IMPLEMENTATION OF A GENERIC MEMBRANE-BASED SYSTEM FOR BENEFICIATION AND TREATMENT OF AGRO-INDUSTRIAL WASTEWATER

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IMPLEMENTATION OF A GENERIC MEMBRANE-BASED SYSTEM FOR BENEFICIATION AND TREATMENT OF AGRO-INDUSTRIAL WASTEWATER

Report to the
WATER RESEARCH COMMISSION

by

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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.

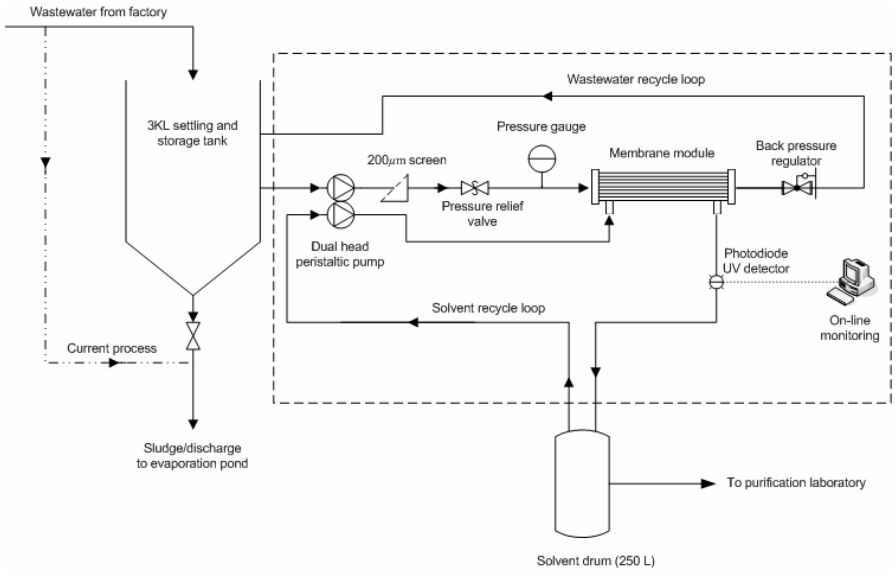
Mass transfer coefficients and associated extraction rates were investigated by means of numerous practical experiments and modelled based on hydrodynamic conditions and other pertinent factors. Calculation of the overall mass transfer coefficient for an extracting solute in a membrane module is a relatively 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.

ACKNOWLEDGEMENTS

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"Implementation of a generic membrane-based system for beneficiation and treatment of agro-industrial wastewaters"

The Reference Group responsible for this project consisted of the following persons:

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CHAPTER 1

1.1 BACKGROUND AND INTRODUCTION

WRC report 1361/1/06 described the development of two technologies for the beneficiation and bioremediation of olive-derived wastewaters, based on which a short research consultancy was established in order to further develop these technologies. Specifically, a membrane-based solvent extraction system was developed to recover valuable phenolic antioxidants from the olive wastewaters. A submerged membrane bioreactor is also described in report 1361/1/06 for the subsequent biodegradation of the wastewater. However, due to time constraints it was not possible to further develop or investigate this avenue, and thus this report deals exclusively with the extraction system.

Olive-derived wastewaters were discussed in detail in report 1361/1/06. In brief, these are darkly-coloured phenolic wastewaters with a complex composition and high organic load (COD can reach up to 200 000 $mg.L^{-1}$). Total phenol concentrations can reach 10 000 $mg.L^{-1}$; this includes low molecular weight monomeric phenols (< 8 kDa), and higher molecular weight polyphenols, tannins and lignin- and humic-like substances. The wastewaters are problematic in terms of treatment and disposal, as they are resistant to biodegradation, and have a high polluting capacity in the environment. Currently in South Africa, they are mostly disposed of in evaporation ponds.

The low molecular weight phenolic components are of interest because they exhibit powerful antioxidant activity, as well as having other biological activities such as antimicrobial and anti-inflammatory. Hydroxytyrosol (3,4-dihydroxyphenyl ethanol), in particular, occurs in the olives, olive oil and the associated wastewaters as the main low molecular weight phenolic component. Its biological activity has been extensively researched (see report 1361/1/06). It is thus of considerable economic interest to recover this compound from the olive wastewaters, where it can occur in concentrations in excess of 1 $g.L^{-1}$. Such an extract can be utilised as a nutraceutical, or as a natural preservative

for foodstuffs or cosmetics. Currently, pure hydroxytyrosol used for research has a market value of around US$1000/gram.

There are two predominant methods for the recovery of phenolic compounds from aqueous streams; these are liquid/liquid extraction and solid phase extraction, as discussed in WRC report 1361/1/06. Solid phase extraction was shown to be unsuitable for the extraction of certain olive wastewaters, particularly the brined olive fermentation wastewater from the production of table olives, and therefore liquid/liquid extraction was investigated. A novel extraction method incorporating the use of a membrane system was then investigated, and was shown to have considerable potential. Membrane-assisted solvent extraction is an emerging technology that offers an appealing alternative to conventional liquid/liquid solvent extraction systems such as mixer-settler units or contacting towers.

Membrane-assisted solvent extraction is similar to liquid/liquid extraction, except that the aqueous (wastewater) phase and the immiscible solvent (extracting) phases are not directly mixed; they are separated by a hydrophobic membrane through which the desired solute diffuses, but the liquid phases remain separated by the membrane. The main advantage of this approach is that subsequent separation and decanting of phases (as in conventional liquid/liquid extraction) is not required, as the phases are not directly dispersed within each other. In effect, a small membrane module replaces the large multi-stage mixer-settler or tower-type contacting systems used for conventional liquid/liquid extraction. There is thus a significant reduction in capital and processing costs compared to conventional extraction methods.

There are also numerous other advantages associated with the membrane assisted approach:

- Interfacial surface area through which mass transfer between the two phases occurs is very large (per unit volume), due to the use of membrane modules that have very high packing densities. In fact, the contact area can be 500 times greater than directly dispersed (conventional) systems, which leads to high extraction rates (Gableman and

Hwang, 1999). In addition, the contact area remains independent of process conditions such as phase flow rates.

- Phase flow rates can be independently controlled and optimised because there is no danger of flooding or washout as in conventional systems.
- The formation of mixed-phase emulsions and foam is avoided as the phases are not in direct contact. Emulsions are problematic in conventional processes because they are difficult, time-consuming and expensive to separate (centrifuges etc.).
- The contacting equipment contains no moving parts.
- There are no significant pressure requirements, and therefore only small pumps are required and energy costs are low.
- Scale-up of membrane systems is straightforward (linear), therefore increased capacity is achieved by simply adding membrane modules. Scale-up with conventional equipment significantly more complicated.
- Aseptic operation is possible.
- Solvent hold-up is low.

Membrane-assisted solvent extraction has been investigated for several applications, including:

- separation-concentration of phenol and cresol from aqueous waste streams (Urtiaga et al., 1992a, 1992b; Gonzalez-Munoz et al., 2003; Ferreira et al., 2005)
- recovery of valeric acid (Rodriguez et al., 1997)
- extraction of aroma compounds from fermentation broths (Baudot et al., 2001).
- recovery of pharmaceutical fermentation products (Prasad and Sirkar, 1989)
- protein extraction (Dahuron and Cussler, 1988)
- recovery of aromatics from hydrocarbon feedstock (Prasad and Sirkar, 1987)

To date there is no published literature describing the use of this method for the extraction of valuable phenolic antioxidants from olive wastewaters.

1.2 PROJECT OBJECTIVES

The objective of this 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.

CHAPTER 2

2.1 MASS TRANSFER THEORY

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. Several mathematical models have been proposed and evaluated for determination of the overall mass transfer coefficient. These include models based on fundamental principles (Urtiaga et al., 1992a, 1992b), Wilson-plot methodology (Viegas et al., 1998) and the Olander and Hatta models (Ferreira et al., 2005). In this work mass transfer within the membrane module was modeled according to Gonzalez-Munoz et al. (2003). These authors provide an analytical solution for the mass transfer coefficient based on solute concentrations in the two phases and various mass balances. The complete mathematical derivation appears in Appendix A. The model was developed for bulk aqueous and organic phases contained in separate reservoirs, with both phases *continuously recycled* through the membrane unit in a co-current manner. It is assumed the initial concentration of solute in the organic phase is zero.

The model chosen here is more complex than the others mentioned; however it is the most applicable for the operating conditions used to determine the mass transfer coefficient, that of solvent and wastewater recycle through a single stage, *i.e.* batch operation. Ultimately it is desirable to have a single pass of solvent and wastewater through several stages, which would allow for continuous operation with reasonable extraction efficiency. However, the mass transfer coefficients should remain unchanged irrespective of the operating regime, as long as fluid dynamic conditions are similar, and therefore the results obtained using this model can be extrapolated for the design of larger, continuously operated systems.

The equation for mass transfer can be described by:

$$J_s = K_a A_m (c_a - c_a^*) \tag{2.1}$$

where J_s = overall solute flux ($g.s^{-1}$)

K_a = overall mass transfer coefficient ($m.s^{-1}$)

A_m = membrane surface area (m^2)

c_a = solute concentration in the aqueous phase at time t ($mg.L^{-1}$)

c_a^* = solute concentration in aqueous phase in equilibrium with organic phase at time t ($mg.L^{-1}$)

The objective is thus to determine the coefficient K_a in equation (2.1). By performing various steady- and unsteady state mass balances, and several integrations, the following expression is obtained for the solute concentration over time in the aqueous phase:

$$c_a(t) = \frac{V c_a(0)}{1+V} + \frac{c_a(0)}{1+V} \exp(-ct) \tag{2.2}$$

where

$$c = \frac{Q_a}{V_a} \frac{(1+V)}{(1+Q)} \left[1 - \exp\left[-\frac{A_m K_a}{Q_a} (1+Q) \right] \right] \tag{2.3}$$

$$V = \frac{V_a}{V_o D}$$

$$Q = \frac{Q_a}{Q_o D}$$

and

$c_a(0)$ = initial concentration of solute in the aqueous phase ($mg.L^{-1}$)

V_a, V_o = volume of aqueous and organic phases respectively (m^3)

Q_a, Q_o = flow rate of aqueous and organic phases respectively ($m^3.s^{-1}$)

D = distribution coefficient of solute between the aqueous and organic phase (-).

Equation (2.2) can be expressed in the form:

$$c_a = a + b\exp(-ct) \tag{2.4}$$

where a and b depend only on known parameters, and the value of c can be obtained from the slope of a straight line plot of $\ln(c_a(t) - a)$, *i.e.* the concentration in the aqueous phase feed tank over time minus coefficient a. Equation (2.3) can be re-arranged to solve for K_a:

$$K_a = \frac{-Q_a}{(1+Q)A_m}\ln\left[1 - c\left(\frac{V_a}{Q_a}\right)\left(\frac{1+Q}{1+V}\right)\right] \tag{2.5}$$

and a value for the mass transfer coefficient can thus be obtained.

2.2 CONCLUSIONS

- The extraction of hydroxytyrosol from olive wastewater was successfully modelled
- Expressions for mass transfer coefficients were derived
- This provides a route for calculation of the mass transfer coefficient for the system.

CHAPTER 3

3.1 MEMBRANE-ASSISTED EXTRACTION SYSTEM DESIGN AND OPERATION

The pilot-scale system was designed to fit into a rectangular metal framework with dimensions 600 x 250 x 600 mm (*l* x *b* x *h*), and weighs approximately 20 kg, making the system readily portable. A schematic representation of the pilot-scale extraction system and process is shown in Figure 3.1, while a photograph of the manufactured system is shown in Figure 3.2. A schematic illustration of the membrane module is shown in Figure 3.3.

The components contained within the dashed box in Figure 3.1 represent the portable pilot-scale extraction system. In terms of operation, it is anticipated that olive production wastewaters will be stored and sedimented on-site in a holding tank. After sufficient settling the wastewater is 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, at the required flow rate (nominally 0.5 $L.min^{-1}$).

Before entering the membrane module, the wastewater is directed through a 200 μm screen to remove residual particulate matter, then through a pressure relief safety valve, in order to protect the membrane module from damage in the case of excessive pressure build-up due to a blockage for instance.

A back-pressure regulator is fitted to the wastewater outlet of the membrane module, in order to control the pressure of the wastewater stream in the membrane module. A slight overpressure (~ 50 – 100 kPa) is required to prevent solvent ingress through the membrane into the wastewater stream. 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 is currently in fabrication; it is to be used 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. Similar to conventional liquid/liquid extraction, several consecutive or parallel stage-wise extractions are required for complete recovery of the product, due to the equilibrium distribution coefficient that exists between the two phases.

The membrane module used in this work was a Liqui-Cel® 2.5x8" Extra-Flow phase contactor, containing ~ 10 000 hydrophobic polypropylene hollow fibers (OD = 300 μm) with a total membrane surface area of 1.4 m^2.

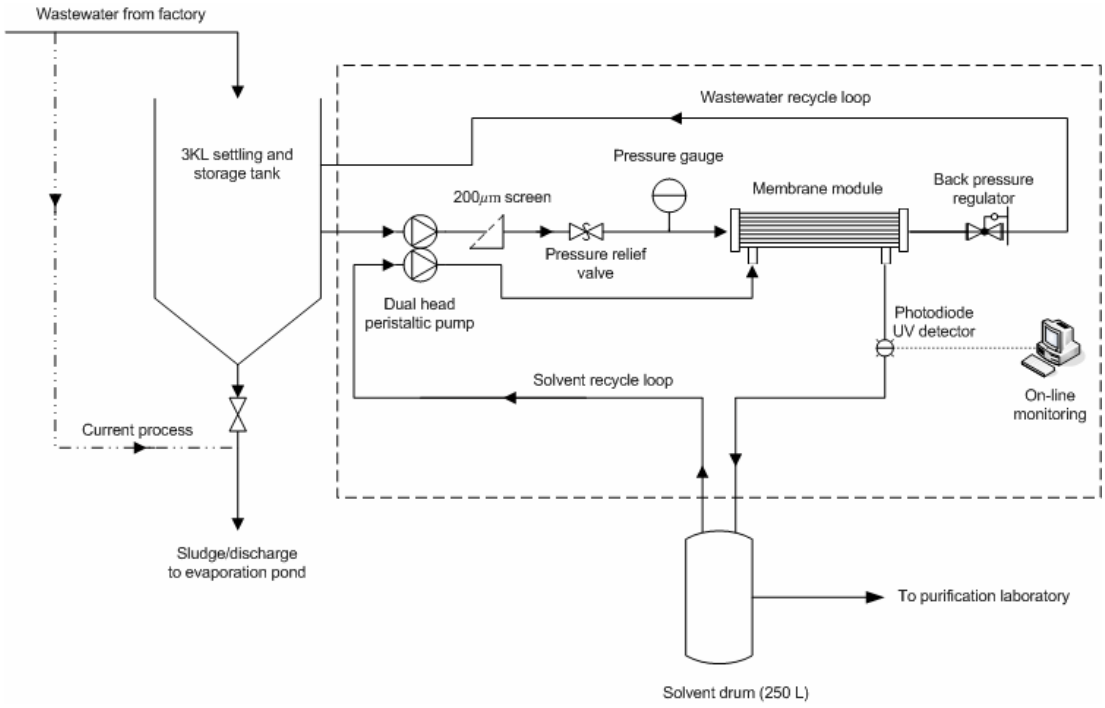

Figure 3.1: Schematic of proposed pilot-scale membrane extraction system and the extraction process

Figure 3.2: Photograph of the pilot-scale membrane extraction system

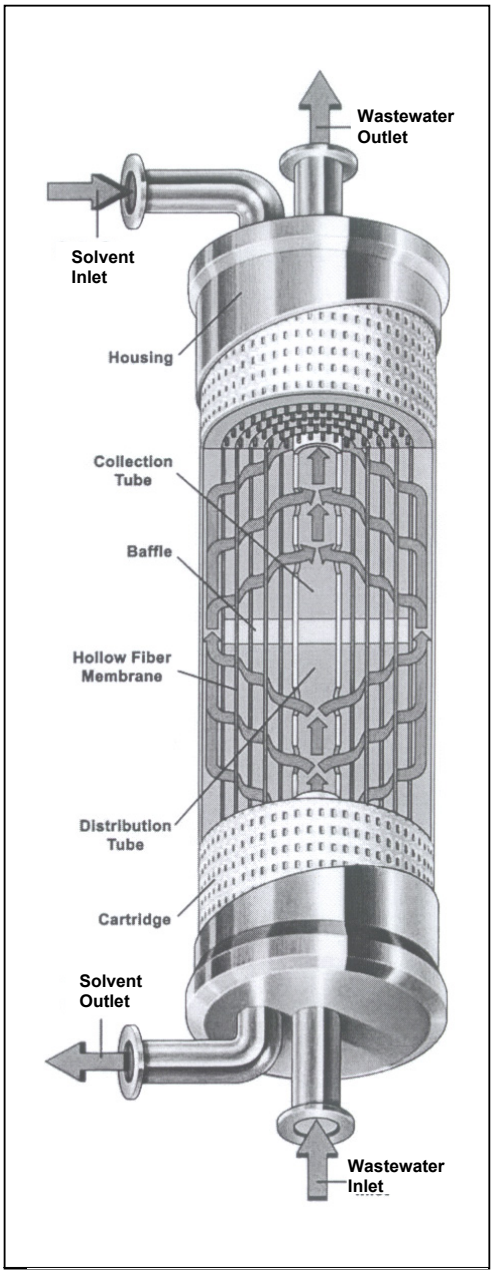

Figure 3.3: The Liqui-Cel membrane module

CHAPTER 4

MEMBRANE-ASSISTED SOLVENT EXTRACTION

4.1 INTRODUCTION

The objective of these experiments was to evaluate the overall mass transfer coefficient of the phenolic antioxidant hydroxytyrosol from the olive wastewater into the organic solvent, and thus to evaluate extraction rates and yields for the process. The mass transfer coefficient is a variable that depends on physical parameters such as flow rates (boundary layer resistance) and membrane properties (pore size, tortuosity, contact angle), and also on chemical properties such as the equilibrium distribution (partition) coefficient of the solute between the two phases.

The equilibrium distribution coefficient of the solute (hydroxytyrosol) between the aqueous (wastewater) phase and the organic (ethyl acetate) phase was thus first evaluated. The distribution coefficient is a function of concentration, relative volumes and pH, therefore several conventional liquid/liquid extraction experiments were performed in order to evaluate the distribution coefficient under various conditions. The experimentally determined distribution coefficients were then used to determine the overall mass transfer coefficients.

To evaluate the overall mass transfer coefficient, the wastewater and solvent were "contacted" within the membrane module as described in section 3. Several experiments were performed in this regard, in order to evaluate the effect of different parameters on the mass transfer coefficient. Firstly, flow rates (and corresponding Reynolds numbers) of the two phases were varied, in order to evaluate the effects of boundary layer resistances within the membrane module. As flow rates increase, concentration boundary layer thickness decreases, which in turn leads to an increase in the overall mass transfer

coefficient (the membrane resistance to mass transfer is expected to remain constant). At some stage a theoretical maximum is reached, whereupon a further increase in the Reynolds number does not significantly improve the mass transfer coefficient, i.e. concentration boundary layers reach a minimum.

Secondly, solvent-to-wastewater ratios were varied, as this ratio affects the steady state distribution coefficient between the wastewater and solvent phases. In terms of obtaining the maximum concentration of product in the solvent extract, a low ratio of solvent-to-wastewater (< 1) is required. As the ratio tends to zero, a maximum concentration of solute in the solvent is reached, equal to the distribution coefficient multiplied by the original concentration in the wastewater. Therefore, the effect of different solvent-to wastewater ratios on the overall mass transfer coefficient and extraction rate was investigated. For given hydrodynamic conditions the mass transfer coefficient is expected to remain constant, however, the relative ratio will affect the final solute yield (due to the change in the equilibrium distribution coefficient).

Once the wastewater has been extracted, the solvent needs to be processed by distillation to obtain a crude extract, and then this crude extract has to be further purified, as several other organics (particularly lactic and acetic acids) are extracted from the wastewater into the solvent. However, in terms of phenolic compounds, ethyl acetate is selective towards low molecular weight (monomeric) phenolic compounds, with larger compounds such as tannins remaining in the aqueous phase.

Since downstream distillation and purification processes are likely to be significantly more cost-intensive than the extraction process, the desired result was to obtain a maximum concentration of the antioxidant hydroxytyrosol in the solvent after extraction, rather than attempt to completely extract all the hydroxytyrosol from the wastewater. This approach is justified because excessive quantities of wastewater are available for extraction.

4.2 MATERIALS AND METHODS

4.2.1 General

All experiments were performed at 25 ± 2^{o}C. All analytical determinations were performed in triplicate with the results expressed as the mean. Standard deviations were in general less than ± 5%, and are thus not stated with results. Error bars are included where appropriate. All reagents were of analytical or HPLC grade as required, and were supplied by Merck. De-ionised reagent water was obtained from a Millipore Elix 3 purification system.

4.2.2 Analytical procedures

Reversed phase HPLC was used to identify and quantify of individual low molecular weight phenolic compounds. A Merck Hitachi L-7000 series system was used. Separation was performed by isocratic elution, using a mobile phase of 80:20:2.5 H_2O:Methanol:Acetic acid at a flow rate of 1 ml.min^{-1}. The column was a Waters Spherisorb® S5 ODS1 4.6x250 mm, fitted with a Phenomenex guard column. UV detection was used to measure compounds at 280 nm. Individual compounds were identified by comparison of retention times against both internal and external standards. Standard curves of concentration vs. peak area were used to quantify components.

Alkali hydrolysis of oleuropein was performed to obtain a hydroxytyrosol standard, according to Garcia et al. (1996) as follows: 100 mg Oleuropein (Extrasynthese, Gamay, France) was added to 6 M NaOH (20 ml) and placed in the dark for 5 hours under N_2. The resulting solution was adjusted to pH 3 with HCl and then extracted 3 times with diethyl ether (1v/v). The combined extracts were mixed with 10 ml 0.1 M HCl, and the organic solvent was removed *in vacuo*. The remaining acidic aqueous solution was treated with 30 mg activated carbon for 20 min., and filtered to give a purified hydroxytyrosol solution at a concentration of 752 mg.L^{-1}.

Total phenol concentrations were determined colorimetrically using the Folin-Ciocalteau reagent according to the procedure of Garcia et al. (2001). The method was scaled down so it could be performed directly in 4ml cuvettes. 400 μL each of sample, Folin-Ciocalteau reagent (Merck) and Na_2CO_3 (20%) were added to 2.5 ml ddH_2O and mixed. This was left to stand for 90 minutes in the dark to allow the reaction to go to completion, and then absorbance was read at 765 nm. Gallic acid in the range 0 – 100 $mg.L^{-1}$ was used as a standard, and all total phenol assays are thus reported as gallic acid equivalents (GAE). Samples were diluted where necessary to fall within the standard range and distilled water was used as a reagent blank.

Organic acids were determined by HPLC on a Varian® chromatography system. The column was a Waters® Fast Fruit Juice 7u (150 mm), which was held at 60°C, while the mobile phase was 0.1% phosphoric acid at a flow rate of 1 $ml.min^{-1}$. UV detection was at 215 nm. Standards were prepared in the range 0 – 1 000 $mg.L^{-1}$.

In the case of analysis of the organic ethyl acetate phase, the solvent was first removed either *in vacuo* or under nitrogen for small samples, and then made up to the original volume with water.

4.2.3 Wastewater

Wastewater from the production of brined table olives was kindly supplied by the Cape Olive Trust, and was subject to numerous physico-chemical analyses as described in WRC report 1361/1/06. This is part of an ongoing project to collate a database of seasonal variation of the different types of wastewater produced. A summary of the properties of the wastewaters used in this study are shown in Table 4.1. [BUF01 and BUF02 are brine wastewaters from the production black *Calamata* table olives. The wastewaters were from two different olive batches, and were quite similar except for a notable difference in hydroxytyrosol concentration].

Table 4.1: Wastewater properties

		BUF01	BUF02
pH		4.58	3.69
Conductivity	(mS/cm)	67	69
Total solids	(g/L)	109.0	128.1
Dissolved solids	(g/L)	108.9	127.8
Suspended solids	(g/L)	0.05	0.32
Total phenols	(mg/L)	5026	5079
Hydroxytyrosol	(mg/L)	1579	2838
COD	(g/L)	54.6	63.2

4.2.4 Distribution coefficient determination

The distribution coefficient of hydroxytyrosol and total phenols between the aqueous and organic phase were first determined, at natural wastewater pH. Six dilutions of wastewater (0 – 100%) were mixed with an equal volume (20 ml) of ethyl acetate, shaken for 24 hours, and left to settle. This allowed for concentrations of solutes in the two phases to reach equilibrium. After separation and centrifugation, concentrations in the aqueous and corresponding organic phases were measured for the different dilutions, in order to establish whether the distribution coefficient is constant over the concentration range. A similar procedure was followed to determine the effect of pH on the distribution coefficient. The pH of undiluted wastewater was adjusted with 1 M NaOH or HCl to the desired value.

4.2.5 Membrane extraction procedures

The general procedure for all extraction experiments was to connect the module to the relevant reservoirs of wastewater and solvent, turn the pump on, and then adjust the over-pressure of the aqueous phase to 75 kPa using the back-pressure regulator. Samples were taken for analysis from both solvent and wastewater reservoirs at T = 0 and every 5 minutes thereafter.

The effect of flow rate on the mass transfer coefficient was measured first. Consecutive experiments were performed at pump speeds of 30, 50, 70 and 90% of the maximum setting. Flow rates were measured volumetrically and the corresponding Reynolds numbers were calculated. The time course of concentration of solute in the two phases was then compared for the different Reynolds numbers. The solvent-wastewater ratio in all experiments was 1:1.

Extraction experiments were next performed with solvent-to-wastewater ratios of 1:1, 1:2 and 1:10, while maintaining a constant flow rate. One litre of solvent was used in all cases, and experiments were performed in triplicate for each ratio. Again the time course of solute concentration in the two phases was measured. The mass transfer coefficients were then calculated as described in Section 2. The 1:10 ratio experiment was successively batch extracted four times, using fresh solvent but the same wastewater. This was done to get a better average estimation of product yield on a sequentially decreasing concentration of wastewater.

4.2.6 Distillation of solvent

After extraction experiments, the bulk combined ethyl acetate extracts were distilled *in vacuo* using a rotovapor with the bath temperature set to 50^{o}C. This resulted in a crude extract which was resuspended in a minimal quantity of methanol or ethanol. The crude extract was then stored at 4^{o}C for further analysis and purification experiments.

4.3 RESULTS AND DISCUSSION

The distribution coefficients of phenolic solutes between the aqueous phase (wastewater BUF01) and the organic phase, at equilibrium, are shown in Figure 4.1 for increasing wastewater concentrations. The slope of the straight line fitted to the data is the effective distribution coefficient. It is evident that the distribution coefficient did not vary significantly over the concentration range studied (least square linear regression coefficients were > 0.99).

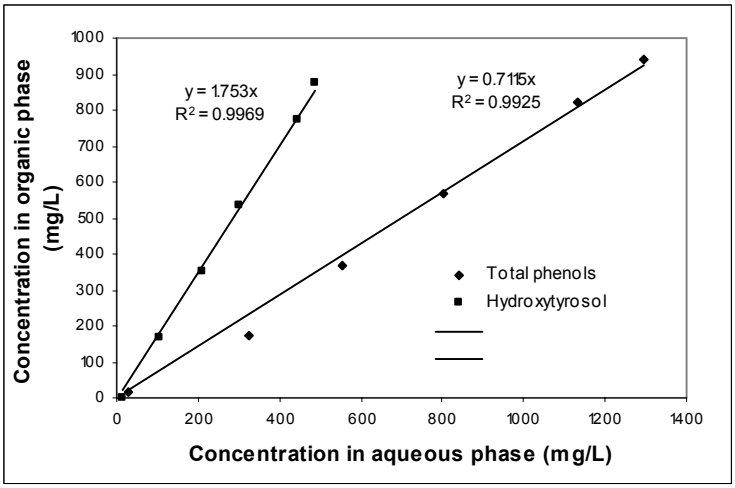

Figure 4.1: Equilibrium solute distribution coefficients for increasing concentrations

The distribution coefficient for hydroxytyrosol was 1.753, while the distribution coefficient for total phenols was 0.712, indicating that the total phenol content remained higher in the wastewater than in the organic solvent. This is because ethyl acetate is selective towards low molecular weight phenolic compounds (Allouche et al., 2004), and the higher molecular weight phenolic components remain in the aqueous phase.

Results for the distribution coefficient as a function of pH are shown in Figure 4.2. pH had only a marginal effect on the distribution coefficient of hydroxytyrosol between the organic and aqueous phases, while for total phenols the effect was more pronounced. In

terms of the recovery of hydroxytyrosol, it is deemed unnecessary to adjust the wastewater pH (at large cost) for the marginal improvement in the distribution coefficient.

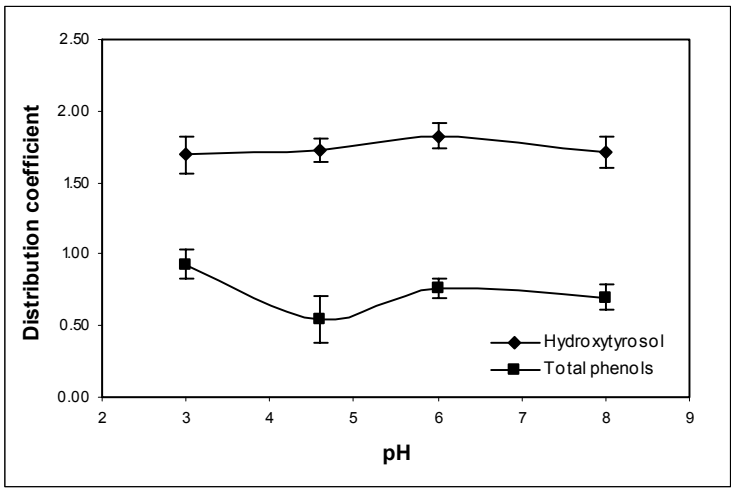

Figure 4.2: Effect of pH on the hydroxytyrosol distribution coefficient between the organic and aqueous phases

It is, however, interesting to note that at the wastewater's natural pH (4.6), the distribution coefficient for total phenols is at a minimum. This would seem to indicate that any adjustment of wastewater pH results in some degradation of the larger phenolic compounds resulting in lower molecular weight subunits, which are then extracted into the organic phase. This was verified by HPLC, as illustrated in Figure 4.3.

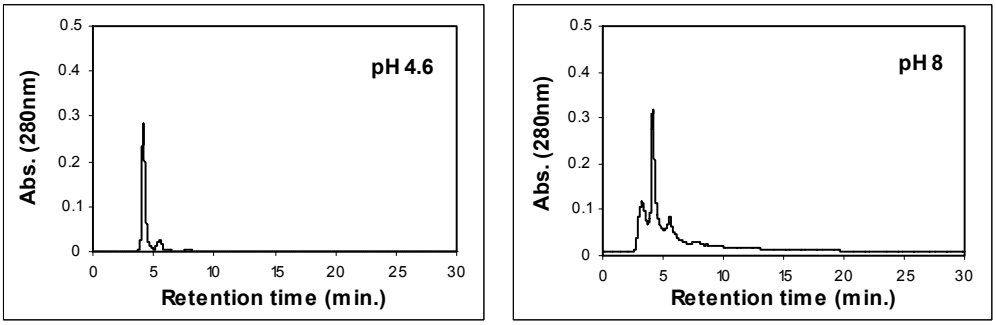

Figure 4.3: HPLC chromatograms of organic extract of wastewater at different pH

At natural wastewater pH of 4.6 the predominant component extracted is hydroxytyrosol, whereas when the wastewater is adjusted to pH 8 the extract contains a significant amount of other low molecular weight components in addition to the hydroxytyrosol peak. This shows that it is in fact undesirable to adjust the wastewater pH before extraction, as subsequent purification of the extract to obtain pure hydroxytyrosol will be more complex.

Figure 4.4 shows results for membrane-assisted solvent extraction experiments, where the flow rates of the aqueous and organic phases were varied, in order to determine the effect of flow rate on the overall rate of mass transfer as described in Section 4.2.5. Table 4.2 lists the relationship between pump speed (in Hz), aqueous and organic phase flow rates and Reynolds numbers.

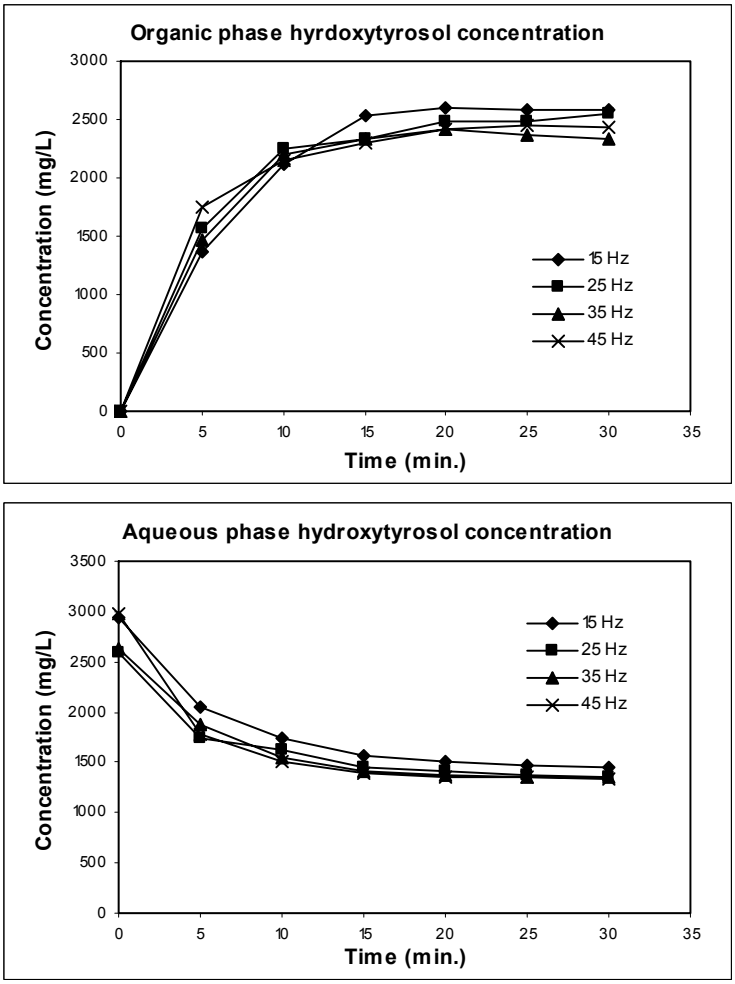

Figure 4.4: Hydroxytyrosol extraction profiles as a function of aqueous and organic phase flow rates

Table 4.2: Relationship between pump speed, phase flow rate and Reynolds number for membrane-assisted solvent extraction experiments

Pump speed (Hz)	**Organic phase flow rate** (L/hr)	**Organic phase Reynolds no.*** (-)	**Aqueous phase flow rate** (L/hr)	**Aqueous phase Reynolds no.*** (-)
15	12.1	0.15	14.2	2.03
25	20.2	0.26	25.5	3.65
35	27.0	0.35	39.6	5.66
45	32.0	0.42	42.3	6.05

* Examples of Reynolds number calculations are shown in Appendix B

Figure 4.4 indicates that over the range of flow rates investigated, there was no significant improvement of the mass transfer coefficient at increased flow rates. This is evident from the fact that there is no major difference in organic and aqueous phase solute concentrations over time for the different pump speeds. These results are in good agreement with those of Gonzalez-Munoz et al. (2003), who investigated the same membrane module and solvent for the extraction of phenol from water. These authors observed that above Reynolds numbers of 0.4 and 4 for the organic and aqueous phases respectively, boundary layer effects (i.e. resistance to mass transfer) are at a minimum, and the predominant resistance to mass transfer is presented by diffusion of the solute through the membrane itself.

It will be noticed from Table 4.1 that for a given pump speed, the organic and aqueous phase flow rates are not the same, despite the pump heads being identical. The reasons for this are that the aqueous and organic phases do not have the same viscosity, and more importantly, resistance to flow in the shell side of the membrane module (organic phase pressure drop) is greater than that in within the membranes (aqueous phase pressure drop) because of the baffle in the shell space (see Figure 3.3). Furthermore, the hydraulic diameter of the shell through which the organic phase flows is significantly larger than that of the membranes, which results in the lower values of the Reynolds numbers. This

is, however, inconsequential, as the boundary layer resistances to mass transfer are negligible compared to the membrane resistance at the operating conditions used in these experiments. The importance of the Reynolds numbers applies to flow rates in modules of different size and geometry, i.e. for scale-up, calculations are based on Reynolds numbers and not flow rates to ensure that hydrodynamic conditions are consistent.

The effect of solvent-to-wastewater volume ratio was then investigated under consistent hydrodynamic conditions (pump speed 25 Hz). Plots of the concentration of hydroxytyrosol in the wastewater and solvent phases over time are shown in Figure 4.5, for the different solvent-to-wastewater ratios. The wastewater used in these experiments was BUF01, and hence the lower initial concentration of hydroxytyrosol in the wastewater compared to Figure 4.4 (BUF02).

It is evident that the lower solvent-to-wastewater ratio (1:10) results in the highest concentration of hydroxytyrosol in the solvent (~ 2000mg/L), although it takes comparatively longer to reach this value. This is as expected from mass balance equilibrium considerations, as a function of the distribution coefficient. It is desirable to obtain the highest possible hydroxytyrosol concentration in the solvent, because downstream processing (distillation, purification) is likely to be much more expensive than the extraction process, and therefore the higher the solute concentration, the better.

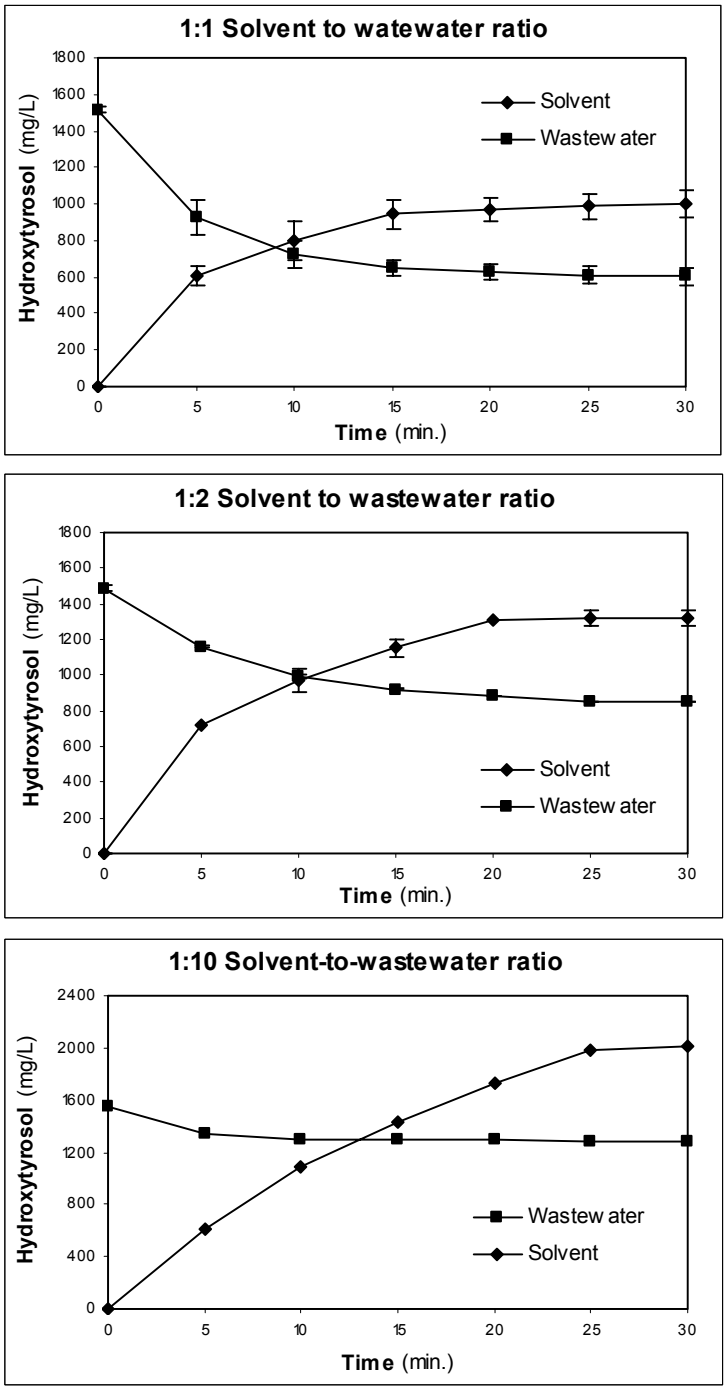

Figure 4.5: Plots of hydroxytyrosol concentrations in the solvent and wastewater phases over time for different solvent-to-wastewater ratios

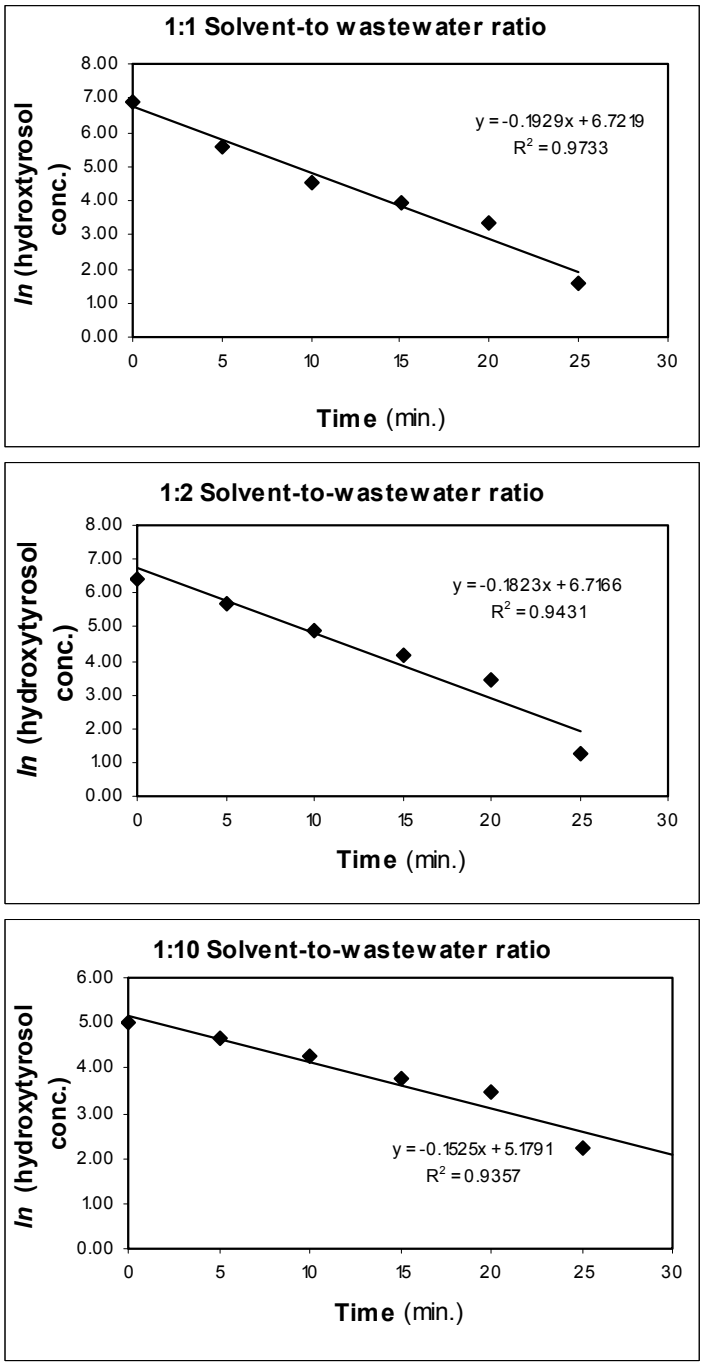

Figure 4.6: Linearised plot of hydroxytyrosol concentration over time in the aqueous phase used for calculation of the mass transfer coefficient

The overall extraction rate is simply the concentration at equilibrium divided by the time taken to reach this point, per unit membrane area. In order to calculate the overall mass transfer coefficients, the data is processed as described in 1361/1/06. This results in the plots shown in Figure 4.6, where the slope of the straight line is the coefficient required for determination of the overall mass transfer coefficient. Results for the overall extraction rates and mass transfer coefficients are shown in Table 4.3.

Table 4.3: Results of extraction experiments using different solvent-to-wastewater ratios

Solvent-to-wastewater ratio	Extraction rate ($g.hr^{-1}$)	Mass transfer coefficient x 10^{-5} ($m.s^{-1}$)
1:1	2.7	1.31 ± 0.06
1:2	2.9	1.37 ± 0.04
1:10	2.8	1.30 ± 0.11

It is evident that both extraction rates and mass transfer coefficients remain relatively consistent at different ratios, and this is as expected, because the rate limiting step of mass transfer across the membrane is not dependant on the distribution coefficient. Based on membrane surface area (1.4 m^2), the average extraction rate was determined to be around 2 $g.m^{-2}.hr^{-1}$, irrespective of solvent-to-wastewater ratio. This extraction rate can be used to estimate yields for a scaled-up process, if operated in the continuously recycled mode. The mass transfer coefficient can be used to model the extraction process, and will be of utility for the design and development of a continuous, single pass extraction process.

Hydroxytyrosol concentrations during successive batch extractions of the 1:10 solvent ratio experiment are show in Figure 4.7. Successive batch extractions can, in theory, be repeated until the hydroxytyrosol concentration in the wastewater is negligible, however, the concentration in successive batches becomes progressively more dilute, and the cost of subsequent downstream solvent processing at some point exceeds the value of product being extracted.

4.4 CONCLUSIONS

- The distribution coefficient for hydroxytyrosol was calculated to be 1.753and that for total phenols was 0.712
- This confirms that hydroxytyrosol is selectively extracted into the organic phase, in the extraction process.
- The pH of the wastewater does not need to be adjusted, for efficient extraction.
- The optimal flow rate for the extraction system and the most suitable characteristics of the pumping system were determined.
- The solvent-to-water volume ratio for most efficient extraction was determined.
- The total yield of hydroxytyrosol was determined to be 0.59g/L wastewater under experimental conditions.
- Evaporative recycling of the solvent was demonstrated.

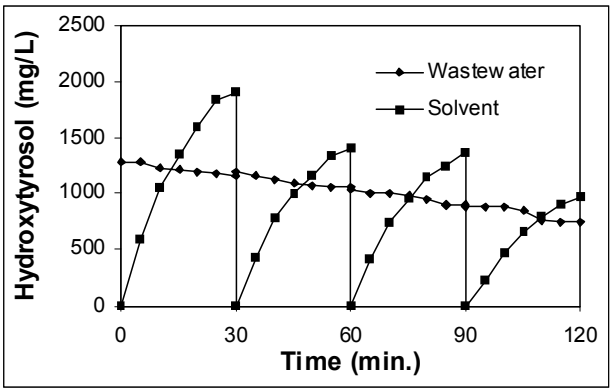

Figure 4.7: Hydroxytyrosol concentrations in the solvent and wastewater phases during successive batch extractions using a 1:10 solvent-to-wastewater ratio

The total yield of hydroxytyrosol, from 10 L of wastewater extracted four times (using a total of 4 L of solvent), was 5.89 g. It is thus possible to anticipate that a yield of at least

1 g of hydroxytyrosol per litre of solvent used, if a 1:10 ratio is employed, with four consecutive extractions. Further consecutive extractions will lead to lower yields, however this is currently deemed to be unnecessary, as downstream solvent processing (distillation) is likely to be the rate limiting step in the overall process, and therefore high concentrations of product are desirable in the solvent after extraction.

After extraction, the solvent batches were combined and distilled *in vacuo*, to obtain a crude extract, and recover to the solvent for re-use. The crude extract was resuspended in a minimal quantity of methanol for further analysis. Hydroxytyrosol accounted for approximately 90% of the total phenols in the crude extract, the remainder being tyrosol (~ 4%) and some other unidentified compounds. Non-phenolic components of the crude extract included predominantly lactic acid (~ 30% w/w) and acetic acid (~ 2% w/w). These values are approximate because there was some variation between the distillate from different extraction experiments.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The membrane-assisted solvent extraction system has been shown to be a viable and attractive 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 appealing business case, and have led to the filing of a provisional patent.

There are some issues that need to be resolved and aspects of the extraction process that need to be further investigated, and these will be the focus of further postdoctoral studies over the next year and a half.

Firstly, all experiments to date have been 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. The overall length of the membrane contactor would need to be increased, while flow rates, pressure drops and associated process control become critical. Having determined the overall mass transfer coefficients, the length of the required membrane contactor (and corresponding surface area) can be calculated, based on the process parameters. Experiments towards this end are planned for the near future.

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.

The planned on-site extraction experiments have unfortunately not been performed as yet, due to extended negotiations with the olive producers. This has turned out to be more complex than anticipated due to the large commercial possibilities on offer. A comprehensive business plan is required before on-site extractions are realistically commenced. Such a business plan in turn requires in-depth market analysis, as well as accurate costing estimates for both capital equipment and operating expenses, the scope of which was too large to be achieved during the course of this short research contract. [At the time of reporting, the plans for implementation are well underway and on-site processing is scheduled to begin in January 2007].

For longer term on-site extraction experiments, a suitably scaled distillation system needs to be designed or acquired in order to process and obtain a bulk crude extract, and to recover the solvent for recycling. Although preliminary purification experiments have been successfully performed on a small scale, this area needs to be investigated in more detail. Large-scale chromatographic purification systems are notoriously expensive in terms of both capital and operating costs, and the exact nature of this process will depend to a large extent on the anticipated customers' requirements.

The Liqui-Cel membrane modules used for this work have performed satisfactorily during experiments over a period of six months with no apparent loss of performance. However, longer-term, continuous operational experience is required, as virtually all membrane processes have a finite lifespan before replacement becomes necessary.

APPENDIX A: DERIVATION OF THE OVERALL MASS TRANSFER COEFFICIENT

The following mathematical model for mass transfer in the membrane-assisted solvent extraction system was adapted from Gonzalez-Munoz et al. (2003). The equation for mass transfer can be described by:

$$J_s = K_a A_m (c_a - c_a^*) \tag{3.1}$$

where J_s = overall solute flux ($g.s^{-1}$)

K_a = overall mass transfer coefficient ($m.s^{-1}$)

A_m = membrane surface area (m^2)

c_a = solute concentration in the aqueous phase at time t ($mg.L^{-1}$)

c_a^* = solute concentration in aqueous phase in equilibrium with organic phase at time t ($mg.L^{-1}$)

The objective is thus to determine the coefficient K in equation (3.1).

With reference to Figure A.1 (where the dashed line represents the membrane), a differential mass balance for solute in the module in terms of transfer of solute from the aqueous phase into the organic phase can be expressed as:

$$Q_a[c_a(x,t) - c_a(x+dx,t)] = -Q_a dc_a(x,t) = K_a dA_m\left(c_a(x,t) - c_a^*(x,t)\right) \tag{3.2}$$

where Q_a = aqueous phase flow rate ($m^3.s^{-1}$), $c_a(x,t)$ is the solute concentration at axial position x at time t, and $c_a^*(x,t)$ is the concentration in the aqueous phase in equilibrium with that in the organic phase at the same time and location, *i.e.* $c_o(x,t)$. This equilibrium relationship can be expressed as:

$$c_a^*(x,t) = \frac{c_o(x,t)}{D} \tag{3.3}$$

where D is the equilibrium distribution coefficient of solute between the aqueous and organic phases. Here the subscript o refers to the organic phase.

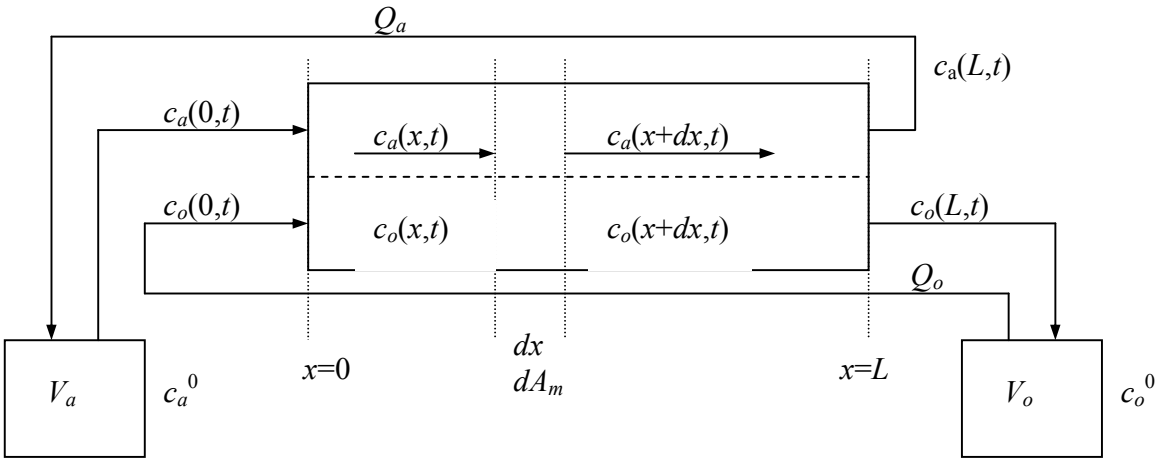

Figure A.1: Schematic diagram of solute transfer in the membrane extraction system

For an overall mass flow rate balance across the module, the decrease in solute in the aqueous is equal to the increase in the organic phase:

$$Q_a\left(c_a(0,t)-c_a(L,t)\right)=Q_o\left(c_o(L,t)-c_o(0,t)\right) \tag{3.4}$$

A similar mass balance can be written for any point (x) of the module:

$$Q_a\left(c_a(x,t)-c_a(L,t)\right)=Q_o\left(c_o(L,t)-c_o(x,t)\right) \tag{3.5}$$

$c_o(x,t)$ from equation (3.3) is then substituted into equation (3.5), and $c_a^*(x,t)$ in equation (3.2). The resulting equation is then integrated between x = 0 and x = L, and the following expression is obtained:

$$\frac{c_a(L,t)-c_o(L,t)/D}{c_a(0,t)(1+Q)-c_a(L,t)Q-c_o(L,t)/D}=\exp\left[-\frac{K_a A_m}{Q_a}(1+Q)\right] \tag{3.6}$$

where

$$Q = \frac{Q_a}{Q_o D} \tag{3.7}$$

Taking into account the overall mass balance equation (3.4), equation (3.6) can then be expressed as:

$$\frac{c_a(L,t) - c_o(L,t)/D}{c_a(0,t) - c_o(0,t)/D} = \exp\left[-\frac{K_a A_m}{Q_a}(1+Q) \right] \tag{3.8}$$

A simultaneous unsteady-state balance on the aqueous phase feed tank (assuming perfect mixing) gives:

$$-V_a \frac{dc_a(0,t)}{dt} = Q_a [c_a(0,t) - c_a(L,t)] \tag{3.9}$$

where V_a is the volume of the tank (m^3).

At any time the depletion of solute in the aqueous phase should be equal to its increase in the organic phase:

$$V_a(c_a(0,0) - c_a(0,t)) = V_o(c_o(0,t) - c_o(0,0)) \tag{3.10}$$

Combining equations (3.4) and (3.10), the concentration of solute in the organic phase at the module outlet can be expressed as a function of the solute concentration in the aqueous phase at the module inlet and outlet:

$$c_o(L,t) = \frac{Q_a(c_a(0,t) - c_a(L,t))}{Q_o} + \frac{V_a(c_a(0,0) - c_a(0,t))}{V_o} + c_o(0,0) \tag{3.11}$$

Combining equations (3.11) and (3.8), an expression is obtained for solute concentration in the aqueous phase at the module outlet as a function of the inlet aqueous phase concentration and some process parameters:

$$c_a(L,t)=\frac{1}{(1+Q)}\left[c_a(0,t)-V(c_a(0,0)-c_a(0,t))+\frac{c_o(0,0)}{D}\right]\exp\left[-\frac{K_a A_m}{Q_a}(1+Q)\right]$$
$$+\frac{1}{(1+Q)}\left[Qc_a(0,t)+V(c_a(0,0)-c_a(0,t))+\frac{c_o(0,0)}{D}\right] \tag{3.12}$$

where

$$V=\frac{V_a}{V_o D} \tag{3.13}$$

Substituting equation (3.12) into equation (3.9) and integrating between $t = 0$ and time t results in:

$$c_a(0,t)=\frac{(c_a(0,0)V-c_o(0,0)/D)}{(1+V)}+$$
$$\frac{(c_a(0,0)V-c_o(0,0)/D)}{(1+V)}\exp\left[-\frac{Q_a}{V_a}\frac{(1+V)}{(1+Q)}\times\left(1-\exp\left(-\frac{K_a A_m}{Q_a}(1+Q)\right)\right)t\right] \tag{3.14}$$

If the initial concentration in the solute $c_o(0,0)$ is zero, then equation (3.14) can be expressed as:

$$c_a(0,t)=\frac{Vc_a(0,0)}{1+V}+\frac{c_a(0,0)}{1+V}\exp(-ct) \tag{3.15}$$

where

$$c=\frac{Q_a}{V_a}\frac{(1+V)}{(1+Q)}\left[1-\exp\left[-\frac{A_m K_a}{Q_a}(1+Q)\right]\right] \tag{3.16}$$

Equation (3.15) can be expressed in the form:

$$c_a(0,t)=a+b\exp(-ct) \tag{3.17}$$

where a and b depend only on known parameters, and the value of c can be obtained from a straight line plot of $\ln(c_a(0,t) - a)$, *i.e.* the concentration in the aqueous phase feed tank over time minus a. Equation (3.16) can be re-arranged to solve for K_a:

$$K_a = \frac{-Q_a}{(1+Q)A_m} \ln\left[1 - c\left(\frac{V_a}{Q_a}\right)\left(\frac{1+Q}{1+V}\right)\right] \tag{3.18}$$

and a solution for the mass transfer coefficient is so obtainable.

APPENDIX B: REYNOLDS NUMBER CALCULATIONS

The dimensionless Reynolds number is defined as:

$$\mathrm{Re} = \frac{D_H v \rho}{\mu}$$

where D_H = hydraulic diameter (m)

v = average linear velocity ($m.s^{-1}$)

ρ = density ($kg.m^{-3}$)

μ = viscosity (Pa.s)

For the aqueous flow through the membrane lumen, D_H is simply the membrane inner diameter. For the organic flow through the shell space:

$$D_H = 4\frac{(\pi/4)D^2{}_{shell}}{N_f \pi d_f} = \frac{D_{shell}{}^2}{N_f d_f}$$

where D_{shell} = inside diameter of the module shell (m)

N_f = number of fibers

d_f = outside diameter of a single fiber (m)

The average linear velocity is given by:

$$v = \frac{Q}{A}$$

where Q = volumetric flow rate ($m^3.s^{-1}$)

A = cross-sectional area (m^2)

For the organic phase flow through the shell space:

$$A = \frac{1}{4}\pi\left(D_{shell}^2 - D_t^2 - N_f d_f\right)$$

where D_t = diameter of the central distribution/collection tube (m)

(see Figure 3.3)

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