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FUNCTIONALIZATION OF CHITOSANE WITH CARBOXYL AND ORGANIC ACIDS

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Introduction

Chitin occupies second place after cellulose and is among the most widespread biopolymers in nature. Chitosan (made from chitin) is a versatile biopolymer and therefore its derivatives are used in various fields such as agriculture, food industry, cosmetics, water treatment and so on. Chitosan is also of interest in the pharmaceutical field because it is biodegradable, biocompatible and has a low toxicity.
The main objective of this paper was the synthesis of some derivatives of chitosan functionalized with dihydroxyfumaric acid and ascorbic acid.

Materials and methods

Chitosan – dihydroxyfumaric (Cht-DFH_4) was prepared in 3 phase. In first phase chitosan – diacetyl tartaric anhydride (C) was prepared according to the method described by *Chen et al* (2013) with some modifications, following the interaction of chitosan (B) with diacetyl tartaric anhydride (A). In second phase hydrolysis is carried out with NaOH (D), and after consumption of the base, the mixture is filtered, washed with acetone and dried. The obtained copolymer (E) is used to oxidize the step with the Fenton reagent to obtain the chitosan grafted with dihydroxyfumaric acid (F).
The functionalisation of chitosan was performed according to the figure 1:

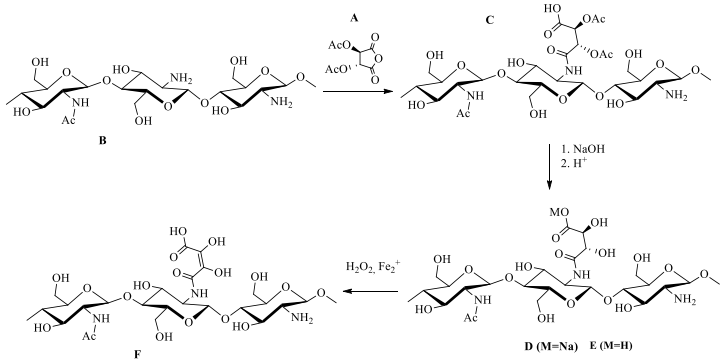

Figure 1. The reaction mechanism of chitosan grafting to dihydroxyfumaric acid

Chitosan ascorbate (Cht-AAs) was prepared according to the method described by *Hafsa et al* (2014) with some modifications. Weigh out 1.00 g of chitosan and dissolve

in 100 ml of 0.5% acetic acid, shake with the magnetic stirrer until the chitosan solubilizes. After that, ascorbic acid (1.10 g) is added and the mixture is heated for 3 hours at 100 ° C. After completion of the reaction time, the mixture is precipitated, filtered, dried under vacuum.
The mechanism of reaction between chitosan and ascorbic acid is represented in Schemes 2.

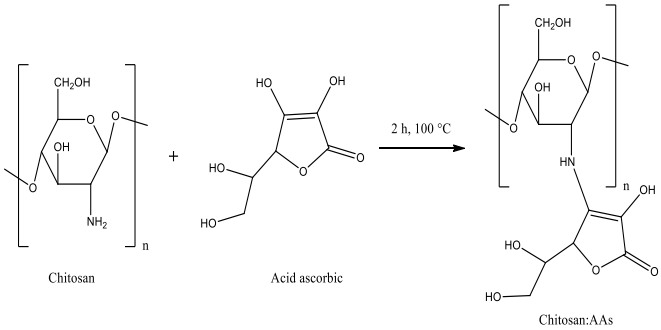

Figure 2. Funcționalizarea chitosanului cu acidul ascorbic, raport echimolar, t= 3 h, t= 100 °C

Results and conclusions
The anti-oxidant activity Cht-DFH$_4$ was determined by the DPPH test and it has been established that the antiradical power of the functionalized copolymer is 2.5 times higher than pure dihydroxyfumaric acid. These composites are to be used to inhibit the formation of N-nitrosamines in drug-nitrosation.
The anti-oxidant activity Cht-AAs was determined by the ABTS test and it has been established that the antiradical activity of the copolymer is 16.7% higher than pure ascorbic acid at the same concentration of AAs.

Table 1.Total antioxidant activity (ABTS • +) of the composite and pure AAs after

[AAs]				
C(AAs), $*10^{-4}$	0	2.03	2.0	2.03
	Cht ($2*10^{-3}$ M)	Cht-AAs	AAs pur	AAs pur
AAT	0.009	0.293	0.232	0.244

It has been demonstrated a functionalization of chitosan with dihydroxyfumaric acid. The antiradical power of the functionalized copolymer was determined. Intermediate and final compounds have been demonstrated by IR, UV and H^1-NMR spectra.
Chitosan was functionalized with dihydroxyfumaric acid and ascorbic acid, increasing the antioxidant power of natural reducers.