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A Review on the Synthesis of Chitosan From Different Waterbodies Exoskeleton Species and Its Application in Treating Water/Wastewater

Kanzul Fikri Achsan[1], **Nor Faizah Razali**[1]*

[1]Department of Chemical Engineering Technology, Faculty of Engineering Technology,
Universiti Tun Hussein Onn Malaysia, 84600 Pagoh, Johor, MALAYSIA

*Corresponding Author Designation

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Abstract: Chitin is the second most abundant biopolymers in the world after cellulose. It can be found in exoskeleton, mollusk, fungi, and many others. Chitosan is the main derivatives of chitin. In this paper, a review on the synthesis of chitosan from different exoskeleton species, its characterization and application treating water/wastewater is discussed. The extraction of chitosan can be done by going through demineralization, deproteinization, and deacetylation process, with decolorization as the optional stage. The characterization of chitosan by Fourier Transform Infrared Spectroscopy (FTIR) was shown in this paper. From the FTIR spectra, several functional group of chitosan can be seen, like NH_2, amide group, C-O. The application of chitosan on treating water/wastewater was reviewed. Chitosan is used as bio-absorbent in treating the water/wastewater. From the data obtained, the use of chitosan can reduce significance value of constituents, and metals. The use of chitosan can reduce the turbidity of water/wastewater.

Keywords: Chitosan, Shrimp, Crabs, Snails, FTIR

1. Introduction

The discovery of chitin happened 30 years before cellulose [1]. It is a structural biopolymer, a component of cell wall of fungi and the component for crustaceans skeletal [2]. It is also known that chitin comprised the major component in arthropod exoskeletons, tendons and it's lining of its excretory [2]. Furthermore, it is also comprises in the respiratory and digestive systems, and also insect's cuticle [2]. Chitosan is the main derivatives of chitin and was introduced by Charles Rouget in 1859 [1]. It is a biological macromolecule that comprising of ß-(1, 4) linked N-acetyl-D-glucosamine units and can be found mostly in crustacean shells, exoskeleton insects, algae, and coral [2]. In recent times, the synthesis of chitosan has been widely used in many areas such medicinal, agricultural and wastewater treatment. Nowadays, the extraction of chitosan for commercial used are usually taken from crabs and shrimps waste from the food industries waste [2].

*Corresponding author: faizahr@uthm.edu.my

Chitosan has been proven useful to be used as flocculants for anionic waste streams. It has been used for removal of metal ions in acidic medium [3]. Chitosan has also been proven useful in colour removal in textile mill effluent [3]. In enhancing the synthesis of chitosan, ultrasonic has been introduced during deacetylation of chitin to improve its structure. When ultrasonication is used in the synthesis of chitosan, it will cause main chain scission at the 1,4-glycosidic bond without changing the degree of deacetylation of chitosan [4]. In the synthesis of chitosan, ultrasonic assisted deacetylation is considered as an effective and efficient method to produce chitosan that avoids further depolymerisation [5]. This is due to the fact that ultrasound wave will accelerate mass transfer and shatter the cell wall of an organism [5].

Fourier Transform Infrared Spectroscopy (FTIR) is a technology that is used for secondary protein structure characterization that offers precision that lies between the purely predictive and approaches molecular coordinate [6]. FTIR is used to determine the functional group in chitosan [7]. Therefore, it is recommended to utilize the shell waste in order to reduce total waste produced in daily lives. This paper will review the synthesis of chitosan from food waste like crabs, shrimps, and snails, and also the application of chitosan in treating water/wastewater.

2. Materials and Methods

This review's writing is compiled based on studies that are related to the synthesis of chitosan from crab shells, shrimp shells, and snail shells. The materials used are primary data, namely international and national journals, and secondary data, where the sources are taken from scientific articles, and research reports. The number of literature reviewed in this paper is 18 journals. The journals were taken from search references in Google Scholar, Science Direct, Elsevier, Springer Link, Research gate, MDPI, and other trusted journal websites ranging from the year 2017 until 2021. Research was conducted in English. Keywords used in searching the literature includes synthesis of chitosan from crabs, synthesis of chitosan from snails, synthesis of chitosan from shrimps, and in wastewater treatment, ultrasonic synthesis of chitosan.

3. Results and Discussion

3.1 Synthesis method of chitosan

The method of synthesis of chitosan from different exoskeleton species is reviewed in this section. Some of the exoskeleton shell used in synthesis of chitosan are blue crab, common shrimp, and rice conch snail. Table 1 shows the method of synthesis of chitosan along with its condition for several named species.

Table 1: Method and condition of chitosan synthesis

Species Name	Treatment Method	Condition	Reference
Gazami Crab *(Portunus trituberculatus)*	Demineralization	5 % HCl, Time:1 h	[8]
	Deproteinization	NaOH, urea, ultrapure water	
	Depigmentation	6 % NaOH, Time: 1 h, Temperature: 80 °C	
	Demineralization	4% HCl, Time: 1 h	
	Deacetylation	Ultrasonic, 50% NaOH, Temperature: 75 °C, Time: 3.5 h	
Blue crab	Deproteinization	2 % CaO, Time: 2 h	[9]

	Centrifugation	4000 rpm, Time: 15 min	
	Deacetylation	6 M NaOH, Time: 2 h	
Unidentified crab 1	Demineralization	0.68 M HCl, temperature: 30 ºC, Time: 6 h	[10]
	Deproteinization	0.62 M NaOH, Temperature: 30 ºC, Time: 16 h	
	Deacetylation	40 % NaOH, Temperature: 120 ºC, Time: 1h	
Unidentified crab 2	Deproteinization	1.25 M NaOH, Temperature: 27 ºC, Time: 3 h	[11]
	Demineralization	1.25 M HCl, Temperature: 80 ºC, Time: 5h	
	Deacetylation	0.5 M NaOH, Temperature: 100 ºC, Time: 2h	
Unidentified crab 3	Deproteinization	1M NaOH, Temperature: 25 ºC, Time: 24 h	[12]
	Demineralization	0.25 M HCl, Temperature: 25 ºC, Time: 15 min	
	Deacetylation	Conc. NaOH, Temperature: 80 ºC, Time: 1h	
Blue crab (*Callinactus amnicola)*	Demineralization	0.7 M HCl, Temperature: 65 ºC, Time: 3 h	[13]
	Deproteinization	1.2 M NaOH, Temperature: 65 ºC, Time: 30 min	
	Deacetylation	50 % NaOH, Temperature: 100 ºC, Time: 3 h	
Fresh mud crab (*Scylla serrata)*	Demineralization	0.1-0.9 M CH_3COOH, Time: 48 h	[14]
	Deproteinization	0.1 M NaOH, Temperature: 45-50 °C, Time: 2 h	
	Decolourization	200mL 10% NaOCl, Time: 30min	
	Deacetylation	250 mL NaOH, Temperature: 100 °C, Time: 2 h	
Common prawn (*Palaemon serratus)*	Demineralization	1 % CH_3COOH, Time: 4 h	[15]
	Deproteinization	2 N NaOH, 2 Time: h	

	Deacetylation	50 % NaOH, Time: 10 min	
	Demineralization	1 % CH_3COOH, Time: 4 h	
	Deproteinization	2 N NaOH, Time: 2 h	[16]
	Deacetylation	50% NaOH, Time: 10 min	
Omani shrimp	Demineralization	50 mL HCl, Temperature: 25-55 °C, Time: 1 h	[17]
	Deproteinization	50 mL 60 % NaOH, Time: 3 h	
	Decolourization	H_2O_2, Time: 1-5 h	
	Deacetylation	50 % NaOH	
White shrimp *(Litopenaeus vannamei)*	Demineralization	0.80 M HCl, Temperature: 27 °C, Time: 12 h	[18]
	Deproteinization	0.75 M NaOH, Temperature: 27 °C	
	Deacetylation	12.5M NaOH	
Whiteleg shrimp	Demineralization	1 L 1 M HCl, Time: 6 h	[19]
	Deproteinization	1 M NaOH, Temperature: 80 °C, Time: 3 h	
	Decolourization	Ethanol, Temperature: 70 °C, Time: 10 min	
	Deacetylation	12.5 M NaOH	
Mediterranean Sea Read shrimp	Demineralization	1.0 M HCl	[20]
	Deproteinization	1.0 M NaOH, Temperature: 80 °C, Time: 6 h	
	Deacetylation	12.5 M NaOH, Time: 12 h	
Unidentified shrimp	Deproteinization	10 % NaOH, Time: 1 day	[21]
	Deacetylation	50 % NaOH	
Rice Conch snail	Deproteinization	3.5 % NaOH, Temperature: 65 °C, Time: 2 h	[22]
	Demineralization	1,0N HCl, Temperature: 27 °C, Time: 2 h	
	Decolourization	Acetone, 0.315 % NaOCl, Temperature: 27 °C, Time: 30 min	
	Deacetylation	50 % NaOH, Temperature:100-150 °C, Time: 6 h	
Periwinkle snail	Deproteinization	4 % NaOH,	[23]

		Temperature: 80 °C, Time: 6h	
	Demineralization	5 % HCl, Temperature: 27 °C. Time: 1 h	
	Decolourization	Acetone, Temperature: 60 °C, Time: 3h	
	Deacetylation	50 % NaOH, Temperature: 30 °C, Time: 4h	
	Deproteinization	4 % KOH, Temperature: 80 °C, Time: 6 h	[24]
	Demineralization	3 % 1M HCl, Temperature: 30 °C. Time: 3 h	
	Decolourization	Acetone, Temperature: 60 °C, Time: 3 h	
	Deacetylation	50 % NaOH, Temperature: 30 °C, Time: 4 h	
Unidentified snail 1	Deproteinization	3 mL 1 M NaOH, Time: 2 h	[25]
	Demineralization	1.2 M HCl	
	Deacetylation	NaOH	

From the table, majority of the synthesis of chitosan undergo 3 major process which are deproteinization, demineralization, and deacetyaltion. Decolourization process is only optional process to be done in order to remove the colour of chitin, and reduce the odour. From there, the demineralization was done by treating the residue with HCl and there are two that used CH_3COOH during the process. Demineralization process was done to remove the mineral found in the shells. Deproteinization was done to remove the protein in it. Usually, the residue is deproteinized by treating it with NaOH. From these two processes, chitin are produced. In order to extract chitosan, the chitin must be treated with concentrated NaOH in a process called deacetylation.

3.2 Characterization of chitosan

Characterization of chitosan was done with FTIR analysis. Several FTIR spectra will be discussed here.

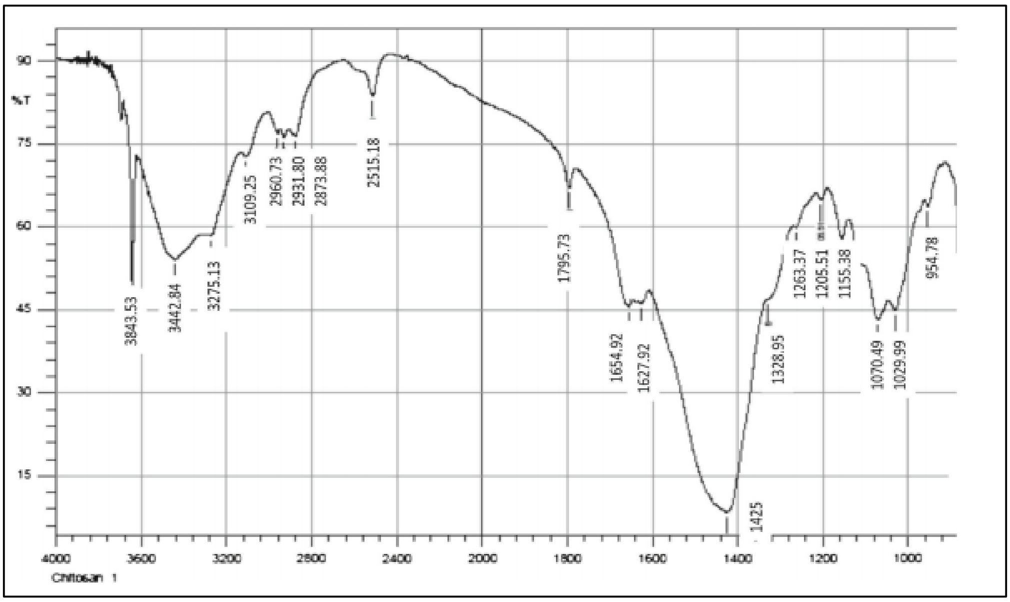

Figure 1: FTIR spectra of synthesized chitosan from unidentified crab 1 [10]

Based on Figure 1, it shows the FTIR spectra of chitosan from unidentified crab species. The FTIR spectra of chitosan from unidentified crab 1, the peak at 3305.99 cm^{-1}, 1645.28 cm^{-1}, 1070.49 cm^{-1} are due to the N-H symmetric stretching vibration that indicates the presence of amino (-NH_2) groups, N-H bending that identify 1° amines, C-N stretching for aliphatic amines [10].

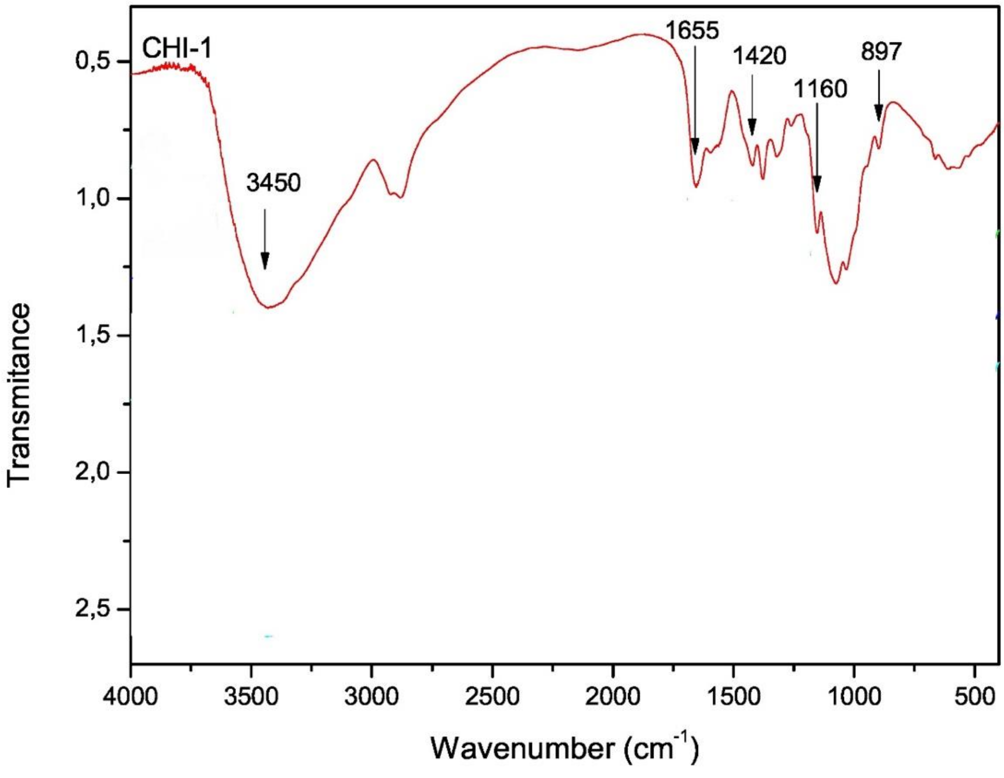

Figure 2: FTIR spectra from whiteleg shrimp [19]

Based on Figure 2, it shows the FTIR spectra of chitosan from whiteleg shrimp. From FTIR spectra on whiteleg shrimp in Figure 4.3 the peaks at 3450 cm^{-1}, 1655 cm^{-1}, 1580 cm^{-1}, and 1320 cm^{-1} indicates O-H stretching, Amide I group, -NH_2 bending, and Amide III group respectively [19].

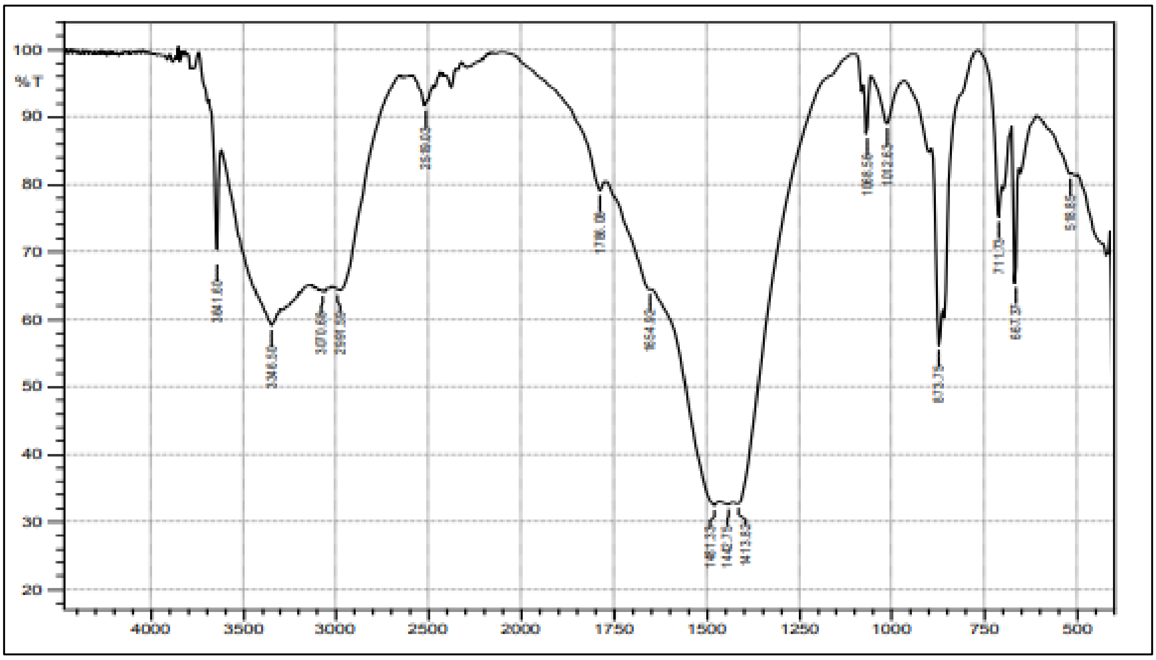

Figure 3: FTIR spectra from Rice Conch Snail [22]

Based on Figure 3, it shows the FTIR spectra of rice conch snail chitosan. At the band 3346.50 cm^{-1}, 2991.59 cm^{-1}, and 1654.92 cm^{-1}shows the function of OH and NH group, CH_2, and the presence of C=O amide respectively [22].

From the FTIR spectra shown above, the presence of certain functional group can be determined based on the band peak. From these figures, the existence of chitosan proved that the synthesized method were successful.

3.3 Chitosan in treating water/wastewater

The synthesized chitosan from unidentified crab 1 are used as adsorbent in treating the effluent. The study done several different experiments to examine the parameters affecting the adsorption of chitosan. Parameters done are effect of temperature, effect of pH, effect of dosage of chitosan, and effect of contact time [10]. The results are shown below, note that some of the values mentioned are approximate to the actual values, and * sign indicates approximate values.

Table 2: Effect of temperature on adsorption of chromium [10]

Temperature (°C)	Initial concentration of Cr (mg/L)	Final concentration of Cr (mg/L)
30	1345	1.20
40	1345	1*
50	1345	0.8*
60	1345	0.2089

Table 2 shows the effect of temperature on the adsorption of Cr by chitosan. From the table, the chitosan works better at a higher temperature where the chitosan adsorbed best at 60 °C, with Cr concentration of 0.2089 mg/L meanwhile at 30 °C, the Cr concentration was 1.20 mg/L. This is because, when the temperature is high, the rate of reaction of adsorption of Cr with chitosan increased [10].

Table 3: Effect of pH on Cr removal [10]

pH	Initial Cr concentration (mg/L)	Final Cr concentration (mg/L)
3	1345	0.07
4	1345	0.2*
5	1345	0.4*
6	1345	0.45*
7	1345	0.6
8	1345	0.995

Table 3 shows the effect of pH on Cr removal. From the table, as the pH change from 3 to 8, the adsorption change from high to low. This means, the Cr adsorption reached its highest peak at pH 3 with Cr concentration of 0.07 mg/L and it hits the lowest adsorption at pH 8, where the final Cr concentration was 0.995 mg/L. It is known that in acidic media, the free amine groups (−NH2) in chitosan are protonated to form −NH+ 3 groups. Chitosan with positive charges can adsorb anions by charge neutralization [10].

Table 4: Effect of dosage on Cr removal [10]

Adsorbent dose (g)	Initial Cr concentration (mg/L)	Final Cr concentration (mg/L)
1	1345	1.17
1.5	1345	0.6*
2	1345	0.5*
3	1345	0.4*
4	1345	0.37
5	1345	0.281

Table 4 shows the effect of dosage on Cr removal. From the table, it can be seen that the highest adsorption of Cr by chitosan are achieved when the dosage is at 5 g, where the final concentration of Cr are at the lowest value of 0.281 mg/L. The higher the dosage of chitosan used, the higher the adsorption. This is because, a high dosage of chitosan will provide a larger amount of reaction sites for the adsorption [10].

Table 5: Effect of soaking time on Cr removal [10]

Soaking time (h)	Initial Cr concentration (mg/L)	Final Cr concentration (mg/L)
0	1345	1000*
1	1345	0.9*
2	1345	0.9*
5	1345	2.0*
6	1345	3.0*
12	1345	0.9*
24	1345	1.0*

Table 5 shows the effect of soaking time on Cr removal. From the table, it shows that the soaking time of chitosan does not provide any remarkable difference in removing Cr. Within 1 hour, the removal efficiency was 99.90 %. Thus, the reaction reached its equilibrium point within 1 hour [10].

Chitosan from Rice Conch Snail has been used as biosorbent in absorption of methylene blue dyes. The result obtained from the experiment is shown in Table 6. Values shown are in approximate range.

Table 6: Results on effect of contact time in absorption of methylene blue dyes [22]

Contact time (h)	Capacity of adsorption (%)
1	58
2	55
3	65
4	70
5	80
6	85

From the Table 6, it shows that the adsorption capacity by chitosan are affected by the time of contact. It can be seen that at 6h the capacity of adsorption was at the highest, at 85.00 % [22]. It can be concluded that the chitosan can be used in treating water/wastewater, although further studies are need to be done.

4. Conclusion

In conclusion, the method of synthesis of chitosan was done with three treatments, demineralization, deproteinization, and deacetylation. These treatments are done by treating the shells obtained with either strong acid or base. For instance, HCl is used for demineralization treatment, and NaOH is used in deproteinization and deacetylation treatments. The characterization of chitosan through FTIR spectra shows that, certain functional group exist in the chitosan synthesized. Chitosan also can be used in treating wastewater by the adsorption method. In the future, the production of chitosan should be utilized from the food waste that come from the restaurant and markets. Further study need to be done in synthesizing chitosan from food waste from these places.

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