V Simpósio Ibero-americano de Quitina
Sociedade Ibero-americana de Quitina
Marzo, 2010, Santiago, Chile

STUDIES ON THE ULTRASOUND-ASSISTED DEACETYLATION OF ALPHA-CHITIN

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Chitin, a polysaccharide soluble only in unusual and toxic solvents, is composed by 2-acetamido-2-deoxy-D-glucopyranose (GlcNAc) units linked by beta-(1-4) bonds. The hydrolysis of the acetamide groups of GlcNAc units generates chitosan, a polymer which is soluble in moderately acid aqueous solution if its average degree of acetylation (DA) is lower than 40-50%.

This work aims the investigation of the high intensity ultrasound irradiation effects on the deacetylation of alpha-chitin. With this purpose, alpha-chitin was extracted from the cephalothorax of *Macrobachium rosembergii* and then it was submitted to the ultrasound-assisted deacetylation (USAD process) while suspended in 40% sodium hydroxide. The ratio chitin/sodium hydroxide was maintained constant in all experiments (0,044g/mL) while the process parameters, such as temperature, irradiation amplitude and duration, were varied. According to the reaction conditions the experiments were organized as Group I and Group II. In Group I the irradiation duration was fixed (30 min) as well as the reaction temperature (60℃) while the irradiation amplitude was varied (low, medium or high). In Group II the irradiation amplitude was fixed to high, the irradiation duration was varied (30, 45 or 60 min) and the temperature was allowed to increase as the process proceeded. In this case the temperature increased from 25 to 100ºC from the beginning to the end of the experiment, according to the irradiation duration. A Branson Sonifier 450S coupled to a ½' stepped probe was used in these experiments and the low, medium and high irradiation amplitude corresponded to $30\%<A_{max}<50\%$, $55\%<A_{max}<70\%$ and $75\%<A_{max}<95\%$, respectively.

The parent chitin and the chitosan samples resulting from the experiments of Group I and Group II were characterized by using infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-rays diffraction (XRD) and thermogravimetric analysis (TGA). The average degree of acetylation (DA) was determined by HNMR spectroscopy or by conductimetric titration while the viscosity average molecular weight (Mv) and average molecular weight (Mw) were determined by capillary viscometry and size exclusion chromatography, respectively.

The data from TG and XRD analyses reveal that the products obtained in Group I and II are less crystalline and thermically more unstable as compared to the parent alpha-chitin. According to the SEM analyses, and regardless of the reaction conditions applied in Group I and Group II, the ultrasound irradiation provoked important morphological changes on the surface of the chitin particles, decreasing the mean particle size and increasing the accessibility to the reactive sites. However, the production of chitosan was strongly affected by the irradiation duration and reaction temperature as the process yield (PY) was lower in Group I ($5\%<PY<20\%$) as compared to Group II ($64\%<PY<83\%$), table 1.

Table 1:Process yield and DA.

Group	Amplitude	Time(min)	Chitosan(%)	DA*(%)
Group 1	Low	30	5,8	-
	Medium	30	9,5	-
	High	30	20,8	-
Group 2	High	30	64,2	45
	High	45	70,3	32
	High	60	82,2	25

*Determinated only for the chitosan fraction.

Thus, it is concluded that the irradiation duration must be longer than 30min and the reaction temperature must be higher than 60^0C to produce chitosan by applying the USAD process to alpha-chitin. Indeed, it was observed from the results of Group II that the longest irradiation duration generates the highest process yield and the lowest average degree of acetylation of the resulting chitosan. Therefore, the average degree of acetylation of the chitosan samples of Group II was 45%, 32% and 25% for irradiation duration of 30, 45 and 60min, respectively. In contrast, regardless of the irradiation duration, severely depolymerized chitosan were produced as $1.4kDa<Mv<1.7kDa$ and $1.5kDa<Mw<2.3kDa$. According to these results one may conclude that the high intensity ultrasound irradiation of alpha-chitin suspended in 40% sodium hydroxide increased the accessibility to reactive sites promoting a more efficient deacetylation, however it also provoked the occurrence of severe depolymerization.

ACKNOWLEDGEMENTS

CNPq, Capes and Fapesp.

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