



## Schiff bases of chitosan

### An overview

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#### Abstract

Chitosan is a polysaccharide that has amino and hydroxyl groups and other functional groups that enable functionalization. Schiff bases, which can be identified using  $^1\text{H}$  NMR, FTIR spectrometry and thermal analysis, can be created when the C2-NH<sub>2</sub> group reacts with primary amines.

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**Keywords:** chitosan, Schiff base, spectral methods, thermal analysis

## 1. INTRODUCTION

Chitosan is a biopolymer comprised of N-acetylated glucosamine and glucosamine units connected by  $\beta$ -(1-4) glycosidic bonds (Scheme 1). It is obtained by the deacetylation of chitin. Chitin can be found in the shells of crustaceans, insects, and various other organisms such as fungi, algae, and yeast [1].

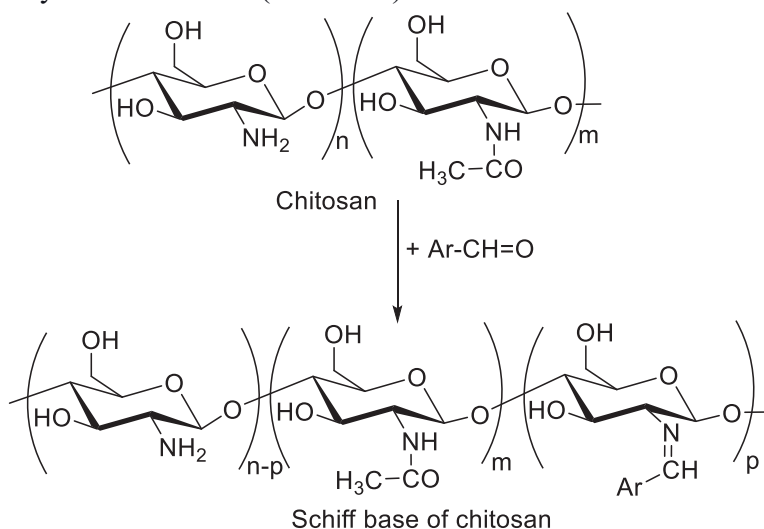
Chitosan molecules contain several functional groups, including C<sub>3</sub>-OH, C<sub>6</sub>-OH, C<sub>2</sub>-NH<sub>2</sub>, and acetyl amino and glycoside bonds. The acetylamino and glycosidic bonds are equally stable and not easily

broken. The C<sub>3</sub>-OH group is a secondary hydroxyl group that cannot rotate freely and has significant steric hindrance, making it difficult to react. On the other hand, the C<sub>6</sub>-OH and C<sub>2</sub>-NH<sub>2</sub> groups are more active chemically, and their presence in chitosan allows for the introduction of other functional groups through various molecular design strategies. They can participate in metal coordination, chemical coupling, chemical crosslinking, graft copolymerization or alkylation reactions. The C<sub>6</sub>-OH group can be esterified and carboxymethylated, too. The C<sub>2</sub>-NH<sub>2</sub> groups can be acylated and Schiff bases are formed. Glycosidic bonds can be cleaved by degradation [2].

This review article centres on the examination of chitosan's Schiff bases, along with their characterization and diverse applications.

### 1. Schiff bases of chitosan characterization

Schiff base compounds which have an imine group ( $-RC=N-$ ) can be produced by the reaction of a primary amine with an active carbonyl. Chitosan, a polymer containing amino groups in its chain, is susceptible to various chemical modifications, such as the creation of Schiff bases via the reaction with aldehydes and ketones (Scheme 1).



**Scheme 1.** Synthesis of Schiff bases of chitosan

Characterization techniques FTIR and <sup>1</sup>H NMR spectroscopy were used to characterize the biopolymeric Schiff bases of chitosan.

Chitosan and Schiff bases of chitosan show an intense band in the region of  $3400\text{ cm}^{-1}$  assigned to the stretching vibrations of the  $-\text{OH}$  and  $-\text{NH}_2$  groups of their structure. A band between  $3000$  and  $2880\text{ cm}^{-1}$  was assigned to symmetrical and asymmetric C-H stretch. Other characteristic bands of chitosan are shown at  $1690\text{--}1630\text{ cm}^{-1}$ ,  $1600\text{--}1560\text{ cm}^{-1}$ ,  $1430\text{--}1380\text{ cm}^{-1}$  and  $1200\text{--}1000\text{ cm}^{-1}$  which were attributed to C=O stretching of the acetamide group (amide band I), N-H stretching of acetamide group (amide band II), C-N deformation of amino group (amide group III) and O-C-O stretching of the glycopyranoside ring, respectively. The spectra of chitosan-Schiff bases derivatives show a new band at  $1650\text{--}1560\text{ cm}^{-1}$  due C=N vibrations. The bands ranging from  $1400$  to  $1500\text{ cm}^{-1}$  are due to the C-C stretching vibrations of the aromatic ring. The absence of the characteristic band of aldehyde in the region  $1660\text{--}1730\text{ cm}^{-1}$  indicates that there is no traceable residue of free aldehydes [1-9].

A significant change in the spectra was observed when comparing the Schiff bases to chitosan, with distinct  $^1\text{H}$  NMR signals characterizing each [5-6, 8-9]. The chitosan spectra and the Schiff base spectra exhibited a singlet between  $1.23$  and  $1.87$  ppm, attributed to the acetyl proton, and a singlet between  $1.91$  and  $2.98$  ppm, corresponding to the (H-2) proton of the pyranose ring. On the other hand, the Schiff bases demonstrated a sharp singlet between  $8.78$  and  $9.79$  ppm due to the imine group's proton ( $-\text{N}=\text{CH}-$ ), and different signals between  $6.0$  and  $10.2$  ppm, mainly resulting from the aromatic rings present in the Schiff bases.

Chitosan-Schiff bases were characterized by thermogravimetric analysis [1-5, 6-8]. Thermogravimetry of Schiff bases derived from chitosan shows that they have nearly the same decomposition temperature as the chitosan, indicating that Schiff bases are thermally stable. The studied Schiff base of chitosan has water elimination up to  $120^\circ\text{C}$ . The second degradation step is observed around  $200^\circ\text{C}\text{--}300^\circ\text{C}$ , due to the decomposition of the polymeric chains followed by the thermal degradation of a new material formed by the residual of the second stage of the degradation process.

**Table 1.** Spectral and thermal data of Schiff bases of chitosan

No	Schiff base of chitosan	Main IR absorption bands (cm <sup>-1</sup> )											<sup>1</sup> H NMR peaks ( $\delta$ /ppm)				TGA analysis	Ref
		VNH <sub>2</sub>	VOH	VC-H	VC=O	VNH	VC-N	V <sub>glyc</sub>	VC-N	VC-C	H- amide	H- imine	H-2	H-	H-Ar	Temp. (°C)		
1	Schiff base of chitosan with 4-chlorobenzaldehyde	3200-3200-3600	3200-3600	2919	1650	1575	1380	1150	-	-	-	-	-	-	-	~100°C 220-350°C t>350°C	[1]	
2	Schiff base of chitosan with benzophenone	3200-3600	3200-3600	2919	1650	1575	1380	1150	-	-	-	-	-	-	-	~100°C 220-350°C t>350°C	[1]	
3	Schiff base of chitosan with -ndole-3-carboxaldehyde	3200-3400	3200-3400	2960	1645	1565	1370	1000-1200	-	-	-	-	-	-	-	ambient- ~100°C 140-200°C	[3]	
4	Schiff base of chitosan with 1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde	3374	3374	2877	1660	1596	1381	1157	1565	1503	-	-	-	-	-	29-87°C 208-404°C 404-694°C	[4]	
5	Schiff base of chitosan with 1-Phenyl-1H-pyrazolo[3,4-b] quinoxaline-3-carbaldehyde	3374	3374	2877	1660	1596	1381	1157	1568	1505	-	-	-	-	-	28-98°C 207-434°C 434-695°C	[4]	
6	Schiff base of chitosan with -1-phenyl-3-(thiophene-2-yl)-1H-pyrazole-4-carbaldehyde	3439	3439	2900-2800	1644	-	1426	1057	1634	1400-1500	1.23	1.91	8.78	8.38	7.87	~92°C ~294°C ~530°C	[5]	
7	Schiff base of chitosan with 1-phenyl-3-(furan-2-yl)-1H-pyrazole -4-carbaldehyde	3439	3439	2900-2800	1636	-	1426	1157	1634	1400-1500	1.23	1.91	9.72	10.17, 9.41	8.0, 7.5	~35°C ~295°C ~530°C	[5]	
8	Schiff base of chitosan with 1-phenyl-3-(pyridine-3-yl)-1H-pyrazole-4-carbaldehyde	3439	3439	2900-2800	1644	-	1426	1057	1634	1400-1500	1.24	1.91	9.11	9.99, 9.39	8.67, 8.33 8.0, 7.5	~70°C ~304°C ~530°C	[5]	

**Table 1. Spectral and thermal data of Schiff bases of chitosan (Continuation)**

No	Schiff base of chitosan	Main IR absorption bands (cm <sup>-1</sup> )										'H NMR peaks (δ/ppm)			TGA analysis	Ref
		VNH2	VOH	VC-H	VC=O	VNH	VC-N	Vglyc	VC=N	VC=C	H <sub>amide</sub>	H-2	H <sub>imine</sub>	H-Ar		
9	Schiff base of chitosan with benzaldehyde	-	3416	2916	-	-	-	1111	1647	1475	1.77	2.88	9.63	7.3-7.6	-	[6]
10	Schiff base of chitosan with 4-(dimethylamino)benzaldehyde	-	3423	2874	-	-	-	1057	1598	1475	1.34	2.45	9.23	7-7.3	-	[6]
11	Schiff base of chitosan with 4-hydroxy-3-methoxybenzaldehyde	-	3425	2870	-	-	-	1022	1646	1507	1.68	2.78	9.26	6.6-7	-	[6]
12	Schiff base of chitosan with 5-Chloro-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde	3400	3400	2984	1690	1600	-	1160	1646	1466	-	-	-	-	55-100°C 260-428°C t>430°C	[7]
13	Schiff base of chitosan with 1-phenyl-3-methyl-5-p-nitro phenyl-1H-pyrazole-4-carbaldehyde	3400	3400	2991	1680	1600	-	1160	1646	-	-	-	-	-	-	[7]
14	Schiff base of chitosan with vanillin	-	-	-	-	1589	-	1026	1636	1520	1.87	2.97	9.47	7.2-7.3	55-230°C	[8]
									1458				6.8	230-320°C		
														320-600°C		
15	Schiff base of chitosan with ethylvanilin	-	-	-	-	1589	-	1026	1640	1520	1.87	2.97	9.45	7.2	55-230°C	[8]
													6.8	230-320°C		
														320-630°C		
16	Schiff base of chitosan with veratraldehyde	-	-	-	-	1589	-	1026	1641	1512	1.86	2.98	9.53	7.4	55-230°C	[8]
									1458				7.2	230-325°C		
													6.9	325-625°C		
17	Schiff base of chitosan with 2,4,6-trimethoxy benzaldehyde	-	-	-	-	1589	-	1026	1610	1520	1.85	2.95	9.79	6	55-220°C	[8]
									1458					220-330°C		
														330-625°C		
18	Schiff base of chitosan with 4-ethoxy 3-hydroxy benzaldehyde	-	-	-	-	1589	-	1026	1640	1512	1.87	2.97	9.48	7.3	55-225°C	[8]
									1458				7.1	225-325°C		
													6.9	325-625°C		
19	Schiff base of chitosan with salicylaldehyde	3368	3368	2880	1655	1598	-	-	1631	1498	-	3.1	9.78	6.8-7.6	-	[9]

## 2. Schiff bases of chitosan with antimicrobial activity

The antimicrobial activities of chitosan and its Schiff bases were tested against *Staphylococcus aureus*, *Bacillus cereus*, *Bacillus subtilis* as Gram-positive bacteria and *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella sp*, *Klebsiella pneumonia* as Gram-negative bacteria. Antifungal activity was tested on *Candida albicans* and *Aspergillus niger*. The antimicrobial activities of the chitosan derivatives were compared with those of chitosan. The antimicrobial activities of the Schiff bases of chitosan were stronger than those of chitosan in most microorganisms.

The Schiff bases of chitosan with vanillin, ethyl vanillin, veratraldehyde, 2,4,6 trimethoxy benzaldehyde and 4-ethoxy-3-hydroxy benzaldehyde showed better antimicrobial activities against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Aspergillus niger* than chitosan. Among all the above-mentioned chitosan derivatives, the Schiff base with vanillin was most effective against *Staphylococcus aureus* and *Bacillus subtilis*. Also, the Schiff bases of chitosan with vanillin and 4-ethoxy-3-hydroxy benzaldehyde showed the best antifungal activity against *Aspergillus niger* [8].

The chitosan Schiff bases prepared via coupling of chitosan with 4-chloro benzaldehyde and benzophenone [1], respectively, were more effective against Gram-negative bacteria than Gram-positive. Chitosan-4-chloro benzaldehyde Schiff base showed the highest activity against *Candida albicans*, *Pseudomonas aeruginosa* and *Bacillus cereus*. The activity of chitosan-benzophenone Schiff base against *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* and *Salmonella sp* was stronger than those of chitosan.

From the study of antimicrobial activity of the chitosan Schiff bases obtained by coupling of chitosan with indole-3-carboxaldehyde and 4-dimethylamino benzaldehyde, respectively, was observed the highest activity for the Schiff base of chitosan with indole-3-carboxaldehyde [3]. However, the chitosan Schiff base with 4-dimethylaminobenzaldehyde was more effective against *Staphylococcus aureus* and *Bacillus cereus* Gram-positive bacteria.

The inhibitory effect of chitosan Schiff bases resulted from the reaction of chitosan with 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-

carbaldehyde, 1-phenyl-3-methyl-5-o-cresyloxy-1H-pyrazole-4-carbaldehyde, 1-phenyl-3-methyl-5-(2-chloro phenyl)-1H-pyrazole-4-carbaldehyde, 1-phenyl-3-methyl-5-(p-Nitro phenyl)-1H-pyrazole-4-carbaldehyde and 3-methyl-1-phenyl-5-(piperidin-1-yl)-1H-pyrazole-4-carbaldehyde, respectively, against *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* was higher than those of chitosan. From the above-mentioned derivatives, 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde showed better antibacterial and antifungal activity (against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Candida albicans*) [7].

### 3. Pollutants removal with Schiff bases of chitosan

The Schiff bases of chitosan with 1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde and 1-phenyl-1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde, respectively were evaluated for the removal of hexavalent chromium from synthetic samples [4]. The optimum pH value for the absorption process of Cr(VI) was 6. The two Schiff bases of chitosan showed high removal efficiency. The best removal efficiency for 1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde was 96.78 % at the optimum dose of 150 mg/L. In case of 1-phenyl-1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde, the best removal efficiency was 98.85 % at the dose of 250 mg/L. From the study of the effect of chromium initial concentration it was observed that the removal efficiency decreased when the initial concentration of Cr(VI) increased.

The salicylaldehyde-chitosan Schiff base was used as an electropositive adsorbent in order to study the electrostatic adsorption behavior of dyes like methylorange, anionic xylenol orange, methylene blue and cationic basic fuchsin, respectively [9]. The results showed that the anionic dyes exhibited a much better adsorption performance than cationic dyes. The color of methylorange and xylenol orange (the anionic dyes) disappeared after 40 min while basic fuchsin and methylene blue (the cationic dyes) exhibited an insignificant adsorption performance.

## 4. CONCLUSION

Some chitosan's Schiff bases obtained by the reaction of C<sub>2</sub>-NH<sub>2</sub> group with primary amines were characterized using FTIR and <sup>1</sup>H NMR spectroscopy and thermal analysis.

The antimicrobial activities of chitosan and its Schiff bases were studied against *Staphylococcus aureus*, *Bacillus cereus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella sp*, *Klebsiella pneumonia*. Antifungal activity was tested on *Candida albicans* and *Aspergillus niger*.

The Schiff bases of chitosan with 1*H*-pyrazolo[3,4-*b*]quinoxaline-3-carbaldehyde and 1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline-3-carbaldehyde were studied for the removal of hexavalent chromium from synthetic samples and it was observed the best removal efficiency for 1*H*-pyrazolo[3,4-*b*]quinoxaline-3-carbaldehyde.

The Schiff base of chitosan with salicylaldehyde was used as an adsorbent in order to study the electrostatic adsorption behaviour of some dyes.

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