EXECUTIVE SUMMARY

This report describes the development of a membrane-assisted solvent extraction process for the recovery of valuable antioxidants from wastewaters. Specifically, in this project, the wastewaters were derived from olive production. These wastewaters are produced in quantities in excess of 1 m^3 per ton of olives produced for table consumption (as opposed to oil). They present a significant environmental disposal problem because they have a high organic load and contain high concentrations of diverse phenolic compounds which do not degrade easily. However, the low molecular weight phenolics, of which the principal compound is hydroxytyrosol, have high antioxidant and other biological activity, and are thus of interest to the nutraceutical, food and cosmetics industries. Pure hydroxytyrosol, such as is used for research purposes, is of extremely high value. At present, its market value is approximately US$1000/gram.

The objective of this consultancy project was to design, construct and evaluate a small-scale, portable membrane-assisted solvent extraction system which could be used on-site to recover valuable phenolic antioxidants from the seasonably produced olive wastewaters at different locations. Extraction of these compounds has the additional benefit of reducing the COD of the wastewater by up to 30%, with the result that the residual wastewater presents less of an environmental burden in terms of subsequent treatment and disposal.

The research was based on the outcomes of a previous WRC-funded project (K5/1366) entitled "Development of a customised bioreactor for the bioremediation of organic-containing effluents and conversion of constituents to high value chemicals" in which one important result was the demonstration of the potential value of hydroxytyrosol and its availability from olive wastewaters. The membrane-based system was developed to selectively extract the low molecular weight phenolic components directly from the wastewater. The membrane-based system has numerous advantages over conventional solvent extraction systems, and in addition, is of small scale and is thus portable, meaning that extractions can be performed on site where the wastewater is produced.

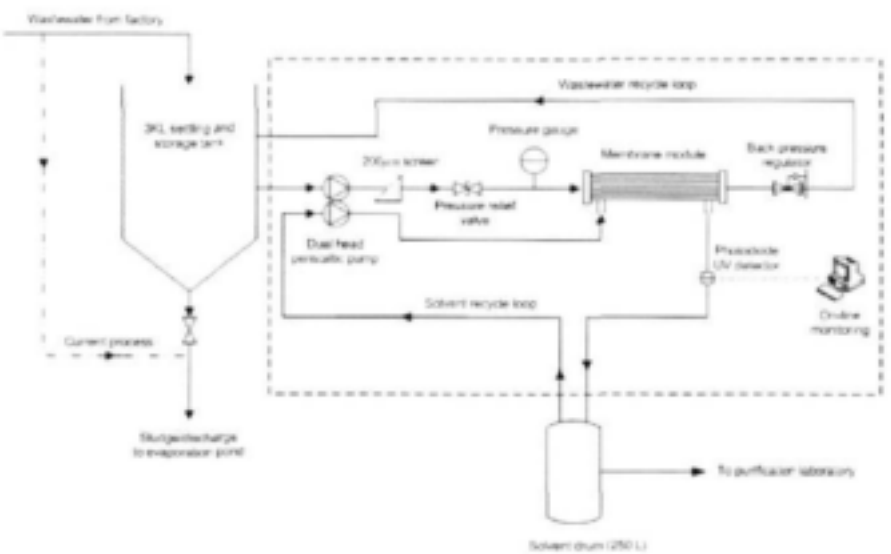
Mass transfer coefficients and associated extraction rates were investigated by means of numerous practical experiments and modelled based on hydrodynamic conditions and other pertinent factors. Calculation of the overall mass transfer coefficient for an extracting solute in a membrane module is a relatively complex mathematical problem due to the variation of concentration driving force along the axial length of the membrane, which is affected by flow rates, concentrations, distribution coefficients and time. The model chosen here was the most applicable for the operating conditions used in batch operation.

The pilot-scale system was designed to be portable and light, as shown below. In operation, it is anticipated that olive production wastewaters will be stored and sedimented on-site in a holding tank. After sufficient settling, the wastewater will be pumped through the lumen side of the membrane module, while the extracting organic solvent (ethyl acetate) is pumped through the shell side, both by means of a dual head peristaltic pump.

Prototype extraction module:

In the process, the wastewater and solvent are both recycled to their respective reservoirs. In this way, the wastewater and solvent are "contacted" in a non-dispersive manner within the membrane, allowing for the diffusion of phenolic antioxidants from the wastewater, across the membrane, and into the solvent. An inexpensive photodiode UV detection system has been designed to measure the on-line concentration of the phenolic antioxidants in the solvent stream. When this reaches steady state, the saturated solvent drum is replaced with fresh solvent. The product-rich solvent drums are then taken away for product and solvent recovery.

The pilot-scale membrane extraction system and process:



The process parameters were investigated in detail, including measurement of distribution coefficients, optimisation of flow rates, pH conditions, and solvent: wastewater ratio. The total yield of hydroxytyrosol, as exemplified in extraction of 10 L of wastewater, extracted four times with a solvent: water ratio of 1:10, and using a total of 4 L of solvent, was 5.89 g. It is thus possible to anticipate a yield of at least 1 g of hydroxytyrosol per litre of solvent used.

CONCLUSION AND PROJECT OUTPUTS

The membrane-assisted solvent extraction system was shown to be a viable method for the recovery of valuable antioxidants from olive wastewaters. The simplicity of the system and its numerous advantages compared to conventional liquid/liquid extraction, in addition to its portability, make for an attractive business case. A provisional patent for the extraction system and procedure has been filed.

Membrane-based solvent extraction is a novel emerging technology that promises a viable and cost-effective alternative to conventional extraction technology thanks to the rapid advances in membrane sciences, and has many other possible applications besides for that discussed here.

RECOMMENDATIONS

In this study, experiments were performed in a recycled batch manner, as indeed have the majority of experiments reported so far in the literature. The reason for this is that it is relatively easy to determine mass transfer coefficients in this manner, and to investigate parameters that affect the mass transfer coefficient. While the recycled batch process is satisfactory, for optimal industrial application a continuous system is desirable. Such a system would ideally be able to almost completely extract the wastewater in a single pass, using the minimal amount of solvent. However the operation would then be significantly more complex and further development is required here. Notwithstanding the above, the current batch recycled system is quite capable of being used for commercial purposes, and although not the optimal solution in terms of process, it is considered to be a simpler and better option than conventional liquid/liquid extraction for the on-site recovery of valuable antioxidants from olive-derived wastewaters.

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