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FT-IR Spectral analysis of Chitosan Coated Carbon biosorbent M. Soundarrajan¹ and P.N. Sudha²

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ABSTRACT

In the present work, chitosan was coated onto the activated carbon and characterized by FT-IR study. The FT-IR spectra of all three chitosan coated carbon showed the characteristic adsorption peaks, which are shifted to lower wave number. The -OH stretching of pure chitosan were observed at 3454 cm⁻¹, whereas the composite showed -OH peak at lower frequency. Due to this, the strong interaction between chitosan and carbon made the bio sorbent effective material for the removal of toxic metal ions from water.

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Keywords

FT-IR Spectra, Chitosan, Carbon, Toxic metal, Biosorption.

Introduction

Chitosan, a hydrophilic natural polymer produced by alkaline deacetylation of chitin, obtained mainly by extraction from shrimp and crab shells, is the most abundant biopolymer occurring in nature, after cellulose. It is composed of both glucosamine and acetyl glucosamine as a monomer in the heteropolymeric network. It is characterized by a high content of nitrogen, present as amine groups capable of adsorbing the metal mechanisms-including ions through several chemical interactions, such as chelation, electrostatic interactions or ion exchange. The interaction type depends on the metal ion, its chemistry and initial solution pH [1]. Chitin is a linear polymer consisting mainly of β -(1-4)-linked-2-acedamido- 2- deoxy- β -dglucopyranose units and partially of β -(1-4)-linked 2- amino- 2deoxy-β-d- glucopyranose.

During the deacetylation of chitin inter and intra molecular hydrogen bonds are changed to give lower crystallinity to chitosan which, ingresses the accessibility to the adsorption sites of biopolymer [2]. At low pH chitosan is water soluble, because of the positive charge on the -NH3+ group. It convert chitosan into water soluble cationic polyelectrolyte but above pH=6 it is water insoluble due to loss of the positive charge on the amine groups [3, 4].

Heavy metals in the environment are non-biodegradable. On the contrary, they can accumulate gradually and transferred into more toxic metal compounds, which causes adverse effects through bio-magnification of the food chain at all levels of the organisms in the ecosystem [5]. Some of the heavy metals like copper (Cu), Nickel (Ni), Zinc (Zn) are essential micronutrients for plants, but in excess all these metals are harmful to human health, animals and plants; as are the non-essential metals Lead (Pb), cadmium (Cd) and mercury(Hg) [6].

Municipal wastes, fertilizers, pesticides, sewage burning of fossil fuels, the mining and smelting of metallic ferrous ores are primary sources of above heavy metals [7]. For normal body functions a specific amount of chromium is required.

Its higher concentration it may cause toxicity, including liver and kidney problems -Genotoxic carcinoge [8,9,10]. Hence the level of toxic metal ions should be minimized in the water. In this study Chitosan was coated on carbon and characterized by FTIR study and used for the biosorbative removal of toxic metal ions from the water.

Materials and Methods

Preparation of Carbon

The coconut shell was broken into small pieces and ground well. This was burnt at a very high temperature for 2-3 hours. The surface of carbon obtained was activated by shaking the same with 7% sulphuric acid for 24 hours. The carbon was then washed several times with de-ionised water till there is no acid in the water. The sulphonated carbon was dried in hot air for over 5 hours at 110°C.

Surface Coating of Carbon with Chitosan

About 400 ml of chitosan gel was diluted with water and heated to 40-50°C. About 400 g of activated coconut shell carbon was slowly added and mechanically agitated using a rotary shaker at 150 rpm for 24 hours.

This gel coated activated carbon was washed with deionized water and dried. This process was repeated to get 1, 2, 3, 4 and 5th coating at chitosan onto activated carbon. 3, 4 and 5th coated carbon were used for the studies.

Characterization

FT-IR measurements of the prepared bio sorbents was recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Perkin Elmer 200 FT-IR spectrophotometer, in the range of 400-4000 cm-1 at 25°C with a resolution of 4 cm-1.

Results and Discussion

The FT-IR spectra of chitosan (Table 1 and Figure 1) showed a strong absorption band at 3454.75 cm-1 due to OH and amine N-H symmetrical stretching vibrations. A peak at 2923.08 cm-1 was due to symmetric -CH2 stretching vibration attributed to pyranose ring [11].

A peak at 1156 cm⁻¹ was assigned to the structure of saccharide. The sharp peak at 1384.01 cm⁻¹ was assigned to CH_3 in amide group. The broad peak at 1021.37 cm⁻¹ and 1098.72 cm⁻¹ indicate the C-O stretching vibration in chitosan and certain peaks observed at 1628.87 cm⁻¹ and 1540.02 cm⁻¹ were due to -C=O stretching (amide I) and N-H bending (amide ID.

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Wave number (cm ⁻¹)	Responsible groups
3454.75	OH stretching, NH stretching, intermolecular
	hydrogen bonding and polymeric association.
2923.08	Symmetric CH ₂ stretching vibration attributed to
	pyranose ring.
1740.23	Carbonyl group vibration
1628.87	C=O stretching (amide I band)
1540.02	NH bending (amide II band)
1384.01	CH ₃ in amide group
1322.23	Secondary alcoholic group, C-C stretching
1151.84	C-O-C in glycosidic linkage
1098.72 and	C-O stretching vibration
1021.37	

Table 1. FT-IR spectra data of pure chitosan





The absorption bands at 1151.84 cm⁻¹ (anti symmetric stretching of C-O-C bridge) 1021.37 cm⁻¹ (skeletal vibration involving the C-O stretching) are characteristics of chitosan polysaccharide structure. The spectral features of pure chitosan were in agreement with previous results [12].

Table 2 and Figure 2 show the FT-IR spectrum of chitosan coated carbon (3rd coating). The prominent peak at 3436.48cm⁻¹ corresponds to inter molecular hydrogen bonded O-H stretching, -NH stretching and also the polymeric association [13].

Table	2	FTIR	spectral	data	of 3 rd	coated	carbon
Laint		1.111/	SULULA	uala	VI .2	UMALUU	vai izni

Wave	Responsible group
number	
(cm ⁻¹)	
3436.48	O-H and N-H stretching, Intermolecular hydrogen
	bonding polymer association.
2924.48	Asymmetric C-H stretching
2857.04	Symmetric C-H stretching
1628.12	N-H bending
1151.87	C-N stretching
1383.51	O-H in plane bending
1017.03	C-O-C skeletal in the backbone
886.27	CH ₃ -C-OH stretching
651.77	OH bending
479.50	C-C bending

The peak obtained at 2924.48 cm⁻¹ and 2857.04 cm⁻¹ corresponds to the asymmetric and symmetric C-H stretching. Certain peaks observed at 1628.12 cm^{-1} , 1151.87 cm^{-1} , 1383.51 cm^{-1} , 1017.03 cm^{-1} and 886.27 cm^{-1} correspond to the N-H bending, C-N stretching, O-H in plane bending, C-O-C skeletal in the backbone and CH₃-C-O-H stretching respectively. The peak at 651.77 cm⁻¹ and 479.50 cm⁻¹ indicate the presence of O-H bending and C-C bending vibrations respectively. Similar observations were made by [14].



Figure 2. FT-IR spectra of 3rd coated carbon

Table-3 and Figure-3 show the FT-IR spectrum of chitosan coated carbon (4th coating). The broad band observed at 3435.11 cm⁻¹ corresponds to the intermolecular hydrogen bonded N-H stretching, O-H stretching and polymeric association. The peak observed at 2923.18 cm⁻¹ corresponding to aliphatic C-H stretching [15].

Table 3. FT-IR	spectral data	of 4 th	coated	carbon
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Table 3. FT-IR spectral data of 4 th coated carbon			
Wavenumber (cm ⁻¹)	Responsible group		
3435.11	O-H and N-H stretching, Intermolecular		
2022 10	ny drogen bonding polymeric association.		
2923.18	Asymmetric N-H stretching		
1627.81	N-H bending		
1383.88	O-H in plane bending		
1098.18	C-O-C in glycosidic linkage		
886.24	CH ₃ -C-O-H stretching		
1229.47	C-O stretching		
98 96 94 92 90 88 86 86 84 82 80 78 76 76	2223.1 (1) 2223.1 (1) 1627.6		

Figure 3. FTIR spectra of 4th coated carbon

Certain peaks observed at 1627.81 cm⁻¹, 1383.88 cm⁻¹ indicate the N-H bending and O-H in plane bending. The peak observed at 1098.18 cm⁻¹, and 886.24 cm⁻¹ and 1229.47 cm⁻¹ ¹corresponds to the C-O-C skeletal, CH₃-C-OH stretching. The peak observed at 1229.47 cm⁻¹ corresponding to the C-O stretching of primary alcoholic group in chitosan [16]. The elimination of moisture reflected the shift of the -OH stretching vibration from 3458cm⁻¹ to 3435cm⁻¹ [17].

Table 4 and Figure 4 show the FT-IR spectrum of chitosan coated carbon (5th coating). The broad band observed at 3456.25cm⁻¹ was attributed to intermolecular hydrogen bonded N-H stretching, O-H starching and the strong polymeric association of chitosan coated carbon. The peak observed at 2924.68 cm⁻¹ and 1628.22 cm⁻¹ indicate the aliphatic asymmetric C-H stretching [18] and N-bending. Certain peaks observed at 1384.35 cm⁻¹, 1115.56 cm⁻¹ and 857.64 cm⁻¹ corresponds to the O-H in plane bending, C-O-C in glycoside linkage and CH3-C-OH stretching respectively.

Wavenumber (cm ⁻¹)	Responsible group
3456.25	O-H and N-H stretching Intermolecular hydrogen bonding polymeric association.
2924.68	Asymmetric C-H stretching,
1628.22	N-H bending
1384.35	O-H in place bending
1225.39	C-O group
1115.56	C-O-C in glycoside linkage
857.64	CH ₃ -C-OH stretching

Table 4. FTIR spectral details of 5th coated carbon

The -NH bending in amides was no longer observed, because the band was shifted to a higher frequency overlapping with the carbonyl stretch in amides. This shifting to a higher frequency indicates that the -NH groups of chitosan are involved in hydrogen bonding leading to a film of higher miscibility [19].





FT-IR spectra of all three chitosan coated carbon (3^{rd} , 4^{th} and 5^{th}) showed the characteristic adsorption peaks of the components. It can be seen that the characteristic absorption bands are shifted to lower wave number. A strong peak around 3200 cm-1to 3400 cm-1 shows the intermolecular hydrogen bonding, presence of –OH stretching and –NH stretching. The – OH stretching of pure chitosan were 3454 cm-1, whereas during the coating on carbon the peak was shifted to lower frequency. The amine, residual amide and hydroxyl groups of chitosan can form intermolecular hydrogen bonds [20]. Similar interaction is seen in chitosan coated carbon, providing strong interaction between chitosan and carbon.

Conclusion

From the results obtained in the region around 3400 cm-1, it can be said that the chitosan coating on carbon has significantly influenced the properties of chitosan typically the relative crystallinity level through the formation of hydrogen bonding which increases the intermolecular forces exist between chitosan and carbon. FT-IR analysis showed that there were strong interactions between carbon and chitosan in the composite. In this study 5th coated carbon has been used for the sorption study of toxic metal ions.

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