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Proceeding Paper

Valorization of Bioactive Compounds from Shrimp Shells: Comparison between Ultrasound-Assisted and Subcritical-Water Extractions †

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Abstract: In the last years, shrimp consumption has increased resulting in massive amounts of wastes**.** In this study, different extraction techniques, namely ultrasound-assisted extraction (UAE), subcritical water extraction (SWE) and conventional extraction (CE), were tested to evaluate their efficiency to recover bioactive compounds from shrimp shells. SWE performed at 200 °C was the extraction technique that allowed the highest recovery of polyphenolic and carotenoid compounds (5.43 ± 0.17 mgGAE/g dw and 59.9 ± 1.0 μg carotenoids/g dw) as well as the highest antioxidant activity by ABTS and FRAP assays (7.93 ± 0.01 and 4.35 ± 0.31 mgAAE/g dw). These results demonstrated the potential of shrimp shells, which can be further incorporated in other products.

Keywords: shrimp shells; sustainability; antioxidants; sustainable extraction techniques

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1. Introduction

Shrimp shells are an abundant residue due to the increase of its consumption on a global scale and they are mostly disposed into landfills or back into the ocean being associated with several environmental issues [1]; therefore, it is urgent to find them a profitable end. Due to its chemical composition, shrimp shells can present themselves as an interesting source of antioxidant compounds, which can be used in high-value products [2].

Usually, the recovery of bioactive compounds from shrimp shells is performed using organic solvents, which can represent a limitation for use in food industries. In the last years, several environmentally friendly extraction techniques, such as such as subcritical water extraction (SWE) and ultrasound-assisted extraction (UAE), has been widely applied to recover bioactive compounds from different food wastes [3]. However, information is still limited on the effect of different solvents and extraction techniques on the extractability of bioactive compound from shrimp shells.

The main goal of the present work was to efficiently extract antioxidant compounds from shrimp shells waste. For that, two environmentally friendly extraction techniques, namely ultrasound-assisted extraction (UAE) and subcritical water extraction (SWE), were optimized and compared to conventional extraction (CE). Then, to determine which one of tested extraction techniques was more efficient, different colorimetric methods, namely total phenolic (TPC) and carotenoid content (TCC), ABTS radical scavenging activity and Ferric Reducing Antioxidant power, were applied.

2. Materials and Methods

2.1. Samples

Shrimp shells, kindly provided by *Marcabo* Company, were dried at 40 °C for 48 h, milled and stored at room temperature in plastic bags until further use.

2.2. Extraction Techniques

Samples were submitted to different extraction techniques:

- UAE: 3.0 g of shrimp shells were mixed with 60 mL of solvent (citric acid, water, ethanol, 50% aqueous ethanol or methanol) for 15 min at 25 °C [4];
- SWE: 7.5 g of shrimp shells were mixed with 150 mL of solvent (water or 50% aqueous ethanol) for 20 min at three temperatures (100, 150 and 200 °C) [5];
- CE: 1.5 g of shrimp shells were mixed with 30 mL of solvent (water, ethanol or 50% aqueous ethanol) for 20 min at 40 °C [6].

2.3. Extracts Charatrization

The TPC and antioxidant activity, evaluated by the FRAP and ABTS assays, were performed as previously described [7,8]. Results were expressed as milligrams of gallic acid equivalents (GAE) and ascorbic acid equivalents (AAE) per gram of dry weight (dw). TCC was also assessed by a colorimetric method and expressed in μg/g dw [9].

3. Results and Discussion

3.1. Total Phenolic Content

Figure 1 presents the TPC obtained for the analyzed samples subjected to the different extraction techniques.

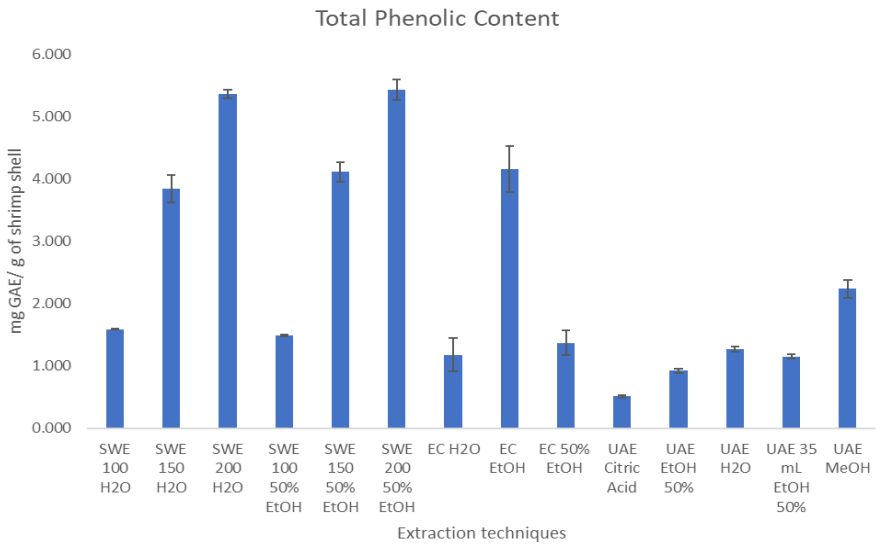

Figure 1. Total phenolic content obtained for shrimp shell extracts; results are expressed as mg gallic acid equivalents/g dry weight (mg GAE/g dw), mean ± standard deviation, n = 3.

For all the analyzed extracts, the TPC ranged from 0.51 ± 0.02 to 5.43 ± 0.17 mg GAE/g dw for UAE performed with citric acid and SWE performed with 50% aqueous ethanol at 200 °C, respectively. From the tested extraction techniques, SWE demonstrated to be the most effective, with TPC at least 5-fold higher than the values reported for the CE (1.18 ± 0.27 mg GAE/g dw).

Despite from the obtained results being lower than the ones reported in the literature [9], it must be highlighted that the differences in shrimp varieties as well as the extraction conditions applied, such as solvents, extraction time and temperature, may exert a huge influence in the amount of phenolic compounds recovered.

3.2. Total Carotenoid Content

Figure 2 presents the TCC obtained for the analyzed samples subjected to the different extraction techniques.

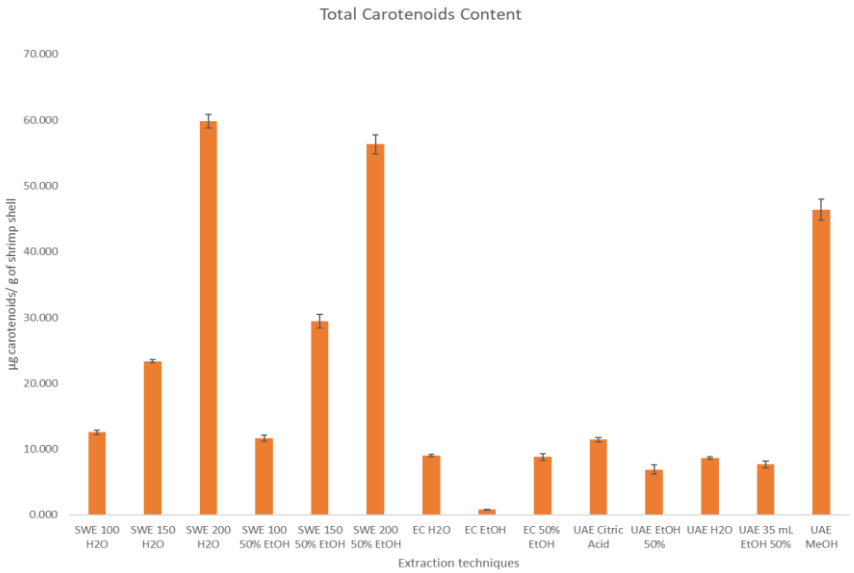

Figure 2. Total carotenoid content obtained for shrimp shell extracts; results are expressed as µg carotenoids/g dry weight, mean ± standard deviation, n = 3.

As previously observed for TPC, the highest amount of carotenoids were reported for the extracts obtained by SWE technique (59.9 ± 1.0 µg carotenoids/g dw). On the opposite, TCC was below 10 µg carotenoids/g dw for UAE and CE, except for the UAE performed with methanol. These values agree with the ones reported by Maia et al. [9], which demonstrated that TCC levels are influenced by shrimp variety, season, and sample location.

3.3. Antioxidant Activity

Figures 3 and 4 shows the obtained results for the antioxidant activity assessed by the ABTS and FRAP assays.

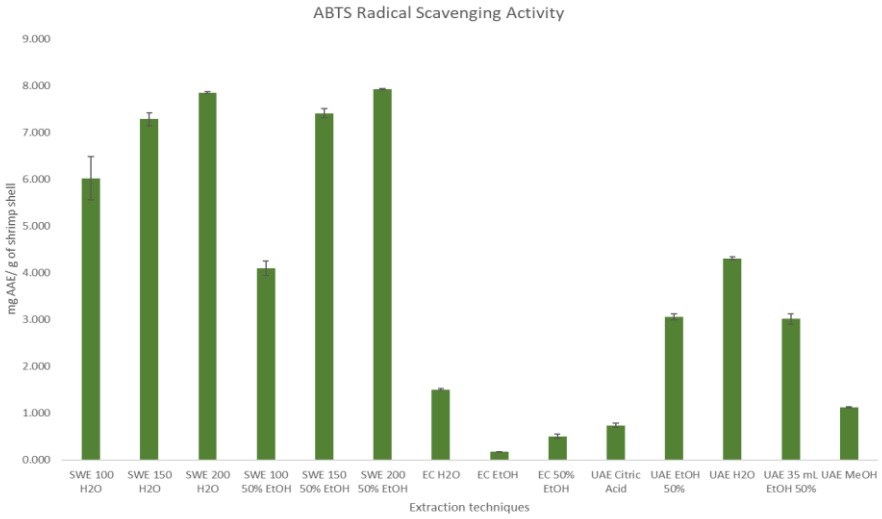

Figure 3. Antioxidant activity evaluated by ABTS assay obtained for shrimp shell extrcts; results are expressed as mg ascorbic acid equivalents/g dry weight (mg AAE/g dw), mean ± standard deviation, n = 3.

The highest antioxidant activity, evaluated by ABTS and FRAP assays (Figures 3 and 4), was registered for shrimp extracts obtained by SWE at 200 °C (7.93 ± 0.01 and 4.35 ± 0.31 mg AAE/g dw, respectively). On the contrary, extracts prepared by CE and UAE presented the lowest antioxidant activity demonstrating to be less efficient. The same correlation was observed for the TPC and TTC results, demonstrating the close relationship between the different spectrophotometric assays.

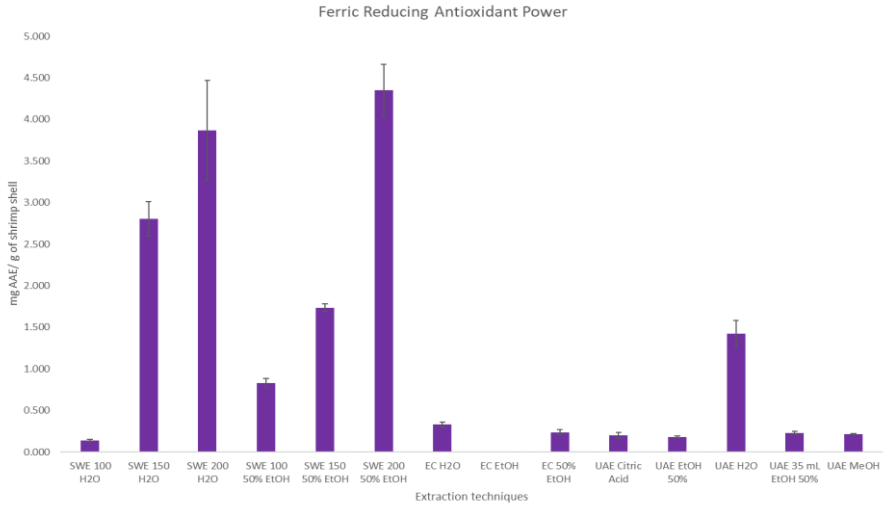

Figure 4. Antioxidant activity evaluated by FRAP assay obtained for shrimp shell extracts; results are expressed as mg ascorbic acid equivalents/g dry weight (mg AAE/g dw), mean ± standard deviation, n = 3.

In general, the extracts obtained by the application of SWE technique, namely at 200 °C either with water or 50% aqueous ethanol, presented the highest amount of bioactive compounds, as well as the highest antioxidant activity. However, additional characterization of the obtained extracts, namely by high performance liquid chromatography with diode array detection, is necessary to determine which individual phenolic compounds can be contributing to the described antioxidant properties.

Overall, the presented results demonstrated that SWE can be an efficient and green extraction technique for obtaining phenolic compounds from shrimp shells, which can be further incorporated in biofilms, creating an added value to this residue.

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Conflicts of Interest: The authors declare no conflict of interest.

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