Intensification of Shrimp Shell Deproteinization Using Subcritical Water: Comparison of Continuous Ultrafast Reactors with Microwave Treatment

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A green strategy employing only water as solvent has been adopted to obtain protein hydrolysates from residual shells of *Litopenaeus vannamei* generated as waste during the production of this species by aquaculture. The goal was to produce a protein hydrolysate through the fractionation of waste biomass, eliminating the need for conventional alkaline treatments and avoiding the environmental and operational issues associated with the use of strong bases. Subcritical water (sCW) refers to the water in the temperature range of 100–374℃ where high pressure (up to 220 bar) is applied to maintain water in the liquid state. At sCW conditions, the physico-chemical properties of water change significantly in comparison with water at ambient conditions; non-polar compounds can be extracted due to the changes of electrochemical properties, such as the decrease of dielectric constant and increase of ionic product of water. The ionic product of water increased from 10^{-14} at ambient temperature to 10^{-12} under subcritical conditions, increasing the concentrations of H^+ and H_3O^- acting as an acid-like catalyst for hydrolysis reactions. Therefore, sCW can hydrolyze some compounds in matrices like shrimp shell [Liu et al., 2023], where proteins are released from the matrix and broken down into valuable peptides and free amino acids. A crustacean exoskeleton is constituted mostly by a three-layered cuticle of chitin (15-30%) with trapped minerals (40-60%), proteins (15-25%) and minor components like astaxanthin. A kinetic study has been performed with sCW using microwaves (Anton Paar Monowave™ 300), in the range 150-230ºC and holding times 0-18min (Fig. 1a). Operational conditions have been optimized to maximize protein extraction yield, leading to 67,5% of proteins at 209ºC and 5 min of holding time.

Continuous ultrafast reactors have successfully been used for the hydrolysis of cellulose and lignocellulose biomass [Martínez et al., 2019]. A suspension of biomass in water (5%w/w) is continuously pumped and mixed with a sCW stream (total flow rate up to 7,5 kg/h) in a "T" piece just before the ultrafast micro-reactor and a sudden expansion with a subsequent cooling down is performed after the reactor. The facility is designed to minimize exposition time of bioactives to high temperatures. In this work, the continuous ultrafast hydrolysis has been applied to marine biomass for the first time, and a kinetic study for protein extraction has been performed in the range 190ºC -270ºC and residence times 1-27s. Kinetic results are presented in Figure 1b, where a first-order kinetics model, assuming a two-stage process for protein extraction (first stage: protein solubilization in water, second stage: protein degradation), has been used to fit the experimental data (Fig. 1b).

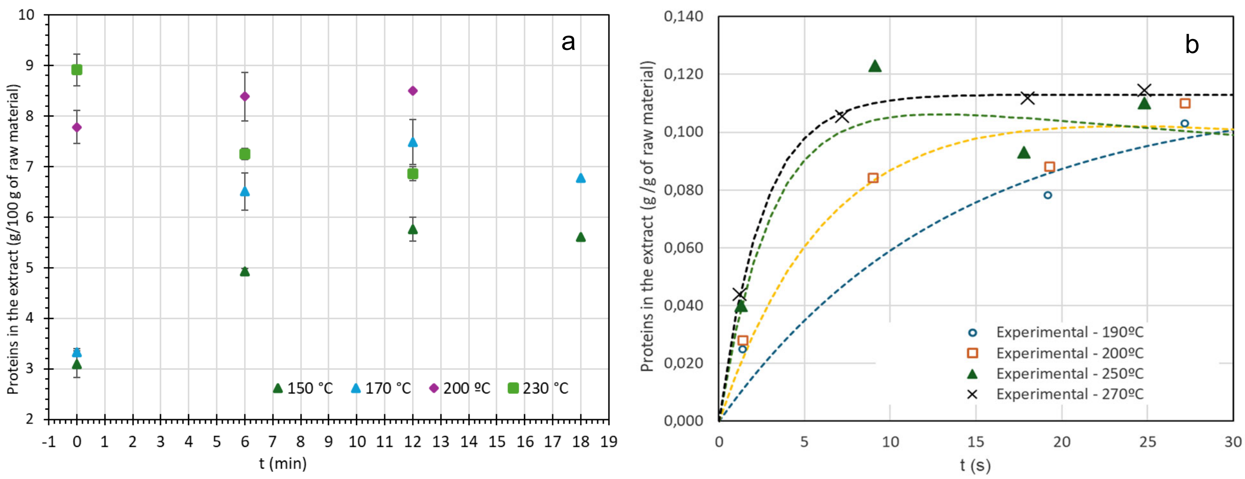

Figure 1. Extraction kinetics of proteins from shrimps' waste shells, a) using microwave treatment, b) using ultrafast continuous micro-reactors

Conclusions

Continuous ultrafast reactors did really intensify the deproteinization of shrimp shells with sCW. 90% of the protein is solubilized and partially depolymerized at 270ºC and 7s of residence time, being solubilized 26% of the initial shell mass. The free amino acid content in the extract accounts for less than 5% of the initial protein, while solubilized minerals were 12.2% of the ash content in the raw material. Residual solid is a biocomposite chitosan-$CaCO_3$, with 18,89% of C (41,5% is inorganic carbon from minerals) and 1,96% of N.

References:

Liu et al. 2023, The Journal of Supercritical Fluids 197, 105902-105912

Martínez et al. 2019, The Journal of Supercritical Fluids 143, 242-250