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学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of extraction and concentration method for phenolics from tomato leaf residue using aqueous crude glycerol solution
（粗製グリセロール水溶液を用いたトマト葉残渣からのフェノール類の抽出と濃縮方法の開発）

Tomato (Solanum lycopersicum) is one of the world's most economically important crops with annual production of 150 million tons. Tomato leaf residue (TLR) removed regularly from the vines for fruit yield improvement is a rich source of phytochemicals, such as phenolics, and flavonoids that can be recycled for a wide range of applications. At the same time, in order to utilize crude glycerol (CG) without complex purification, application of CG as a solvent is becoming a hot topic. The main objectives of the research are: (1) to recover phenolics from TLR by the hydrothermal processes using aqueous CG solution; (2) to concentrate extracted phenolics by nanofiltration (NF); and (3) to evaluate the potential environmental impacts of whole processes using life cycle assessment (LCA).

1. Hydrothermal extraction optimization of phenolics from TLR

The first study evaluated the potential of aqueous CG solution for the recovery of phenolics in TLR. The extraction parameters, including the CG concentration, liquid-to-solid ratio, and extraction temperature, were optimized using response surface methodology (RSM) while the total phenolic content (TPC), 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging activity, and total flavonoid content (TFC) were selected as the response variables. The regression analysis results showed that TPC was significantly affected by extraction temperature ($p < 0.001$). This suggests that TLR releases large amounts of phenolics when exposed to high temperatures. The interaction between CG concentration and liquid-to-solid ratio ($p < 0.05$) also contributed significantly to TPC, as glycerol increased the polarity of water, thereby increasing the solubility of phenolics. After fitting, the optimal conditions are shown as follows: CG concentration of 39.14%, temperature of 130.87 °C, and liquid-to-solid ratio of 152.65 mL/g. Validation experiments conducted under the predicted conditions derived from the RSM ridge analysis showed that the actual values were quite close to those predicted, which confirmed the validity and adequacy of the predictive model. The high correlation indicated that a second-order polynomial model could be used to optimize the extraction of phenolics and flavonoids from TLR to maximize the total antioxidant activity.

2. NF concentration and quantification of phenolics

NF is a pressure-driven membrane technology which currently used to concentrate heat-sensitive phenolics with significant biological activity from natural extracts at low temperatures. The membrane's permeation performance and cleaning efficiency were evaluated at transmembrane pressures (TMPs) of 0.5, 0.6, 1.0, 1.2, 1.5, 1.8, and 2.0 MPa. Although a cross-flow filtration mode was utilized, some degree of fouling was observed regardless of TMP. The higher TMP can lead to a compression effect of the fouling layer and make cleaning procedures less effective. The contents of individual phenolics (allic acid, caffeic acid, ferulic acid, chlorogenic acid, naringenin, rutin, and quercetin) of crude extract, retentate, and permeate were determined by high-performance liquid chromatography. The results showed that quercetin was the main polyphenol in the extract, and its highest concentration of 113.74 mg/L in the concentrate was obtained with a pressure of 1.5 MPa and showed obvious differences ($p < 0.05$) with the values obtained at 0.5, 0.6, and 1.0 MPa.

3. LCA of the whole processes

LCA is a systematic method which could be used to evaluate the potential environmental impacts of low-temperature vacuum drying and mechanical grinding of TLR, hydrothermal extraction and NF concentration of TLR. It acts as a guide before scaling up for industrial applications based on ISO 14040 and ISO 14044. For the overall effects of human carcinogenic toxicity, human noncarcinogenic toxicity, mineral resource scarcity, and water consumption, the contribution of low-temperature vacuum drying was higher than 15%. The contribution of the mechanical grinding process was negligible across all categories. The most tedious process steps are those with high demands on electrical energy. The hydrothermal extraction process showed the highest environmental impact of all categories, accounting for more than 90% of the impact caused by marine eutrophication and land use. Additionally, NF is driven by pressure and does not require heating. It had approximately 7.5% effects on stratospheric ozone depletion and water consumption. An uncertainty analysis between electricity production from renewable sources and energy mixes of hard coal and natural gas was performed. Under most environmental impact categories, the electricity factor was a sensitive parameter and using electricity from renewable sources will be more environmentally friendly in future production.

4. Conclusions

In this study, the potential of aqueous CG solution to recover phenolics from the TLR was verified. The main component in the extract was quercetin. Membrane-based separation technology provided efficient recovery of phenolics from the crude extract in the cross-flow NF mode. A volume reduction of 50% was successfully achieved without a significant loss of the bioactive polyphenols, and the rejection rate of quercetin was kept at approximately 90%. An LCA based on laboratory-scale research showed that the largest contributor was the electricity used to heat the extraction system. For future improvement, electricity from renewable energy sources could effectively reduce the overall environmental effects.