13th International Symposium on Supercritical Fluids
Montreal, Canada, May 15-18, 2022

Value-added Compounds Obtained from Shrimp Shells using Pressurized Fluids with Carboxylic Acids

Zhengjie Liu, Mashaer Matouri, Marleny D.A. Saldaña*
Department of Agriculture, Food and Nutritional Science
University of Alberta, Edmonton, T6G 2R3, AB, Canada
*marleny.saldana@ualberta.ca

1. Introduction

The conversion of food residues into value-added compounds has become imperative to alleviate the environmental impact associated to their final disposal[1]. Emerging technologies like subcritical water processing has shown to be a promising and environmentally friendly technique to obtain valuable compounds from biomass[2]. In 2020, the shrimp production reached 5.03 million tons worldwide with an expectation to increase to 7.28 million tons by 2025. Approximately 50-60% of solid waste, containing the head and shells, is generated as byproducts during the shrimp processing[3]. Large quantities of these byproducts are being wasted, resulting in the loss of valuable bioactive compounds with an increment of environmental pollution. While shrimp shells can be further processed to obtain value-added compounds such as proteins, chitin and chitosan for food, pharmaceutical and biomedical uses. However, the isolation of chitin from crustacean requires very high temperatures and long hydrolysis times. The main objective of this study was to determine the optimum conditions of temperature, pressure, time, and carboxylic acid concentration to hydrolyze chitin and chitosan from shrimp shells.

2. Materials and Methods

Shrimp shells were obtained from shrimps bought in the market in Oman. The materials used in this study including acetic acid, citric acid, malic acid, sodium hydroxide, hydrochloric acid, formic acid, acetonitrile, dichloromethane, 1-methylimidazole, acetic anhydride, sodium borohydride, myo-inositol, sulfuric acid, glacial acetic acid, and D-glucose (≥ 99.5 %) were acquired from Sigma Aldrich (Oakville, ON, Canada).

The hydrolysis of shrimp shells was carried out using subcritical water at a pressure of 50 bar and temperatures of 140, 180, 220, and 260ºC for 10, 20, 40 and 60 min. Then, 1%, 5%, and 10% citric acid was used as a solvent to hydrolyze shrimp shells at 260ºC for 40 min.

Reducing sugar, total protein, and amino acid contents in the hydrolysates were analyzed by dinitrosalicylic colorimetric method, Lowry's method, and OPA, respectively.

3. Results and discussion

The shrimp shells used in this study contain 48.65% of protein, 22.54% of ash, 18.25% of carbohydrates, 7.23% of moisture, 1.68% of carotenoids, and 1.65% of fat. These contents are similar to previously reported values by Sanchez-Camargo et al. (2011)[4]. However, moisture and fat contents were not consistent with values reported by Hongkulsun et al. [5] and Klomklao et al. [6], which could be due to the different type of shrimps used.

The highest protein yield of 34.20±2.86 mg/g shrimp shell (Fig. 1), and the highest amino acid yield of 49.11±1.09 mg/g shrimp shell (Fig. 2) were obtained by sCW hydrolysis at 260°C for 40 and 60 min, respectively. The amount of recovered protein by sCW treatment was consistent with the results obtained through the conventional method conducted by alkali extraction using 2.0 M NaOH (1:16 w/v) at ambient temperature (46.09± 1.85 mg/g shrimp shell of protein). The amino acid content was comparable to the results of the study by Quitain et al. [7]. In this study, a yield of 70 mg amino acid/g shrimp shell was reached by hydrolyzing shrimp shell proteins using water at a temperature of 250°C (at its corresponding saturated vapor pressure) for 60 min. The increase in the hydrolysis of protein with water at high temperature was due to the increase in the concentration of hydronium and hydroxide ions, as the dissociation constant of water increases at high temperature. The increase of hydronium and hydroxide ions could lead to the cleavage of proteins into smaller molecules of soluble protein and amino acids with lower molecular weight and higher quality of amino acids, which could also further break down the amino acids to form carboxylic acids with low molecular weight.

Fig. 3 shows that the addition of citric acid improved the hydrolysis of protein. Up to 34.7% protein was hydrolyzed by 10% citric acid at 260ºC for 40 min.

At hydrolysis temperatures between 140 and 220°C, only a small amount of reducing sugars was produced at all reaction times. At higher temperature, production of reducing sugar increased significantly. The highest amount of reducing sugar (40.96±0.54 mg/g shrimp shell) was reached at 260°C and 60 min of hydrolysis (Fig. 4). These values were comparable to the study reported by Uddin et al. [8]. In their study squid viscera were hydrolyzed at 180-280ºC by subcritical water and the highest yield of reducing sugar was obtained at 280ºC. The increase of reducing sugar yield by increasing the temperature is probably due to the cleavage of chitin into smaller molecules of glucosamine and glucose.

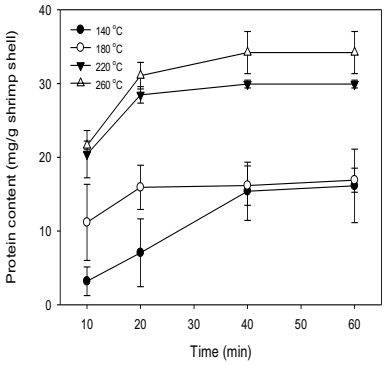

Figure 1. Effect of temperature and time on total protein content of hydrolysates.

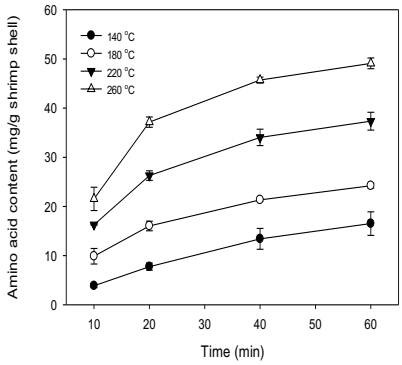

Figure 2. Effect of temperature and time on amino acid content of hydrolysates.

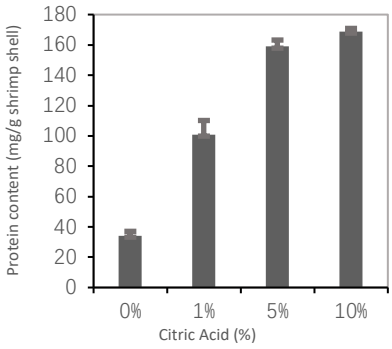

Figure 3. Effect of citric acid concentration on total protein content of hydrolysates.

4. Conclusions

In this study, the highest yield of total protein (34.20±2.86 mg/g shrimp shell) was obtained after 40 min of hydrolysis at 260°C. Higher amount of total amino acids (49.11±1.09 mg/g shrimp shell) was produced during hydrolysis at 260°C for 60 min. The addition of carboxylic acid improved the hydrolysis of protein up to 168.77±2.12 mg/g shrimp shell. The amount of reducing sugar had an increasing trend during hydrolysis, and its amount reached 40.96±0.54 mg/g shrimp shell at 260°C and 60 min of hydrolysis. Overall, subcritical water technology has shown to be a feasible and sustainable alternative to obtain bioactive components from shrimp shells.

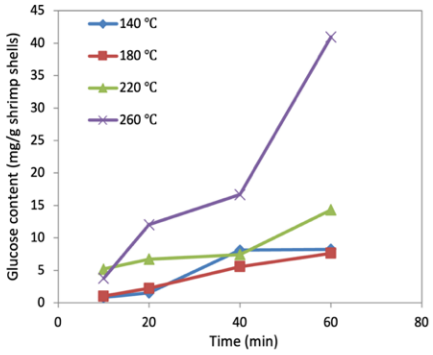

Figure 4. Effect of temperature and time on reducing sugar content of hydrolysates.

Acknowledgement: This study was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC, #04371-2019).

References

1. Saldaña, M.D.A., dos Reis Coimbra, J.S. & Cardozo-Filho, L. *Current Opinion in Food Science*, 2015, 5, 76-85.
2. Saldaña, M.D.A., Valdivieso-Ramirez, C.S. *J. Supercrit Fluids*, 2015, 96, 228-244
3. Nirmal, N.P., Santivarangkna, C., Rajput, M.S. & Benjakul, S. *Trends Food Sci Technol*, 2020, 1, 20-35.
4. Sánchez-Camargo, A.P., Meireles, M.Â.A., Lopes, B.L.F., & Cabral, F.A. *J. Food Eng,* 2011, *102*, 87-93.
5. Hongkulsup, C., Khutoryanskiy, V.V. & Niranjan, K. *J. Chem. Technol. Biotechnol,* 2016, *91*, 1250-1256.
6. Klomklao, S., Benjakul, S., Visessanguan, W., Kishimura, H. & Simpson, B.K. *J. Food Biochem* 2009, *33*, 201-217.
7. Quitain, A.T., Faisal, M., Kang, K., Daimon, H. & Fujie, K. *J. Hazard. Mater,* 2002, *93*, 209-220.
8. Uddin, M.S., Ahn, H.M., Kishimura, H. & Chun, B.S. *J. Environ. Biol,* 2010, *31*, 675-679.