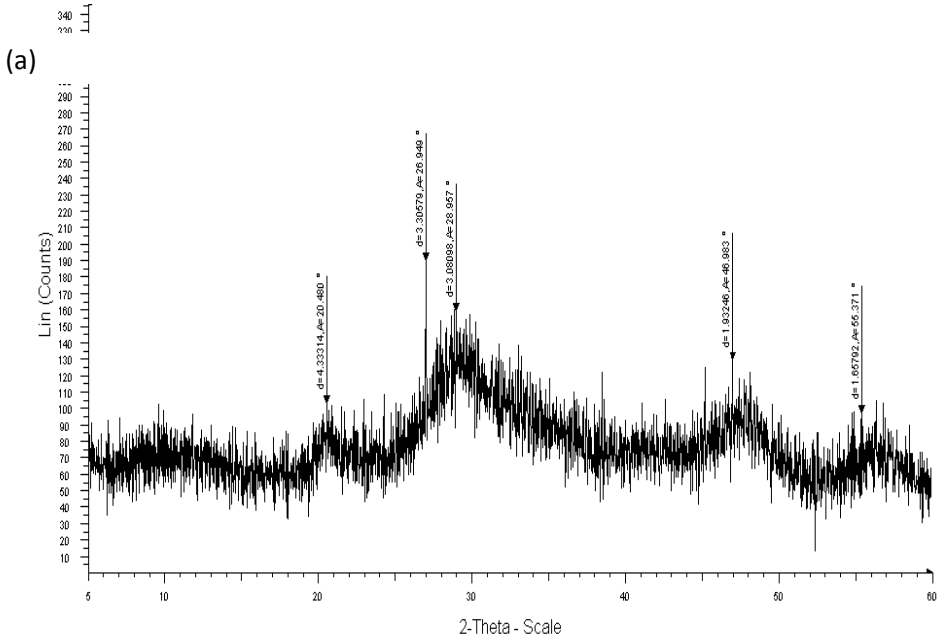



**Figure 3: FTIR spectrum of Copper Schiff base complex**

**XRD studies**

The X-ray diffraction analysis is used to determine the structure, complexation and crystallization of the polymer matrix [14]. The X-ray pattern of the CMC, CMC-SB and its copper complexes are shown in Figure 4a, 4b and 4c. As compared with CMC alone, the CMC-SB shows the weaker and broader peak at 2θ = 40°. For copper Schiff base complexes the 2θ values are at 28°, 47° and 56° were observed. This observed change in the peak positions are due to the coordination of metal with CMC-SB Schiff base.



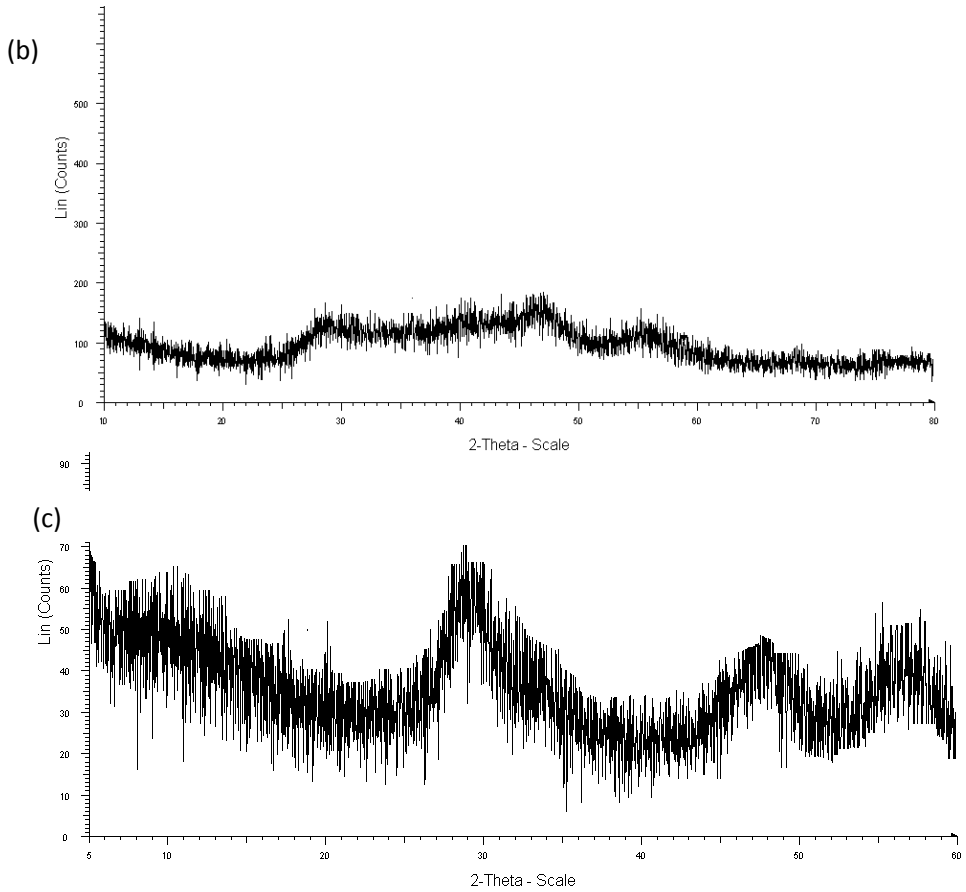



**Figure 4: XRD pattern of (a) CMC; (b) CMC-SB and (c) Schiff base Copper complex**

**SEM analysis**

In order to observe the changes in the morphology of the Carboxymethyl Cellulose (CMC), Carboxymethyl Cellulose/p-dimethylamino benzaldehyde (CMC-SB) and Carboxymethyl Cellulose/ p-dimethylamino benzaldehyde copper complex (CMC-SB-Cu), a study of scanning electron microscopy was carried out. The following figures show the SEM images of the prepared derivatives.

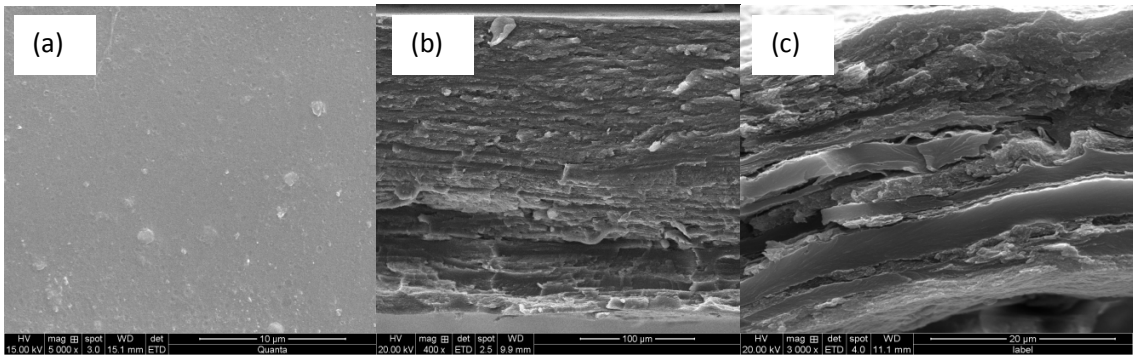



**Figure 5: SEM images of (a) CMC; (b) CMC-SB and (c) Schiff base Copper complex**

The surface morphology of the CMC shows a homogeneous smooth surface, whereas the rough and dense surfaces was seen for CMC-Schiff base and its copper complexes. Comparing the bare Schiff base with its copper complexes, the images of copper complex shows the continuous matrix with pores. Due to the metal-ligand coordination, the

Schiff base matrix comes closer to each other and give a regular, fibrous and large number of small pores and makes suitable for biomedical applications.

**Antioxidant activity**

Antioxidants play an important role as health protecting factor. The antioxidant activity has mainly been designated as the peroxide value of oxidation prodents and the oxidation rate of coexisting lipids. To study the antioxidant potential through free radical scavenging by the metal complexes, the change in optical density of DPPH radicals is monitored.

The scavenging activity for CMC-SB-Cu is 92%, whereas for bare CMC and CMC-SB the activity is 97% and 92% respectively. After the coordination of Cu in carboxymethyl chitosan Schiff base, the complex shows higher activity.

## CONCLUSION

Carboxymethyl Chitosan/ p-dimethylamino benzaldehyde Schiff bases (CMC-SB) and its copper (CMC-SB-Cu) complexes were prepared and characterized by FTIR, XRD and SEM studies. FTIR studies confirm the effective formation of Schiff bases and its metal complexes with modified properties. The antioxidant activity of the copper complexes was studied. The results reveal that the metal complexes have antioxidant activity. The XRD and SEM results proved that the prepared material is suitable for biomedical applications.

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