

Two step chitosan modification based on glycidylmethacrylate and triethylenetetramine - synthesis, characterization and cation removal

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Abstract – Chitosan biopolymer was chemically modified in two steps: (i) chitosan reacted with the epoxy ring of glycidylmethacrylate in water and (ii) the α - β -unsaturated part of glycidylmethacrylate modified chitosan reacted with triethylenetetramine in methanol in presence of triethylamine. The modified biopolymer characterized by elemental analysis, IR and solid state NMR for ^{13}C nuclei. This new biopolymer has ability in copper cation removal from aqueous solution.

Chitosan is a biopolymer of glucosamine repeating units, which is the N-deacetylated derivative of chitin. Recently, researcher demonstrated great interest in chitosan modification due to variety of its applications, such as, encapsulating agent for the sustained release of drugs, support for immobilization of enzymes and chelating agent for toxic metal removal from industrial effluents [1].

The present investigation based on chitosan modification by glycidylmethacrylate and triethylenetetramine. In first step a sample of 8.0 g of chitosan was suspended in 200 cm³ of water, followed by the slow addition of 5.3 ml of glycidylmethacrylate at 353 K, under mechanical stirring for 2 h. The final product was filtered, washed with water and ethanol. In a second step, a sample of 4.0 g reacted with 2.98 cm³ of triethylenetetramine under reflux with mechanical stirring for 72 h. The material obtained from the reaction was filtered and washed with ethanol.

The IR spectra for chitosan and modified chitosan are shown in Fig. 1, present bands at 3435 cm⁻¹ in (a), (b) and (c) is due to OH and NH stretching. Glycidylmethacrylate modified chitosan shows bands at 1719 and 1635 cm⁻¹, which are due to C=O and C=C stretching of glycidylmethacrylate moiety Fig (1-b). The band at 1635 cm⁻¹ disappeared when glycidylmethacrylate modified chitosan reacted with triethylenetetramine, that confirm the reaction of triethylenetetramine with vinyl carbon Fig (1-c).

^{13}C NMR spectra for chitosan biopolymer and modified chitosan are shown in Fig. 2. Glycidylmethacrylate modified chitosan shows peaks at 175, 137 and 128 ppm, which are attributed to the carbon of C=O and C=C bonds of glycidylmethacrylate moiety Fig. (2b). The reaction of triethylenetetramine with glycidylmethacrylate modified chitosan was confirmed by the disappearance of peaks at 137 and 128 ppm Fig (2c).

Carbon, nitrogen elemental analysis results for chitosan and for all modified polymers as well as the C/N relationship are summarized in Table 1. These listed results shows a decrease in the amount of nitrogen in the glycidylmethacrylate modified chitosan and an increase in reaction with triethylenetetramine biopolymers, respectively, which on comparison with the precursor chitosan confirmed such modification. The investigation demonstrated the successful modification of chitosan, which have the ability for copper removal from aqueous solution.

Table 1. Amount of nitrogen (N), carbon (C) and molar ratio for chitosan and chitosan derivatives (mmolg⁻¹)

Sample	C	N	C/N
A	33.86	5.27	6.42
B	36.69	4.21	8.71
C	34.04	5.70	5.97

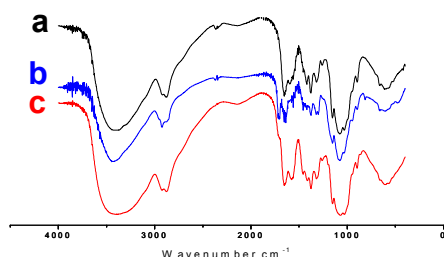


Fig 1: IR spectra of chitosan (a) glycidylmethacrylate modified chitosan (b) and triethylenetetramine modified chitosan (c)

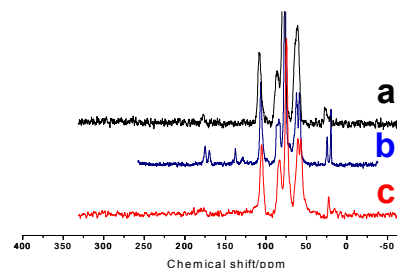


Fig 2: ^{13}C NMR of chitosan, (a) glycidylmethacrylate modified (b) and triethylenetetramine modified chitosan (c)

References

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