Development of Integrated Process for the Recovery of Bioactive Compounds from Olive Mill Water
(オリーブミル水からの生理活性成分回収のための統合化プロセス開発)

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Olive production for obtaining olive oil is mainly concentrated in the Mediterranean countries with an average annual production around 3 million ton/year. Olive oil extraction of generates a large amount of by-products (15 million ton/year), especially olive mill water (OMW) requiring specific management to minimize its potential negative impact on the environment. This residue represents a serious environmental problem, not only due to the large amount produced (10 million ton/year), but also because of its phytotoxic effect. However, OMW is a rich source of polyphenols having a wide range of bioactivities. For that reason, the selective recovery of polyphenols from OMW provides the double opportunity to obtain bioactive compounds and to reduce its phytotoxicity.

In order to elucidate olive oil processing by detailed material balance, the mass flow analysis of olives during processing was carried out for a three-phase virgin olive oil extraction factory, whereas oil extraction yield was around 85.5 wt%. The effect of each industrial operation on the distribution of olive major components, water content, carbohydrates, oil, proteins and minerals were investigated and estimated material balances based on mass flow were obtained. Moreover, the material balance of polyphenols, major bioactive compound found in olive fruits, was also evaluated. Results showed an increase of polyphenols content during malaxation step, which was correlated to the several chemical and enzymatic reactions directly reflecting in the composition of final product. Distribution analysis of polyphenols in the oil and water phases, after oil separation by centrifugation, showed that a majority of these compounds are discharged in the two major by-products, OMW (73 wt%) and olive cake (23 wt%). The OMW has 20 times higher levels of polyphenols than that of olive oil. This is a particular advantage that OMW, which is an undesirable by-product of the olive oil manufacturing process, can be productively used.

In order to develop a suitable separation process, with low cost and high efficiency, for the recovery of polyphenols from OMW, we have selected membrane separation technology due its low energy consumption and high productivity. To elucidate the important factors that control the transport mechanism of polyphenols through nanofiltration (NF) membrane, we have chosen oleuropein, as typical major polyphenol compound containing in olive fruit in high amounts (60 to 90 mg/g dry weight), to conduct quantitative analysis of NF membrane performance.

The filtration of oleuropein model solution by NF membrane using different feed concentrations (0.3–0.9–2.7 kg m^{-3}) enables the correlation of a transport model, comprising of concentration polarization and osmotic pressure model, to membrane retention performance, which was evaluated using the Spiegler-Kedem model. Moreover, the osmotic pressure was observed and interpreted using van’t Hoff equation at different levels of feed concentration and applied pressure. The transport parameters reflection coefficient, water and oleuropein permeability, mass transfer coefficient were obtained experimentally, by developing transport models that relate the flux decline by increasing osmotic pressure. The obtained results can be useful for forecasting separation efficiency not only of oleuropein but other polyphenols as well. In the second part of membrane experiments, a study was conducted to examine Donnan effect on the rejection of oleuropein in aqueous solution by negatively charged polymeric NF membranes. Model studies were performed in order to provide quantitative process prediction data of oleuropein separation in aqueous solution by nanofiltration based on physical properties available. A model for the description of mass transport of oleuropein through NF membrane, based on the extended Nernst-Planck equation, was applied to predict mass transfer of oleuropein using feed solutions with various pH values. The generalized model allows a simple calculation of the separation efficiency not only of oleuropein but also of other polyphenols as well.

Following membrane basic research, we have proposed to analyse the potentialities of an integrated membrane system for the recovery and concentration of polyphenols from OMW. The proposed system included three membrane operations microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). After preliminary centrifugation of OMW which resulted in the reduction of 45% of total dissolved solid, the supernatant was subjected to a MF operation. This step allowed achieving 8% reduction of total organic matter. Moreover, most polyphenols were recovered in the produced permeate stream. The MF permeate stream was then submitted to a UF treatment. Most polyphenols initially present in OMW were recovered in the permeate stream using the discontinuous diafiltration mode, with 70% reduction on total organic matter. A concentrated solution enriched of polyphenols was obtained by treating the UF permeate using NF. In particular, the proposed integrated system allows the recovery of 88% of total polyphenols in the NF retentate, with hydroxytyrosol and oleuropein representing nearly 50% of the total polyphenols.

Besides membrane process, drowning-out process by ethanol was found useful to achieve the main target for the recovery of polyphenols from OMW, using clean technologies, for obtaining a polyphenols concentrate from OMW was developed. The process integrate centrifugation, evaporation and drowning-out separation process, for the isolation of polyphenols from the total solids present in OMW based on the solubility behavior changing after addition of ethanol, a food-grade solvent. Furthermore, batch evaporation was carried out for the regeneration of ethanol, which can be reused in the process. Experimental data demonstrated evidence of successful application of a novel and efficient process for the recovery of polyphenols from OMW to obtain bioactive compounds of interest for foods, cosmetics, or pharmaceutical industry.

Conceptual work done for the evaluation of the present process was been considered for industrial application using process simulator and design tools, the integrated process was decomposed for two sections: pretreatment section for the preparation of raw material to the next purification section. Results from economic analysis indicated that the throughput of main product polyphenols, around 33 kg/batch, which corresponds to an annual throughput of polyphenols around 21 tons, was obtained after optimization of equipment time occupancy. The economic evaluation of the profitability gained during investment in such project could be a real profit in the economic view: around 4 years needed to payback the total capital investment (~ 3 million USD).

Considering these material balance results, the annual production of olives in Tunisia, olive oil production and the proposed process was coupled and the mass balance of main products (olive oil and recovered polyphenols) indicated that the revenue in the sector of olive oil could be enhanced 3.26 times, by an useful application of a simple and efficient process for isolating polyphenols from OMW, hence, obtaining value-added biomolecules of interest for food, cosmetics and pharmaceutical applications.