

Synthesis and Properties of Bionanocomposite - Nanochitosan Reinforced with Microcrystalline Cellulose

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Abstract: *Bio-nanocomposites in different ratio were successfully developed using microcrystalline cellulose extracted from sisal fibers as the reinforcement and nanochitosan as the polymeric matrix. MCC was extracted by adopting steam explosion technique and nanochitosan was prepared using ionotropic gelation method. The effect of reinforcement on the structure, morphology and properties of the bio-nanocomposites were characterized by SEM, FTIR, XRD, TGA, DSC and swelling analysis. The results indicated that the bio-nanocomposites can be used as efficient materials for heavy metal removal in water treatment.*

Keywords: Nanochitosan, MCC, Bio-nanocomposite, Structure, Properties

1. Introduction

71% of the total surface of earth is water. Most of the water bodies have become polluted due to population expansion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources [1]. The removal of toxic heavy metal ions discharged in water bodies has received prime importance by many researchers. Over the past few years, several research studies have been conducted globally on natural polymers and various methods have been developed to enhance their metal binding [2] properties.

Since biosorption process is recognized as a scientific method for the removal of toxic heavy metal ions from water, numerous adsorbents such as Chitin, Chitosan and Cellulose which are eco friendly, cost effective but are also effective in the remediation of common effluents present in waste water [3] are well known. Chitin and chitosan are versatile and promising bio-polymers for its special features such as biocompatibility, biodegradability, hydrophilicity, nontoxicity, non- antigenicity, antimicrobial activity as well as bioadherence.

In spite of the unique properties of chitosan, it needs modification to improve the physical and mechanical properties of chitosan. Much research has been done in synthesizing composites using chitosan as the polymeric matrix. Wan Ngah et al., 's (2011) [4] review highlights the application of chitosan composites in the removal of dyes and heavy metals and the future for commercial application. Cellulose fibers in micro and nanoscale are attractive reinforcement to develop "Green" composites.

Adsorption with nanomaterials has emerged as one of the potential technologies in treatment of waste water due to their high adsorption capacity and selectivity [5]. From the vast literature available, the excellent properties of Chitosan and Cellulose as efficient adsorbents of heavy metals for water treatment, our work focused on the preparation and characterization of Nanochitosan using ionotropic gelation and extraction of micro-crystalline

cellulose from Sisal fibers (Agave sisalana plant) by adopting steam explosion technique.

Bio-nanocomposites using Nanochitosan as the polymeric matrix and extracted micro-crystalline cellulose as the reinforcement in varying ratios were prepared by casting and hope to use for bio-sorption studies of heavy metals in waste water. Synthesis and characterization of chitosan nanoparticles by ionic gelation of chitosan and TPP and its sorption capacity for Cr (VI) was studied and first reported on sorption property of chitosan nanorod in the conversion of Cr (VI) to Cr (III) [1].

2. Materials and Methods

2.1. Chemicals and reagent

Chitosan (deacetylation 92% and MW 12, 000) was procured from India Sea Foods, Cochin, Kerala, India. Sodium tripolyphosphate and acetic acid of AR grade were used without any further purification.

Sisal fibers used were supplied by Vibrant Nature, Chennai, Tamil Nadu, India. The chemicals used for the extraction of microcellulose from sisal fibers, NaOH (Commercial grade), acetic acid (Commercial grade), sodium hypochlorite (Commercial grade) and oxalic acid (Commercial grade).

2.2. Preparation of chitosan nanoparticles

The method adopted is as reported by Tang et al., (2007) [6]. 20mg chitosan was dissolved in 40ml of 2.0% (V/V) acetic acid. 20ml of 0.75mg/ml sodium tripolyphosphate was dropped slowly with stirring. Chitosan nano particles as a suspension were collected and stored in deionised water. Supernatant was discarded and chitosan nanoparticles were air dried for further use and analysis.

2.3. Extraction of microcrystalline cellulose from sisal fibers

The isolation of microcrystalline cellulose from sisal fibers was obtained by steam explosion method as adopted by Cherian et al., (2008) [7]. This process is the removal of other components such as lignin, hemicellulose and pectin and was achieved by the treatment of alkaline solution followed by bleaching.

2.4. Preparation of microcrystalline cellulose – nanochitosan bionanocomposite

The prepared nanochitosan and the extracted microcrystalline cellulose from sisal fibers were mixed in varying ratios of 1:2, 1:3, 2:1, 3:1 and 4:1 by stirring for 20 minutes and casting in polystyrene plates. The dried bionanocomposite was used for further analysis.

2.5. Characterization of bionanocomposite

2.5.1. Swelling Index

The swelling behaviour of the bionanocomposites was investigated by immersing the samples in deionised water at room temperature. The wet weights of swollen samples were measured after blotting with a filter paper to remove surface water, followed by immediate weighing. This process was repeated at the time intervals of 1 hour, 2 hours, 3 hours, 4 hours, 5 hours and 24 hours respectively and the results are discussed.

2.5.2. Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR analysis of dried bionanocomposite prepared in different ratio were carried out in the range between 4000-

375 cm^{-1} using Thermo Nicolet AVATAR 300 FTIR spectrometer using KBr pellet method.

2.5.3. X-ray Diffraction (XRD) Spectra

X-ray diffraction profiles of all the samples were recorded by Bruker, Germany, powder X-ray diffractometer, model D8 Advance, source 2.2 kW Cu anode, Ceramic X-ray tube. The relative intensities were recorded within the range of $10^\circ - 90^\circ$ (2θ) at a scanning rate of 5°min^{-1} .

2.5.4. Thermogravimetric (TGA) and Differential thermogravimetric (DTG) analyses

Thermogravimetric (TG) analysis and differential thermogravimetry of the samples were carried out on a SDT Q600 V8.0 Build 95 instrument at a heating rate of 10°C per minute in nitrogen atmosphere. The weight losses at different stages were analyzed.

2.5.5. Differential Scanning Calorimetry (DSC) analysis

DSC curves of all the samples were obtained using a NETZSCH DSC 200PC in a Al pan, pierced lid in the N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The results were recorded and analyzed.

2.5.6. Scanning electron microscopy (SEM)

For SEM analysis, all the samples were cut into pieces of various sizes and wiped with a thin gold – palladium layer by a sputter coater unit (VG – microtech, UCK field, UK) and the cross section topography was analyzed with a Cambridge stereoscan 440 scanning electron microscope (SEM, Leica, Cambridge, UK).

3. Results and Discussion

3.1. General discussion

Plate 1: Bionanocomposites in the ratio (a) NC/MCC (1:2), (b) NC/MCC (1:3), (c) NC/MCC (2:1), (d) NC/MCC (3:1) and (e) NC/MCC (4:1)



Several studies show that both chitosan and cellulose are found to exhibit excellent sorption potential for multivalent metal ions. Chitosan, partially deacetylated product of chitin is β - (1, 4) – D – N – acetyl glucosamine and β - (1, 4) – D – glucosamine. Chitosan has three types of reactive functional groups, an amino group as well as both primary and secondary hydroxyl groups at the C–2, C–3, and C–6 position respectively which allows modification feasible. Nanochitosan/ microcrystalline cellulose bionanocomposites of various ratios (1:2), (1:3),

(2:1), (3:1) and (4:1) were prepared. The characterizations of the bionanocomposites were studied by the swelling index, FTIR, XRD, TGA, DSC and SEM analyzes.

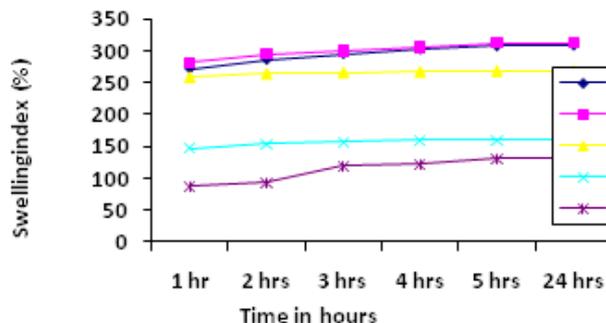
3.2. Swelling index

From **Table- 1** and **Figure-1** shows a gradual increase in weight upto five hours in the bionanocomposites NC/MCC (1:2) and (1:3) with increase in the cellulose content where as the bionanocomposites (2:1), (3:1) and (4:1), there is

very slow increase in weight with increase in the nanochitosan content. For the bionanocomposites NC/MCC (1:2) and NC/MCC (1:3) the gradual increase in the water sorption capacity is due to the increase in cellulose content. Since in pure cellulose, each unit has three free – OH groups, the water absorption rate increases

with cellulose content [8]. Considering the water sorption capacity of the bionanocomposites NC/MCC (2:1), NC/MCC (3:1) and NC/MCC (4:1) there is no sharp raise in the water sorption capacity as the content of nanochitosan increases which is amorphous and hydrophobic in nature.

Table 1 and Figure 1: Water sorption capacities (%) of NC/MCC bionanocomposites



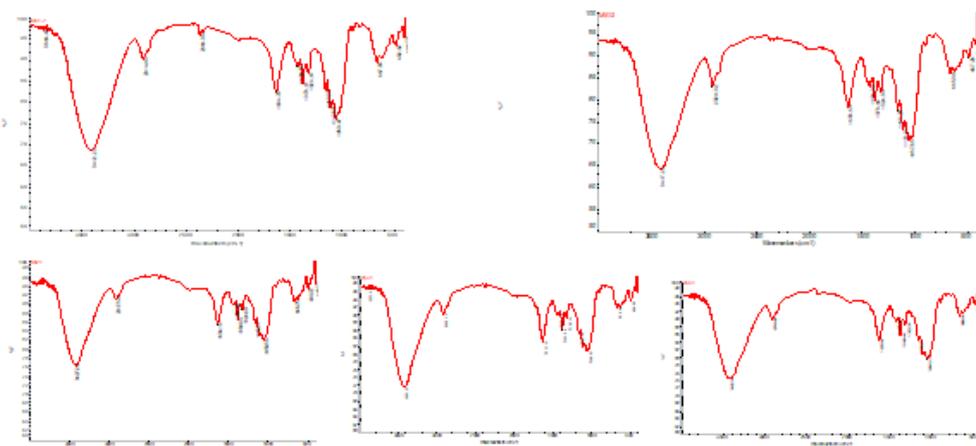
Samples	% water sorption					
	1 hr	2 hrs	3 hrs	4 hrs	5 hrs	24 hrs
NC/MCC 1:2	272	286	295	302	307	308
NC/MCC 1:3	282	295	300	305	312	312
NC/MCC 2:1	259	264	266	267	268	268
NC/MCC 3:1	147	154	158	159	160	160
NC/MCC 4:1	88	94	119	122	131	131

3.3. FTIR spectroscopy analysis

The FTIR spectra of the bionanocomposites in the different ratio are shown in **Table2 and Figures- 2 a- 2e**

Table 2: FTIR – Spectral details of NC/MCC bionanocomposites

Wave number cm ⁻¹					Responsible group
NC/MCC (1:2)	NC/MCC (1:3)	NC/MCC (2:1)	NC/MCC (3:1)	NC/MCC (4:1)	
3412.23	3417.23	3427.61	3427.31	3428.17	N-H stretching and O-H stretching of H-bonded OH group
2911.03	2920.32	2917.50	2922.73	2919.89	aliphatic saturated C–H stretching
1634.78	1633.65	1634.16	1633.77	1633.87	Carbonyl stretching (amide I)
1430.57	1431.22	1430.00	1431.72	1431.84	- CH ₂ scissoring
1379.13	1378.66	1380.33	1380.94	1380.48	-CH ₃ symmetrical scissoring of amide group
1324.01	1324.93	1324.60	1324.30	1323.33	N-H bending (amide III)
1266.8	1266.4	1268.40	1268.00	1268.20	P=O stretching
1163.35	1163.29	1162.57	1162.69	1162.71	C-O-C bridge anti symmetric stretching
1112.89, 1059.07	1113.27, 1057.85	1059.56	1058.67	1059.33	C-O stretching vibrations of polysaccharide structure



Figures – 2 a- 2e FTIR spectral details of bionanocomposite(a) NC/MCC (1:2), (b)NC/MCC (1:3), (c)NC/MCC (2:1), (d)NC/MCC (3:1) and (e) NC/MCC (4:1)

From **Table- 2 and Figures- 2 a- 2e**, the FTIR spectra of all bio nanocomposites show high intensity peak around $3412 - 3428 \text{ cm}^{-1}$ due to the N-H and O-H stretching vibration of chitosan [9] and which may be also due to the hydrogen bonded O-H stretching vibration of cellulose [7].

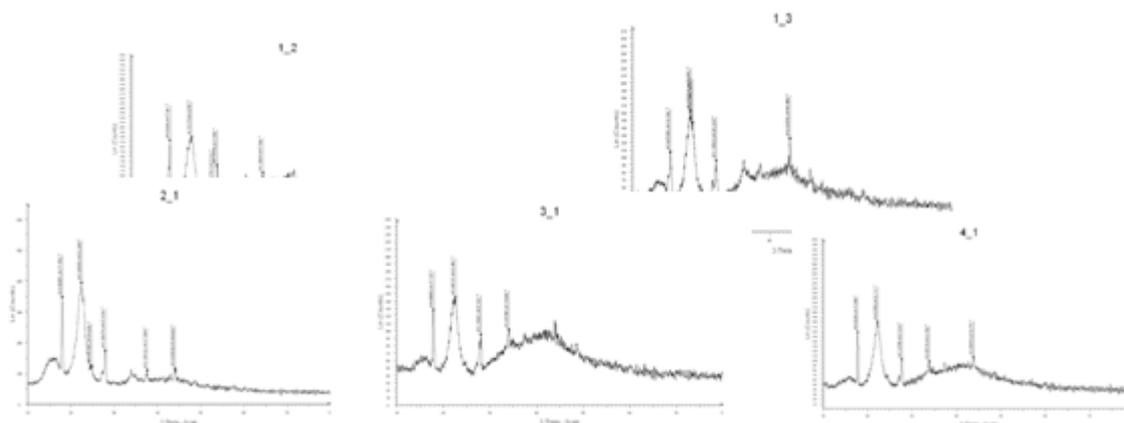
Comparing the FTIR spectra of nanochitosan and bionanocomposites, the appearance of sharp peak in the range $2911 - 2922 \text{ cm}^{-1}$ which is rather blunt in nanochitosan confirms the microcrystalline cellulose loading in the composite characteristic of C-H stretching vibration of cellulose [9]. The absorption band at around $1633 - 1634 \text{ cm}^{-1}$ in all the bionanocomposites is assigned to carbonyl stretching vibration of acetylated amino group (amide I) [11] of nanochitosan and at $1430 - 1431 \text{ cm}^{-1}$ characteristic band due to $-\text{CH}_2$ scissoring [12].

3.4. Crystallinity of bionanocomposites

The XRD profiles of the bionanocomposites are given in **Table –3 and Figures – 3 a- 3e**

Table 3: XRD details of the bionanocomposites

Samples	2 θ Values			Ic%
NC/MCC 1:2	17.981°	22.597°	27.969°	31.0
NC/MCC 1:3	18.192°	22.653°	28.236°	31.4
NC/MCC 2:1	17.852°	22.294°	27.834°	31.5
NC/MCC 3:1	17.737°	22.483°	27.221°	31.4
NC/MCC 4:1	17.654°	22.111°	27.614°	28.3



Figures 3 a- 3e: XRD details of bionanocomposite (a) NC/MCC (1:2), (b) NC/MCC (1:3), (c) NC/MCC (2:1), (d) NC/MCC (3:1) and (e) NC/MCC (4:1)

From **Table-3 and Figures- – 3 a- 3e**, the XRD profiles of the bionanocomposites indicate an increase in the number of crystalline forms with three peaks at $2\theta=17-18^\circ$, 22° and $27-28^\circ$. An intense peak at $2\theta=22^\circ$ in all the bionanocomposite corresponding to (200) plane of cellulose I [17] confirms the strong adhesion of microcrystalline cellulose onto nanochitosan. The sharp peak at $2\theta=17^\circ-18^\circ$ is assigned to nanochitosan and also to (110) plane of cellulose I [17] and the third peak shifts from $2\theta=34^\circ$ observed in acid treated fiber to $2\theta=28^\circ$ thus supporting the formation of the composite.

The peak at $1378 - 1380 \text{ cm}^{-1}$ is assigned to the $-\text{CH}_3$ symmetrical deformation mode (scissoring) in amide group [13]). The peak at $1323 - 1324 \text{ cm}^{-1}$ is characteristic of absorption of amide III [11]. The appearance of a new peak at $1266 - 1268 \text{ cm}^{-1}$ indicating P=O stretching [13] in all the bionanocomposites shows the strong interaction between the nanochitosan matrix and the microcrystalline cellulose reinforcement. The crystalline nature of the microcrystalline cellulose in the composite is further supported by the sharp peak at $1430 - 1431 \text{ cm}^{-1}$ [15].

The bands at $1162 - 1163 \text{ cm}^{-1}$ is assigned to the antisymmetric stretching of C-O-C bridge and at $1057 - 1059 \text{ cm}^{-1}$ is the C-O stretching vibration, characteristic peak of polysaccharide structure in chitosan [16]. Thus FTIR analysis confirms the successful development of the bionanocomposite.

The diffraction peaks of cellulose observed in all the bionanocomposite around $2\theta=22^\circ$ suggests the crystallinity of the composites increased because of highly crystalline reinforcement [9]. The crystallinity index (Ic) determined for the bionanocomposite maintained a high percentage of crystallinity around 31%.

3.5. Thermal properties of bionanocomposites

TGA thermograms of the bionanocomposites NC/MCC (1:2), NC/MCC (1:3), NC/MCC (2:1), NC/MCC (3:1) and NC/MCC (4:1) are shown in **Figures – 4 a- 4e**

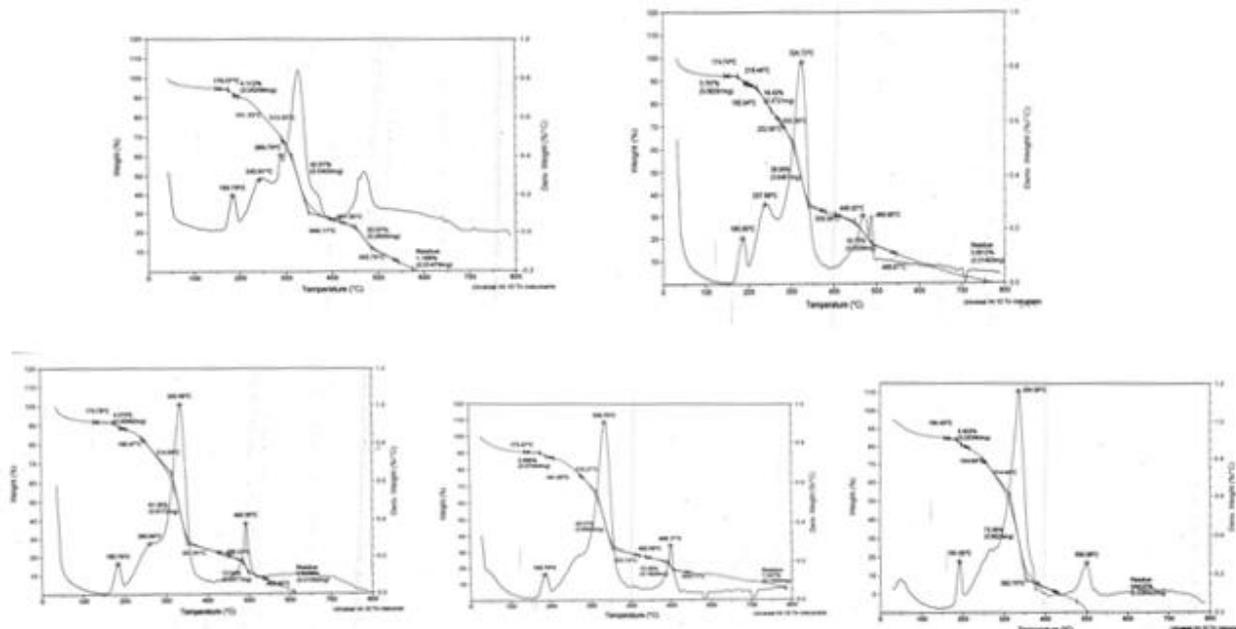
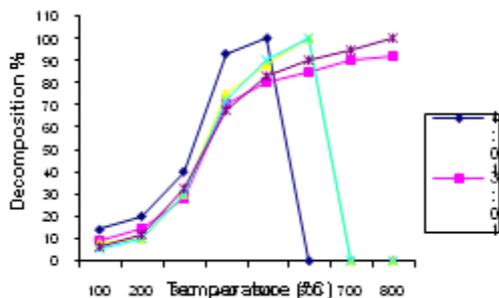


Table 4: Rate of decomposition percentage of bionanocomposite in the ratio 4:1, 3:1, 2:1, 1:2 and 1:3 and Figure-5

Temperature °C	Decomposition %				
	4:1	3:1	2:1	1:2	1:3
100	14	9	8	5	7
200	20	14	10	10	12
300	40	28	30	30	33
400	93	70	75	72	68
500	100	80	88	90	83
600	-	85	100	100	90
700	-	90	-	-	95
800	-	92	-	-	100



From **Table- 4** and **Figures- 4a-4e**, the decomposition temperature between 335-355°C was attributed to the decomposition of cellulose [18] and also a 50% weight loss in all the bionanocomposites happened at 320-340°C. The thermal degradation of nanochitosan happens well

above 485°C almost in all composites. **Table-4** and **Figure-5** confirms that the rate of decomposition percentage of all the bionanocomposites increases with increase in temperature in the range of > 400-800°C. This evidenced the enhanced thermal stability of the bionanocomposites. The thermal studies of nanochitosan reveals that the residual temperature was 800°C with a residue of 45.63% indicating the increased thermal property of the bionanocomposites by the incorporation of nanochitosan.

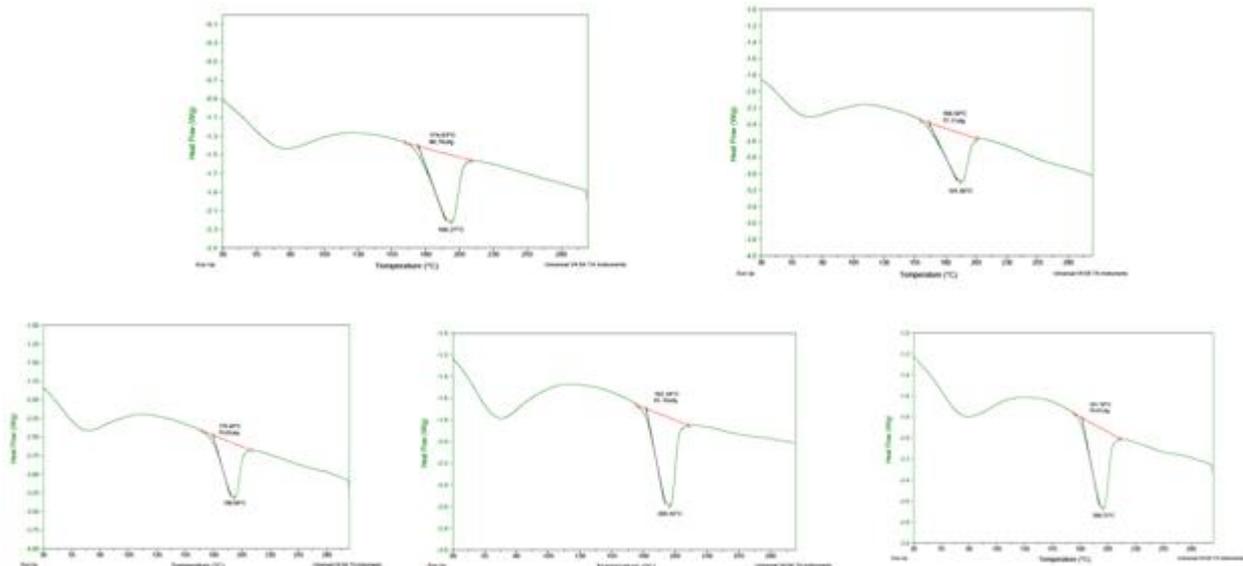
Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is an analytical tool which helps to understand the thermal behavior and to determine the glass transition temperature of polymers, polymer blends and polymer composites.

The DSC curves of the bionanocomposites NC/MCC(1:2), NC/MCC(1:3), NC/MCC(2:1), NC/MCC(3:1), and NC/MCC(4:1), are given below in **Table – 5** and **Figures – 6a-6e**.

Table 5: DSC Thermogram of the bionanocomposites

Sample	Tg°c	Tc°c	Tm°c
NC/MCC 1:2	141.7	75.8	198.25
NC/MCC 1:3	135.2	70	191.95
NC/MCC 2:1	145.6	73	198.04
NC/MCC 3:1	145.6	70	200.55
NC/MCC 4:1	149.5	80	200.72



Figures –6 a-6e: DSC Thermogram of the bionanocomposite

Table-5 shows that all the bionanocomposites had a single transition temperature. The appearance of single T_g confirm the formation of NC/MCC composites. T_g of NC/MCC (1:2), NC/MCC (1:3), NC/MCC (2:1), NC/MCC (3:1) and NC/MCC (4:1) are 141.7°C, 135.2°C, 145.6°C, 145.6°C and 149.5°C respectively. All the bionanocomposites showed the melting temperature above 300°C confirming the high thermal stability of the bionanocomposites.

Two endothermic peaks were observed for all the bionanocomposites. The first peak at 75.8°C, 70 °C, 73°C, 70°C and 80 °C for NC/MCC (1:2), NC/MCC (1:3), NC/MCC (2:1), NC/MCC (3:1) and NC/MCC (4:1) respectively indicating the removal of absorbed moisture and the second endothermic peak at 189.25°C, 191.95°C, 198.04°C, 200.55°C and 200.72°C for the bionanocomposites showing the crystalline temperature.

The T_c increases with increase in nanochitosan content and the decomposition temperature of all the

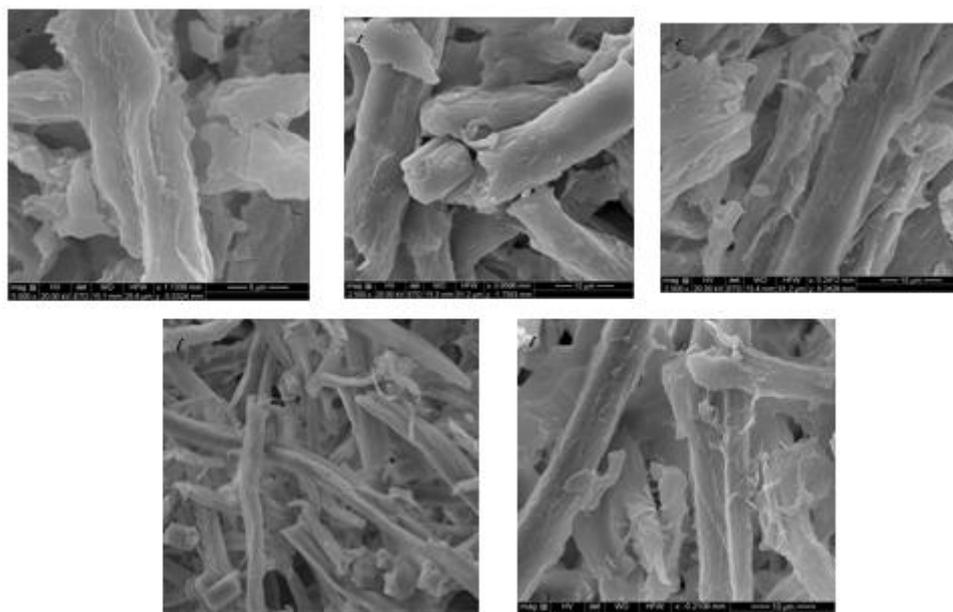
bionanocomposites was found to be above 300°C since there is no exothermic peak up to 300°C.

3.6. Scanning Electron Microscopic Analysis.

The SEM micrographs of the bionanocomposites NC/MCC (1:2), NC/MCC (1:3), NC/MCC (2:1), NC/MCC (3:1) and NC/MCC (4:1) are shown below in **Figures – 7a-7e**

The scanning electron micrographs of the nanochitosan, microcellulose bionanocomposites 4:1, 3:1, 2:1, 1:3 and 1:2 (**Figures – 7a-7e**), the higher concentration of nanochitosan in 4:1 is clearly shown in the SEM image 7a.

All the figures show the rough and coarse nature of the surfaces of the composites showing the suitability of the composites for adsorption. The $-NH_2$ and $-OH$ functional groups in chitosan and cellulose make the composite a suitable material for the adsorption of ionic pollutants such as heavy metals.



4. Conclusions

Study on water sorption capacity for the bionanocomposites in varying ratios showed water absorption rate increases with increase in cellulose content while no sharp increase with increase in Nanochitosan content which is amorphous and hydrophobic in nature. FTIR spectral details confirm strong interaction between the nanochitosan matrix and the microcrystalline reinforcement which may be attributed by the appearance of a new peak due to P=O stretching in all the bionanocomposites. XRD profiles of the bionanocomposites indicate an increase in the crystallinity which confirms the strong adhesion of highly crystalline reinforcement microcrystalline cellulose onto nanochitosan. TGA and DSC results evidenced the enhanced thermal stability of the bionanocomposites due to the incorporation of nanochitosan. SEM images show the rough and coarse nature of the surfaces of the composites suitable for the adsorption of ionic pollutants such as heavy metals. Thus the bionanocomposites prepared from renewable resources for heavy metal remediation from aqueous solutions, industrial and municipal waste water can serve as potential biosorbents.

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