

# CHITOSAN CROSSLINKING BY GLUTARALDEHYDE AND EPICHLOROHYDRIN AND THEIR INTERACTION WITH $\text{Cu}^{2+}$ IONS IN AQUEOUS MEDIUM

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## INTRODUCTION

The ability of chitosan to complex metal ions is attributed to its chemical structure, mainly due to the presence of numerous primary amino groups which are proposed to be the active adsorption sites. The application of chitosan as a coadjutant agent in wastewater treatment has been tested, making it a promising material to be utilized in purification systems<sup>(1)</sup>, however chitosan is highly soluble in acidic aqueous media and its cross-linking with bifunctional agents, such as glutaraldehyde and epichlorohydrin, can significantly enlarge its application. In fact, the establishment of enough covalent cross-linkings among the chitosan chains prevents its dissolution and allows its utilization as membranes and also in packed columns. Glutaraldehyde is the most used cross-linking agent but some of the available amino sites of chitosan are consumed when the cross-linking reaction is carried out with this agent, decreasing its ability to complex metal ions. In this context, epichlorohydrin has been suggested as an alternative cross-linking agent since it will mainly react with the hydroxyl groups, preserving the amino sites which are essential to complex the metal ions. In the present work, a set of chitosan samples cross-linked with glutaraldehyde and epichlorohydrin are prepared and their abilities to complex  $\text{Cu}^{2+}$  ions in aqueous medium are compared.

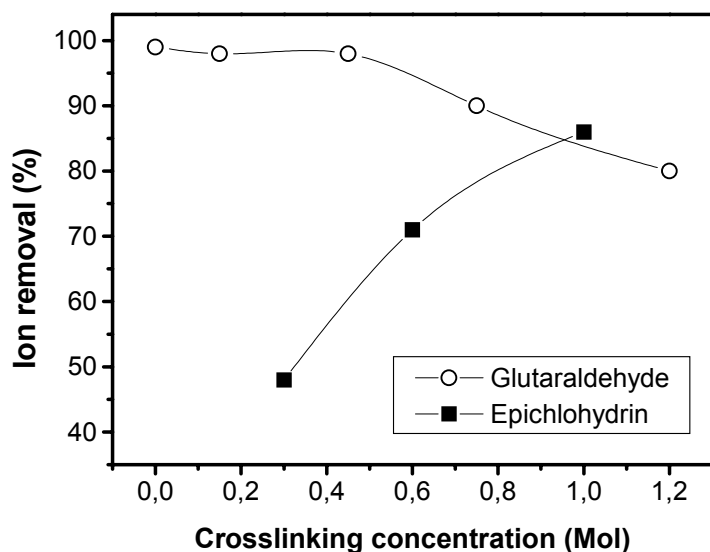
## EXPERIMENTAL

The chitosan sample employed in this work to prepare the cross-linked derivatives was obtained after the deacetylation of commercial chitin (Fluka/Biochemika from crab shells) and it was previously purified as described elsewhere<sup>(2)</sup>. To carry out the cross-linking of chitosan with variable amounts of glutaraldehyde (0.15, 0.45, 0.75 and 1.2 mol), the polymer was dissolved in methanol/aqueous acetic acid and the desired volume of glutaraldehyde dispersed in methanol/water was added. The reaction proceeded for 4 hours at room temperature with constant stirring, an excess of acetone was added to the reaction medium, the cross-linked derivative was recovered by filtration and it was then extensively washed with acetone. The dried product was ground and washed with methanol for 14 hours in a Soxhlet system. To carry out the cross-linking of chitosan with variable amounts of epichlorohydrin (0.3, 0.6 and 1.0 mol), the polymer was dissolved in aqueous acetic acid, and then sodium hydroxide and the desired amount of the cross-linking agent were added to the chitosan solution. The reaction proceeded for 4 days at room temperature with constant stirring, the reaction medium was then dialyzed against deionized water until the conductivity of the dialyzed attained that of the pure water, and the cross-linked derivative

was obtained after freeze-drying. To determine the ability of the cross-linked chitosans to complex  $\text{Cu}^{2+}$  ions, these derivatives were equilibrated with  $\text{CuCl}_2$  aqueous solution ( $C_0 = 5 \cdot 10^{-4} \text{M}$ ;  $\text{pH} = 5.2$ ) with constant stirring during 3 days at room temperature. After this period, the suspension was centrifugated and the concentration of  $\text{Cu}^{+2}$  ions in the supernatant was determined by absorption atomic spectrometry<sup>(3)</sup>.

## RESULTS

The plot of the percent removal of  $\text{Cu}^{2+}$  ions against the molar concentration of cross-linked agent employed to cross-link the chitosan sample is shown in the figure below. Following these results, it is concluded that the unmodified chitosan and its cross-linked derivatives



obtained in the presence of the lower amounts of glutaraldehyde were the most effective materials to remove the cooper ions from the solution. In fact, the increase in the excess of glutaraldehyde resulted in lower efficiency to complex the cooper ions, probably due to the consumption of amino sites by the cross-linking reaction and as a consequence of the decreased porosity of the material. In the case of the chitosan samples which were obtained after cross-

linking with epichlorohydrin, it was observed that the efficiency to remove cooper ions was strongly dependent on the stirring speed due to the much lower density of these derivatives as compared to the chitosan sample and to its derivatives cross-linked with glutaraldehyde. The increased efficiency of cooper ions removal with increasing amount of epichlorohydrin can be attributed to morphological effects and to the higher porosity of these materials as compared to the other chitosan derivatives studied in this work.

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