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## Physicochemical Characterization of Chitin/ Cellulose Binary Composite for Fluoride Removal from Water

### G. Jayapriya<sup>1,2</sup> and P.N. Sudha<sup>3</sup>

<sup>1</sup>Department of Chemistry, C. Kandaswami Naidu, College for Women, Cuddalore, Tamil Nadu, India <sup>2</sup>Department of Chemistry, Manonmanium Sundaranar University, Tirunelveli, Tamil Nadu, India and <sup>3</sup>Department of Chemistry, D.K.M. College for Women (Autonomous), Vellore, Tamil Nadu, India

### KEYWORDS

Chitin; Cellulose; Composite; Defluorination.

### ABSTRACT:

The fairly new idea of biodegradable composites is a relatively recent concept that has the ability to produce the next generation of novel eco-friendly products with excellent performance and a vast range of medical uses, coatings, packaging, automobile applications, and other areas. Biopolymers can be put to use to produce biodegradable composites with stronger thermal, barrier, and mechanical properties than today's biomaterials. For these novel composites, natural biopolymers would be the place to start (chitin and cellulose). The production of composites will be investigated in order to improve one's knowledge of phase compatibility and reinforcement dispersion in the biopolymer matrix. The most important polysaccharides that shape sustainable natural fibers are cellulose and chitin. We used glutaraldehyde, a cross-linking agent, to prepare and describe the chitin/cellulose composite in this analysis. FT-IR, XRD, DSC, and TGA quantities were used to classify the composite. The formulated composite was also used to illustrate defluorination, and the findings were examined.

### Introduction

Fluoride is the most common inorganic contaminant in India, its natural origin can be discovered in groundwater<sup>1,2</sup>. Fluoride contamination of drinking water has emerged as one of the most popular serious public health issues of the twenty-first century, as it has a direct impact on human health, including dental fluorosis and skeletal. The only practical solution to the problem of harmful fl uoride in drinking water is defluoridating the water. In the years since fluoride was discovered to be the cause of fluorosis, several approaches for removing fluoride from water and wastewater have been extensively investigated. The principles behind these methods are adsorption<sup>4-6</sup>, ion-exchange<sup>7,8</sup>, precipitation-coagulation process<sup>9,10</sup>, membrane separation electrolytic defluoridation<sup>11</sup>, Donnan dialysis<sup>12,</sup> and electrodialysis<sup>13-</sup> <sup>15</sup>. Among these technologies, adsorption is the most widely employed for removing fluoride from water. Biosorbent chitin is a kind of chitin. Adsorption processes that use biomaterials as adsorbents are referred to as biosorption. Chitin has received little research as a biosorbent, and fluoride biosorption is no exception.

However, when compared to other biosorbents, particularly chitosan, chitin's chemical tolerance, and cheaper cost may be significant benefits for its application in fluoride or other pollutant adsorption procedures. A biocomposite based on chitin and polymeric matrixes efficient of adsorbing fluoride from an aqueous medium has recently been created based on these benefits<sup>16</sup>. Because chitin and cellulose have comparable chemical structures, compatibility and homogenous mixing should be possible. In this study, we chitin/cellulose created а composite utilizing glutaraldehyde as a crosslinking agent. The composite was classified using FT-IR, XRD, DSC, and TGA measurements. The prepared composite was also used to illustrate defluorination, and the findings were discussed. **Experimental** 

### Material

All of the substances utilised in this research were analytical reagent grade. Chitin was purchased from India Seafoods Cochin, Kerala. Sodium fluoride and  $C_5H_8O_2$  were obtained from E. Merck India Ltd., Mumbai, India.



# Preparation of chitin/cellulose composite with C5H8O2 as a crosslinking agent

Chitin/cellulose binary composite the film was created by combining 1:1 chitin and cellulose solutions. One gram of Chitin was stirred for 18 hours in 100 mL 15% calcium chloride dissolved in DMSO. Cellulose was made into a paste with 50 mL water, and the two polymers were combined in a 1:1 ratio with 10 mL glutaraldehyde added as a crosslinking agent. The solution was rapidly agitated for one hour and kept at 5°C overnight to get a dry film.

### Characterization

The prepared composites were analyzed in solid-state using KBr pelletization and FT-IR in a broad wavelength range between 400 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>. A spectrophotometer from Perkin-Elmer was used. The NET Z SCH-Geratebau GmbH thermal analyzer developed a DSC thermogram. Vacuum desiccators were used to dry the samples, which were then powdered in a regular aluminum tray. 2.0 mg of this sample was heated in the DSC analyzer at a rate of 10 °K/min from 33 to 350 °C under continuous nitrogen atm purging. TGA was done on 2.0 mg of this sample, which was heated from 30 to 870°C at a rate of 10°C/min under nitrogen atm. Graphite-monochromatized Cu Κ radiation (K=1.54178Å) was used to obtain X-ray diffraction with a D/max-2200 X-ray diffractometer.

#### Experimental process of removal of F<sup>-</sup> ion

Batch tests with varying amounts of NaF were carried out to determine the level of adsorption. By varying the adsorbent dose, solution pH, and shaking duration of the adsorbent metal solution combination, each of the three parameters related to fluoride removal was examined separately. Using either NaOH or HCl, the pH of each solution was changed to a different value. An orbital shaker set at 250 rpm and operated at 30°C for varying periods of time was used to shake the stoppered bottles. The whattman filter paper was used to separate the adsorbates, and the liquid supernatant was examined using an ion-selective electrode for residual fluoride ion concentration. Triplicate runs were conducted with a deviation of less than 1% of all measures, assuring data repeatability.

### **Results and Discussion**

Characterization's main goal is to understand more about a material's efficiency, such as strength, durability, and thermal qualities. Characterization of cross-linked chitin bio-composites was carried out in this study to investigate their interacting group vibrations, thermal analysis, and crystallinity. In this part, we specify the characterisation of pure chitin and chitin/cellulose 1:1, 1:2, and 2:1 biocomposites in the company of  $C_5H_8O_2$  as the cross-linking agent.

### FT-IR studies

FT-IR spectroscopy is a great technique for qualitative investigation since, excluding optical isomers, each compound's spectra is unique. It's best for deciding identity, purity, and gross structural detail. Below are the FT-IR frequencies of pure chitin and chitin composites.



Fig. 1 FTIR Spectrum of pure chitin

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Fig. 2 FT-IR spectrum of chitin/cellulose (1:1)-GLU composite



Fig. 3 FT-IR spectrum of chitin/cellulose (1:2)-GLU- composite



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JCHR (2024) 14(1), 1799-1810 | ISSN:2251-6727



Fig. 4 FT-IR spectrum of chitin/cellulose (2:1)-GLU composite

When the FT-IR spectral descriptions of chitin/cellulose binary composites made with glutaraldehyde in different ratios (1:1, 1:2, and 2:1) were examined, it was found that the composites made with  $C_5H_8O_2$  as the cross-linking agent had more peaks<sup>17</sup>. The maximum absorbance at around 3428 cm<sup>-1</sup> was relocated lower wave number during composite creation due to O-H and N-H stretching vibrations, as seen in **Figs 1-4**. Furthermore, when comparing the FT-IR spectra of pure chitin with the absorption peaks of chitin/cellulose composites in the existence of  $C_5H_8O_2$ , the peaks expand owing to hydrogen bonding, and the rate of  $CH_2$  stretching and C-O stretching rises. The peak shift shows that the cross– linking agent glutaraldehyde had a good interaction with chitin/cellulose.

#### Thermogravimetric Analysis

When a substance is subjected to a controlled temperature programme, TGA is a method that calculates the mass of the material as a function of temperature.



Fig. 5 TGA thermogram of pure chitin





www.jchr.org JCHR (2024) 14(1), 1799-1810 | ISSN:2251-6727





Fig. 8 TGA thermogram of chitin/cellulose (2:1)-GLU composite

400

500 ature (\*C)

When composites (1:1, 1:2, and 2:1) were compared with pure chitin, the composites' temperatures for thermal breakdown and dehydration were lower, suggesting that chitin's thermal stability decreased marginally after composite formation. For the composites, a four-stage decomposition method was used to construct the thermogravimetric profiles. The key result in these systems was that composites decomposed at a lower temperature than pure chitin. This is an odd behavior since similar systems normally have higher thermal stability than pure polymers<sup>18-19</sup>, and this phenomenon could have something to do with crystalline or different morphologies between pure polymers and composites.<sup>20</sup>. The TGA results show that **Figs 5-8** when comparing chitin/cellulose composites in different ratios of 1:1, 1:2, and 2:1 with  $C_5H_8O_2$  as the crosslinking agent, because of the gradual breakdown of linkage and breaking of hydrogen bonds, the 1:2 chitin/cellulose composite containing  $C_5H_8O_2$  exhibited the greatest initial decomposition temperature. In general, the crosslinking agent enhances the composites' thermal stability.

#### Differential scanning calorimetry (DSC) studies

DSC is an analytical method that aids in the understanding of polymer thermal behavior. It assists in the determination of polymer, polymer mix, and polymer composite glass transition temperatures.

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Fig. 9 DSC thermogram of pure chitin



Fig. 10 DSC thermogram of chitin/cellulose (1:1) – GLU composite



Fig. 11 DSC thermogram of chitin/cellulose (1:2) – Glu composite

www.jchr.org JCHR (2024) 14(1), 1799-1810 | ISSN:2251-6727





Fig. 12 DSC thermogram of chitin/cellulose (2:1) – glu composite

Through the release of heat, the device appeared to be able to overcome the activation energy barrier in DSC, allowing trapped absorbed water molecules to be adsorbed by hydrogen bonding <sup>21</sup>. Both materials exhibit favourable molecular interactions and a strong sense of compatibility, as seen by the single glass transition. The restricted thermal motion of the polymer was blamed for the rise in glass transition temperature. As a consequence, various ratios of chitin/cellulose (1:1), (1:2), and (2:1) are stable in the prepared composite. This suggests that chitin and cellulose are compatible and that prepared composites have greater thermal stability than chitin. The glass transition temperature of chitin/cellulose (1:1)–  $C_5H_8O_2$  was found to be higher when the DSC curves of the different samples were

examined. As a consequence of the observations, it was determined that the chitin/cellulose hybrid prepared in a 1:1 ratio is highly thermally stable. Furthermore, the single glass transition temperature was obtained for each composite based on the DSC studies described above **Figs 9-12**. This clearly shows that in the existence of the  $C_5H_8O_2$  crosslinker, the heavy interaction was present in chitin/cellulose composites.

### X-ray diffraction studies

To investigate the shift in crystalline nature of solids, XRD patterns of various samples were calculated. The use of X-ray diffraction analysis to assess the crystallization of polymer matrices with different polymers is a valuable technique shows in **Figs 13-16**.



Fig. 13 XRD of pure Chitin

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2-Theta - Scale







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| JCHR (2024) 14(1), 1799-1810 | ISSN:2251-6727 |
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|  | S. No | Polymer          | $2\theta$ value | Percentage degree of |
|--|-------|------------------|-----------------|----------------------|
|  |       | composites       |                 | crystallinity (%)    |
|  | 1.    | Chitin           | 9°, 19°         | 22                   |
|  | 2.    | CT/CL(1:1) + Glu | 17°             | 26.45                |
|  | 3.    | CT/CL(1:2) + Glu | 17°             | 26.47                |
|  | 4.    | CT/CL(2:1) + Glu | 42°             | 34.78                |

The **Table 1** displays the XRD results of binary composites prepared with  $C_5H_8O_2$  as a crosslinking agent.

According to the results in **Table 1**, the X-ray diffractograms of the binary composite generated with a cross-linking agent show nearly two separate peaks at around 17° and 42°. The composites displayed a weaker and larger peak at roughly 2=20° when compared to pure chitin. This was due to a lack of crystallinity, which might have been produced by a hydrogen bonding disruption<sup>22</sup>. If the crystallinity of one polymer is decreased as a consequence of the presence of another polymer, the crystallinity of the other polymer will eventually decrease. The diffraction strength of composites decreased significantly with rising cellulose content at 2 value 20°. These findings suggested that the intermolecular interactions between the two substances in the composites caused the chitin to lose its crystalline regularity, indicating that the constituent parts of the composites were miscible. When the alginate content was raised, the crystallinity of carboxymethyl chitosan was shown to be lowered in a comparable fashion<sup>23</sup>.

**Table 1** summarizes the percentage crystallinity of chitin and chitin/cellulose composites, showing that the percentage crystallinity decreased as cellulose was additional to the composite. As a result, For the composite chitin/cellulose (1:1) - glutaraldehyde, it is suggested that there be greater amorphous existence, lower water vapour permeability, strong mechanical proportion, and enhanced gas barrier properties.

#### Factors influencing the adsorption of F<sup>-</sup> ion

The influence of different operational factors such as adsorbent dose, pH, and contact time was studied.

### Effect of contact time

Fluoride ion removal increased with increased contact time before equilibrium was reached, according to the results (**Fig. 17**). Other factors to consider are adsorbent dose and solution pH were maintained constant. The results showed that 180 minutes was the optimal contact period for full fluoride ion removal (88%).



Fig. 17 Percentage removal of F<sup>-</sup> ion using 1:1 chitin/cellulose composite at different time interval

#### Effect of adsorbent dose

According to **Fig. 18**, the dependency of  $F^-$  ion adsorption was explored by Increasing the number of

adsorbents is a good idea from 1 to 5 gms while maintaining other parameters (pH and contact duration) constant. It was revealed that increasing the adsorbent



dosage enhanced the removal effectiveness of the adsorbent. There was no additional increase in adsorption once a particular amount of adsorbent was added, according to the data. The optimal percent elimination of  $F^-$  ion was around 67.2 % at a dosage of 3 gms.



Fig. 18 Percentage removal of F<sup>-</sup> ions using 1:1 chitin/cellulose composite with different dosages of adsorbents

#### Effect of pH

As demonstrated in **Fig. 19**, the removal efficiency of the fluoride ion in the aqueous solution was impacted by pH. The results revealed that when the pH climbed from 4 to

9, fluoride ion removal peaked and thereafter declined. At pH 6.5, the fluoride ion elimination rate is the greatest about 79 %.



Fig. 19 Percentage removal of F<sup>-</sup> ion using 1:1 chitin/cellulose composite at different pH

### Conclusion

The polymer composites thus prepared were FT-IR spectral analyses that have been used to describe it. The spectra revealed the fingerprint of matching groups at hand in the two polymers involved in composite

synthesis. The identification of additional peaks related to hydrogen bonding revealed the development of stable composites. TGA and DSC data show that the CT/CL composites made with the crosslinker glutaraldehyde have high thermal stability. According to an X-ray

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JCHR (2024) 14(1), 1799-1810 | ISSN:2251-6727



examination, the inclusion of cellulose during composite synthesis lowered the crystallinity of chitin. The information that the produced composites have a lower percentage degree of crystallinity implies that they might be used as an effective adsorbent for F- removal from H<sub>2</sub>O. The adsorbent dosage was varied from 1g to 5g, and the contact period was varied from (1) 30, (2) 60, (3) 90, (4) 120, (5) 150, (6) 180, (7) 210, and (8) 240 minutes. The authority of pH on the adsorption effectiveness of the polymers was examined by altering the pH from 4 to 9. For the CT/CL composites, the findings demonstrated that a 3g adsorbent dosage was sufficient to treat the wastewater with a 180-minute contact period. According to the findings, fluoridecontaminated wastewater may be treated with properly prepared polymer composites. The prepared Chitincellulose composites prove to be an efficient candidate for the fluoride removal from water.

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www.jchr.org

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