Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

PERVAPORATION-BASED HYBRID PROCESSES IN TREATING PHENOLIC WASTEWATER: TECHNICAL ASPECTS AND COST ENGINEERING

F. Lipnizki[a]; R. W. Field[b]
[a] Danish Separation Systems AS, Nakskov, Denmark [b] University of Bath, Bath, UK

To cite this Article Lipnizki, F. and Field, R. W.(2001) 'PERVAPORATION-BASED HYBRID PROCESSES IN TREATING PHENOLIC WASTEWATER: TECHNICAL ASPECTS AND COST ENGINEERING', Separation Science and Technology, 36: 15, 3311 — 3335

To link to this Article: DOI: 10.1081/SS-100107905

URL: http://dx.doi.org/10.1081/SS-100107905

SEPARATION SCIENCE AND TECHNOLOGY, 36(15), 3311–3335 (2001)

PERVAPORATION-BASED HYBRID PROCESSES IN TREATING PHENOLIC WASTEWATER: TECHNICAL ASPECTS AND COST ENGINEERING

F. Lipnizki* and R. W. Field

University of Bath, Claverton Down, BA2 7AY Bath, UK

ABSTRACT

In this study, the feasibility of combining pervaporation with adsorption in a hybrid process to recover phenol from wastewater is analyzed with the technical aspects and the cost of the processes taken into account. The pervaporation unit in the hybrid process is combined with a decanter on the permeate side and an adsorption unit on the retentate side. Two modes of regeneration, steam and heat, are considered for the adsorption unit. Through comparisons of the stand-alone units with the hybrid processes, we found that hybrid processes were feasible economic alternatives. In addition to meeting the environmental standard, the hybrid processes also recovered over 98% of the phenol at a concentration of 76% (wt). Even though the cost data showed that the use of heat regeneration for the adsorption unit is the cheaper option, the integration of steam regeneration improves the phenol recovery rate to over 99%. A sensitivity analysis of the economic boundaries of the hybrid

---

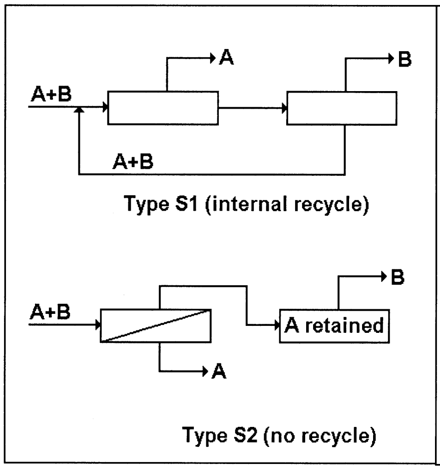
*Corresponding author. Current address: Danish Separation Systems AS, Stavangervej 10, DK-4900 Nakskov, Denmark. Fax: +45 7020 4910; E-mail: fl@sepsys.com

processes revealed that the membrane life cycle and not the membrane cost is the key cost parameter in the hybrid processes. The advantages of the hybrid process are further increased when the processes are scaled up. Overall, this study demonstrates that pervaporation-based hybrid processes that combine pervaporation, adsorption, and a decanter could be used effectively to recover phenol from industrial waste streams.

INTRODUCTION

Since the mid 1980s, hydrophilic pervaporation units have been successfully used on an industrial scale to dehydrate alcohols and to overcome chemical equilibrium in the esterification process by removing the water by-product. In both applications the successful implementation of pervaporation lies in the combination of pervaporation with other processes units, i.e., distillation and chemical reactors, in a hybrid process. Worldwide several hundred hydrophilic pervaporation units on various scales have been implemented (1). Despite the success of hydrophilic pervaporation in industry, hydrophobic pervaporation applications are developing at a slower pace; however, many potential applications are available for hydrophobic applications in biotechnology (2), food technology (3), and wastewater treatment. Even though the first commercial unit was reported in 1997 (4), only a few units had been installed by 2000. The reasons for this trend can be found in both membrane development and process integration. While for hydrophilic pervaporation 2 membrane types, polyvinylalcohol and polyacrylonitrile (PVA and PAN) membranes, and more recently, zeolite membranes have established themselves as successful membranes for water permeation, hydrophobic pervaporation often requires case-specific modified membranes because the permeating component varies with the application. Furthermore, the success of hydrophilic pervaporation can be related to its integration in hybrid processes with distillation and chemical reactors, while hydrophobic pervaporation units have only been installed as stand-alone units (4). To increase the employment of the potentially successful hydrophobic pervaporation process, improved membranes and an integration strategy for hydrophobic pervaporation are required.

Our aim was to develop a rigid approach for the successful integration of hydrophobic pervaporation in hybrid processes for the treatment of phenolic wastewater. We also considered the technical aspects and cost of the processes. In this paper, after the concept of hybrid processes is presented within the framework of wastewater treatment, the position of pervaporation in hybrid processes for wastewater treatment is analyzed, and then previously published pervaporation-based hybrid processes used to treat phenolic streams are reviewed. Based on this review and our goals, a novel pervaporation-based hybrid process, in which



Examples of Type S1:

- Pervaporation – Decanter
- Pervaporation – Reverse Osmosis
- Perstraction – Pervaporation
- Pervaporation – Steam Stripping

Examples of Type S2:

- Pervaporation – Adsorption
- Pervaporation – Oxidation
- Pervaporation – Biological Treatment
- Pervaporation – Extraction

Figure 1. Hybrid process types and potential combinations.

cumene oxidation was used (Hock's Process), for the treatment of a phenolic waste stream is developed and analyzed.

DEFINITION OF PERVAPORATION-BASED HYBRID PROCESSES FOR WASTEWATER TREATMENT

Generally, both conventional separation units and reactors can be combined with pervaporation methods to form a hybrid process. In wastewater treatment, pervaporation-based hybrid processes to date have been only studied in combination with separation units to remove organic compounds.[1] Two concepts of hybrid processes combining pervaporation with a separation unit can be distinguished (Fig. 1):

Type S1 is an interlinked combination that achieves a binary split, and

Type S2: is a combination of consecutive separation processes that achieves a split that could neither technically or economically be achieved independently.

The full integration of pervaporation in a hybrid process seems to be a crucial aspect for the success of pervaporation-based hybrid processes. Furthermore,

---

[1] The closest to a pervaporation-(bio)reactor hybrid process for wastewater treatment is found in the work of Livingston (5–7). The hybrid consisted of a combined bioreactor with a selective permeation process through a dense membrane.

a previous study (8) on hydrophilic pervaporation revealed that all hybrid-processes realized on an industrial scale are of Type S1. The importance of pervaporation is further highlighted in cases in which wastewater treatment is considered a part of clean production, which is a strategic undertaking in chemical-industry production. While Type S1 achieves a clear separation of component A and B, Type S2 requires a regeneration or disposal step that eliminates the portion of component A that is retained in the second process. This need for further action reduces the potential economic and ecological benefits of the process and is therefore the less favorable option.

POSITION OF PERVAPORATION IN HYBRID PROCESSES

Compared to other processes, such as decantation or distillation, pervaporation is not restricted by thermodynamic limitations, such as chemical equilibrium, and can therefore be used as both preconcentration and polishing steps in a hybrid process. However, an analysis of hydrophilic pervaporation in hybrid processes revealed that pervaporation was rarely used as a polishing step in industrial scale operations because of the purity required in production and the driving force limitation at low feed-side activity. This limitation of the transmembrane driving force leads to an exponential increase in membrane area when low concentrations are targeted, and pervaporation is considered a less favorable economic mechanism. This finding has direct implications on the selection of processes suitable for integration in pervaporation-based hybrid processes. On the retentate side, hydrophobic pervaporation must often be followed by a final polishing step.

Furthermore, while in hydrophilic pervaporation, zeolite membranes working as molecular sieves can achieve permeate streams with very low organic concentrations, the selectivity of polymeric membranes in hydrophobic pervaporation is often limited and generates permeate streams that cannot be directly recycled within the process. Consequently, pervaporation must be followed by another concentration step on the permeate side. Based on this low selectivity, hydrophobic pervaporation is often seen as a preconcentration step in front of a polishing step on the retentate side and a further concentration step on the permeate side in a hybrid process (Fig. 2).

BACKGROUND

Phenol

Phenol represents a family of important chemicals and its synthesis commonly involves the production of a contaminated wastewater stream. Phenol is

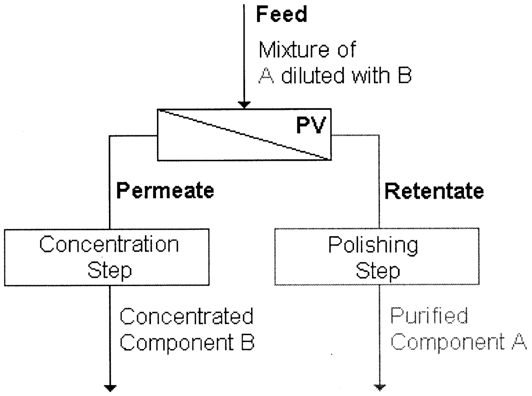


Figure 2. Position of hydrophobic pervaporation in a hybrid process.

used in the production of phenol-formaldehyde resins, caprolactam, adipic acid, bisphenol A, and aniline, which are required for the production of a wide range of consumer goods and product materials. Table 1 gives an overview of potential sources of phenol-contaminated effluents.

Phenol itself is acutely toxic, affecting the central nervous system, and the main absorption route is through the skin. Beyond a temperature of 68.4°C, phenol is totally miscible with water (9). Miscibility of phenol decreases with decreasing temperature, and at 20°C, approximately 7.5% (wt) phenol is present in water. The discharge limit for phenol in the United States, as mandated by the Environmental Protection Agency (EPA), is about 5 ppm.

Table 1. Sources of Phenol Contaminated Effluents

Industry	Production of Chemicals
Chemical industry	Bisphenol A
	Cumol-hyperoxide
	Phenol-formaldehyde-resin
	Phenol production
Coking plants	Carbonization of brown coal and hard coal
	Coking of brown coal and hard coal
	Production of charcoal
Petrochemical industry	Cracking installations

Pervaporation-Based Hybrid Processes for the Recovery of Phenol

The recovery of phenol from wastewater was one of the first applications proposed for hydrophobic pervaporation.

The simplest process design that has been suggested is the combination of pervaporation with a decanter and a recycling loop. Böddeker (10) patented several designs of pervaporation-decanter hybrid processes to separate phenol and water. In a typical process, a pervaporation unit was combined with a decanter to form a series process. Using high-selective hydrophobic sweep gas pervaporation, a phenol-rich (approximately 70% phenol) permeate stream is separated from a feed stream with less than 10% phenol. After condensation of the 2 immiscible permeate phases, a phenol-rich phase with about 70% phenol and a water-rich phase with 10% phenol spontaneously develop. The water-rich phase is then either removed from the process or recycled in front of a pervaporation unit. A further extension of this process is possible through the combination of 2 pervaporation units with 2 phase separation units as shown in Fig. 3 (10,11). The use of pervaporation in the recovery of phenol offers a simple, highly efficient, and inexpensive way (no additives are required and low temperature waste heat can be used within chemical plants) to remove phenol from contaminated water. The limitations of this hybrid process are the solubility of phenol in water on the phenol-rich side, and flux and selectivity of the pervaporation membrane, which along with the target concentration define the required membrane area, on the water-rich side.

Ray et al. (12,13) proposed a hybrid process combination of pervaporation and reverse osmosis to reduce a 500-ppm phenol level of contaminated wastewater to less than a 14-ppm level. The proposed system can treat 3.785×10^5 kg wastewater per day by combining a pervaporation unit with hydrophobic elastomeric polymeric membranes and a reverse osmosis unit with hydrophilic FT-30 spiral wound membranes (Dow Liquid Separations/Filmtech, Minneapolis, MN,

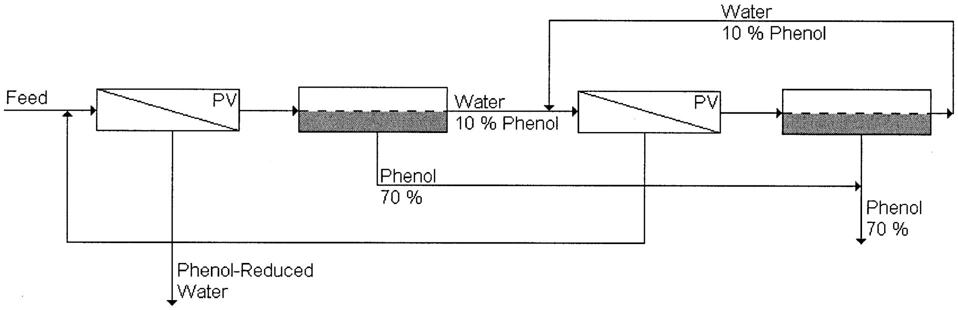


Figure 3. Separation of phenol from wastewater: Simplified process layout of a pervaporation-liquid-liquid separation hybrid process. Adapted from (11).

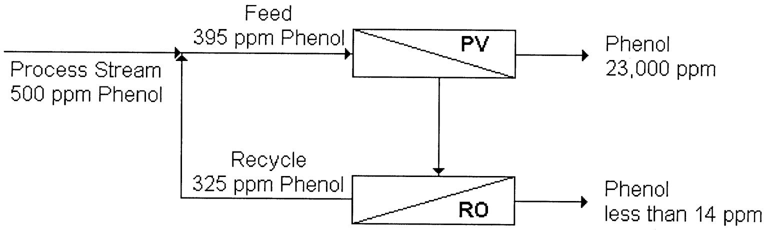


Figure 4. Separation of phenol from wastewater: basic process layout of the pervaporation–reverse osmosis hybrid process. Adapted from (14).

USA) (Fig. 4). The initial process feed stream was mixed with the recycled stream of the reverse osmosis unit to reduce the phenol concentration in the feed of the pervaporation unit to 395 ppm. The pervaporation unit separated the feed into a permeate stream enriched with phenol and a retentate stream with a low phenol concentration. The retentate from the pervaporation unit was further processed in the reverse osmosis unit. The permeate stream of the reverse osmosis unit contained 14 ppm phenol and could be directly discharged without further treatment (depending on the environmental regulations). The retentate stream containing 325 ppm phenol was recycled to the pervaporation unit. This layout allowed the hybrid process to handle a large range of feed stream concentrations and flow rates. A cost comparison revealed that for a low concentration feed the overall costs of the hybrid process were 5.4 times lower than the costs of pervaporation alone (13). The selectivity and the flux of the reverse osmosis and pervaporation membranes set the limitations of this process. Even though the pervaporation unit enriched the phenol by a factor of 60, the phenol concentration in the permeate of 2.3% (wt) was still too low for phase separation or recycling to occur and had to be further concentrated.

Bemquerer Costa (15) analyzed 2 layouts of a hybrid process that combined a reverse osmosis unit with a SU 700 membrane (ROPUR/Toray Industries, Münchenstein, Switzerland) and a pervaporation unit with hydrophobic PEBA 55 membranes (GKSS Forschungszentrum, Geesthacht, Hamburg, Germany). The process was set up to separate a feed stream of between 500 and 3500 ppm phenol into a product of 91.5% (wt) phenol and a water stream with less than 100 ppm phenol. In the first layout, shown in Fig. 5, the wastewater was initially treated by the reverse osmosis unit. Permeate from the reverse osmosis unit was directly discharged, and the phenol-rich retentate was further processed by the pervaporation unit. The retentate stream of the pervaporation unit was recycled to the reverse osmosis unit, while permeate was further treated in an additional step of liquid-liquid phase separation. The water-rich phase of the phase separation was recycled to the pervaporation unit and the phenol-rich stream was further concentrated in an evaporator to reach the final concentration.

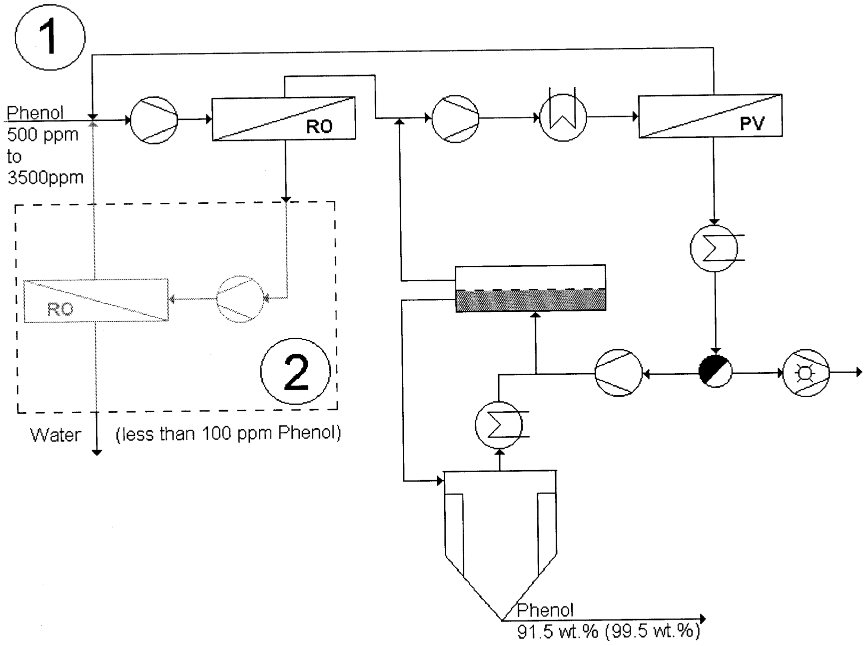


Figure 5. Separation of phenol from wastewater: process layout by a pervaporation–reverse osmosis hybrid process. 1) Simplified and 2) extended layout. Modified from (15).

In the second layout (Fig. 5), the latter steps of the process were similar to those of the first layout. However, because a single reverse-osmosis unit may not achieve the target of 100 ppm phenol in the water stream, a second reverse-osmosis unit was integrated into the process. The retentate of the second reverse-osmosis unit was mixed with the initial process stream. A comparison of the 2 layouts with systems in which pervaporation alone was used, shows that the hybrid processes are more economical because they do not require as much membrane area as do the stand-alone pervaporation units.

Klatt and Klatt and Rautenbach (16–18) proposed 2 layouts of a hybrid process with reverse osmosis upstream of pervaporation. The pervaporation process was equipped with hydrophobic polybutadiene-polyhydantoine composite membranes to recover phenol from water. In this case, the processes were to separate feed streams between 0.04 and 5% (wt) phenol to a final concentration of 99.5% (wt) and to reduce the phenol concentration in the discharge water to 20 ppm. The energy-intensive posttreatment of the final product by phase separation and evaporation to achieve the desired phenol purity in layouts by Bemquerer Costa (15) was overcome by replacing the phase separation and evaporation by a 2-stage condensation process. Also, the elimination of separation and evaporation steps reduced the investment costs. The improved layout, using a moderately selective membrane, reportedly achieves a high purity phenol in which only 1 pervaporation stage is needed and with the flexibility of having final phenol concentrations varied through a change in condenser temperature. Replacing the 2-stage reverse osmosis by a 4-stage osmosis with ideal cascades further extended the layout and all mixed streams had similar concentrations. In a cost comparison of this final layout with liquid-liquid extraction and adsorption (which included recycling either the extract or the adsorbents), the extraction was found to be economically superior to the hybrid process. On average, the costs of the hybrid process were 15% higher than they were for the liquid-liquid extraction but 30% lower than they were for adsorption. In addition, the costs of the hybrid process depended on phenol concentration of the feed, while the costs of liquid-liquid extraction were nearly independent of the feed composition. However, even in the case of low phenol concentration (0.075% (wt)) the hybrid process was not competitive with extraction. Even the use of membranes with the same selectivity but higher fluxes did not put the hybrid process in a more favorable position compared to liquid-liquid extraction. Overall, this process layout was highly dependent on flux and selectivity of the reverse osmosis and the pervaporation membranes. Furthermore, even though the process achieved a highly concentrated phenol stream, the phenol concentration in the water-rich output stream (under 100 ppm) was not justified by the complexity of the process; liquid-liquid extraction can achieve a concentration of 20 ppm with a process of lesser complexity.

We propose a new pervaporation-based hybrid process that overcomes the limitation of previous processes regarding selectivity and flux of the membranes and reduces the overall complexity of the process. In the analysis of the new hybrid process, we present both technical aspects and costs of the processes.

PROCESS DEVELOPMENT

On the basis of a preliminary screening, both adsorption and liquid-liquid phase separation were selected as conventional processes to be combined with pervaporation in a hybrid process (19). The initial stage of the process development is the modeling of the process units involved. The different modeling approaches for the technical aspects and evaluations are introduced. In our study, we aimed to reach the accuracy level of a study estimation as defined by the American Association of Costs Engineers 1958 (20). This parameter gives the study a probable range of accuracy of between ±20 to ±30%.

Modeling and Costs of Adsorption

The modeling and design of the adsorption unit was based on a short-cut method. The size of the adsorber was based on industrial adsorption data. The adsorption of the phenol from water onto powered activated carbon was described by a Freundlich isotherm. The applicability of the isotherm ranged from 1 to 100 000 μg/kg and was defined by the 2 Freundlich constants: *K* was 44.442 mg/g and the constant l/*n* was given as 0.3144 (21). The design approach used in this study is based on a procedure suggested by Faust and Aly (22). The relevant equations have been combined in a design spreadsheet.

Typical residence times in adsorption during industrial water treatment are between 20 to 120 minutes because mass transfer time is lower than that of gas separation (21,23). Taking industrial experience and a comparison of different carbons into account, we set the contact time to 120 minutes. In addition, we assumed that the mass transfer zone covers less than 10% of the total bed. For the regeneration of the carbon, both heat- and steam-regeneration modes were investigated. We assumed that during each regeneration cycle 20% of the carbon must be replaced due to carbon and efficiency losses. Because design data for steam regeneration in the literature is very limited, an industrial maxim was used to determine the steam requirement: 6 bed volumes of water as steam should be used for the regeneration (24).

The cost calculations of the adsorption unit were based on data collection sponsored by the EPA for the removal of volatile organic chemicals from potable water (25). The costs cover

investment costs of the main apparatus, contactors, and backwash pump;
investment-related construction costs, e.g., charges and site costs, as 18% of the investment costs of the main apparatus;
main operating and maintenance costs, i.e., carbon replacement and energy costs;
investment-related operating and maintenance costs as 7% of the total investment costs; and
investment and operation costs of a multiple hearth furnace in case of heat regeneration or off-site regeneration (carbon consumption is less than 910 kg/day) and operating costs in case of steam regeneration.

The costs were updated with the chemical engineering plant cost index (26). The annual operating time is set to be 8000 h/a. To ensure a continuous process, all adsorption units consisted of 2 sets of columns in which 1 was used for regeneration. For the cost comparison with other processes, the annual costs consisted of a combination of annual operating costs and annuities based on a 5-year write-off period and an interest rate of 8%.

Model Design and Cost Calculations of Pervaporation and Decanter

The pervaporation unit was modeled using PVModel, a design tool developed at the University of Bath (27,28). This simulation program is based on the resistance-in-series model and describes the mass transfer through the membrane and concentration boundary layer. The simulation of the process includes the influence of the pressure gradient and the heat balance through a finite elements-in-succession method. Using this simulation, pervaporation units can be sized and optimized while the influence of process parameters are taken into account. Both sizing and optimization was founded on the guidelines for applying hydrophobic pervaporation (28).

After an initial screening, 3 membranes were selected for this study:

1. an unfunctionalized PDMS (polydimethylsiloxane) membrane
2. a functionalized PDMS membrane loaded to 20% with an acetate group, and
3. a functionalized PDMS membrane loaded to 10% with a pyridyl group.

The thickness of the selective layer for all membranes was 0.025 mm. Their base membrane parameters are given in Table 2.

The PDMS membrane functionalized with an acetate group can be described as a high-flux low-selectivity membrane, while the PDMS membrane functionalized with a pyridyl group is a low-flux high-selectivity membrane. The unfunctionalized PDMS membrane is included in this study because it is the commonly used hydrophobic membrane.

For the process design of the pervaporation unit, vacuum pervaporation with plate-and-frame modules was selected as the standard process design for industrial applications of hydrophilic pervaporation. For the cost calculations, we assumed that the condenser on the permeate maintains the vacuum and the vacuum pump is only used for the start-up and the removal of inerts from the system. Hence, we assumed that the vacuum pump only works for 2% of the total opera-

Table 2. Base Parameters of Membranes for the Recovery of Phenol (29)

Membrane Type	Chemical Structure	Loading (%)	P_w^* (kmol/m·s)	P_o^* (kmol/m·s)	$\alpha_{o/w}$
Unfunctionalized PDMS	n.a.	0	2.48 E−10	2.22 E−10	17.7
Acetate group	—$CH_2CO_2CH_3$	20	1.14 E−09	7.82 E−10	13.1
Pyridyl group	—C_5H_4N	10	3.34 E−10	5.74 E−10	31.8

Temperature = 343.15 K.
n.a. Not applicable.

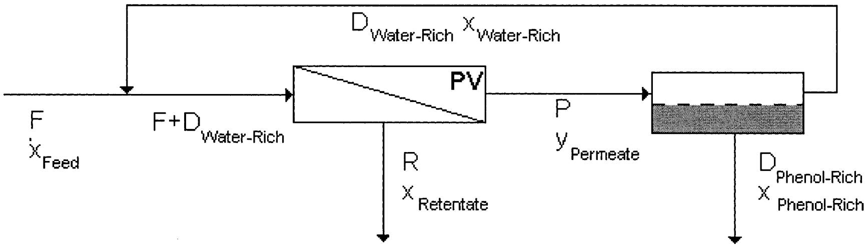


Figure 6. Simplified arrangements of pervaporation unit and decanter.

tion time. However, the sizing of the vacuum pump is based on the total permeate stream needed to start up the system.

For this study, the original simulation program was modified to include a decanter and a recycling loop (Fig. 6). For this design, the mass and concentration balances of the overall systems were solved through an integration of an iteration loop in the simulation with an resulting error equal to less than ±1%.

The cost analysis was based on simulation results because no uniform database on hydrophobic pervaporation was found, the different data sources are combined in a datasheet for the cost calculations. This spreadsheet covers

investment costs of the main apparatus, feed and vacuum pumps (30), membranes and modules (29), a vacuum vessel (32), re-heater (33), condenser (33), decanter, piping, and control (34);
investment-related construction costs, e.g., charges and site costs, as 18% of the investment costs of the main apparatus;
main operating and maintenance costs, i.e., membrane replacement and energy costs; and
investment-related operating and maintenance costs as 7% of the total investment costs.

The pervaporation costs were updated in a way similar to the adsorption costs. The calculations of the operating costs were based on 8000 hours per year and included the replacement costs of the membranes after a life cycle of 2 years. No refund for recovered phenol from the phenol-rich phase of the decanter was included in the cost analysis. Based on these parameters, the annual costs for the pervaporation were calculated for comparison.

PROCESS DESIGN AND COST CALCULATIONS

The process design and cost calculations for all processes were based on a feed stream of 1000 kg/h and a phenol concentration of 3% (wt), which represents a typical concentration from phenol production through the use of cumene oxidation (Hock process), the most common process for phenol production (9). At this concentration, phenol is completely miscible with water. The discharge limit in all cases was set at 5 ppm.

Previous studies revealed that the required membrane area of pervaporation increases with a decrease in retentate concentration (Fig. 7.1). This trend is independent of the membrane and the organic compound selected, and can be related to the diminishing feed-side driving force at low concentrations (27,28). However, a decreasing feed concentration in the case of adsorption leads to lower carbon consumption and longer cycle times. Hence, pervaporation was selected as the first unit followed by adsorption as the polishing step on the retentate side. To reach high phenol concentrations on the permeate side, the pervaporation unit was followed by a decanter. The phenol-rich phase of the decanter concentrated the phenol in the permeate by a factor of 3.5 (Fig. 7.2). This enrichment factor of the phenol-rich phase in the decanter is independent of the permeate concentration as long as the solubility limit of the phenol is reached in the permeate. Even though the water-rich recycling stream from the decanter in front of the pervaporation unit was slightly smaller in the case of the low-flux high-selectivity pyridyl functionalized PDMS membrane, the overall membrane area required was over 40% larger than that of the high-flow low-selectivity acetate functionalized PDMS membrane. Although the acetate functionalized membrane has a smaller area, additional costs associated with the increased condensation (due a larger permeate stream) can be found. However, these additional expenses, as defined for the cost data and related assumptions, were lower than the additional costs of the pyridyl functionalized PDMS membrane. Furthermore, in this arrangement, the type of membrane has little affect on the size of the retentate stream. Consequently, the choice of membrane does not affect the size of the secondary process, i.e., adsorption. The selectivity of any candidate membrane must be sufficiently high to overcome the solubility limit, while the final choice depends on the economic boundaries set by the study.

The different process parameters selected for the pervaporation unit were based on the guidelines for applying hydrophobic pervaporation (28) and are summarized in Table 3.

The change-over concentration between the processes was defined after the process units were independently optimized through comparisons of total annual costs of processes at different retentate concentrations, which are based on the pervaporation unit/feed concentrations of the adsorber. The optimum changeover concentration was case specific for adsorption. With a multiple hearth furnace and off-site regeneration, adsorption was 0.4% (wt), but it was 0.2% (wt) for steam regeneration. The two optimum process layouts with flow rates and concentrations shown are presented in Fig. 8.

The annual costs of all processes are summarized in Table 4. The most economic options are the 2 hybrid processes combining pervaporation either with off-site heat or steam regeneration. Both processes have different advantages. While the hybrid process combined with off-site heat regeneration is the most economic option,

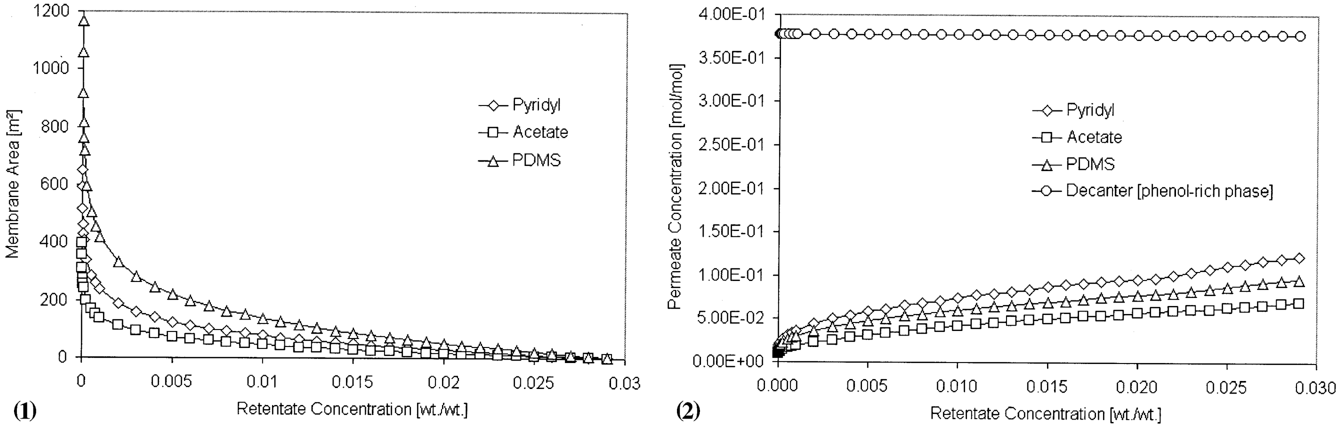


Figure 7. 1) Retentate concentration versus membrane area for pervaporation-decanter hybrid process with different membranes. 2) Retentate concentration versus phenol concentration of pervaporation unit without decanter and a stand-alone decanter.

Table 3. Parameters for Simulation of Pervaporation Unit

Process Parameters		
Process mode	(–)	Vacuum pervaporation
Feed stream	(kg/h)	1000
Initial feed temperature	(K)	343.15
Minimum module inlet temperature	(K)	333.15
Permeate pressure	(bar)	0.01
Flow pattern	(–)	Co-current flow
Module Geometrics		
Module type	(–)	Plate-and-frame
Module length	(mm)	500
Module width	(mm)	500
Feed channel heights	(mm)	1
Permeate channel heights	(mm)	1

the hybrid process combining pervaporation with steam regeneration is the most integrated process and has the maximum phenol recovery rate. In the steam-regeneration hybrid, over 99% of phenol is recovered for recycling at a concentration of 76% (wt) compared to a recovery rate of 98% in case of off-site heat regeneration.

The economic advantages of the heat-regeneration hybrid process are directly related to the regeneration step of the adsorbent. While the reduced operation costs of this process can be related to subcontracting the regeneration, the reduced investment costs can also be related to a reduced feed stream that goes to the pervaporation unit because no steam must be recycled.

In Fig. 9 a detailed analysis of the annual costs is given. For both hybrid processes the cost structure is relatively similar except for the operating costs for ad-

Table 4. Breakdown of Annual Costs

Process	Investment Costs (£)	Operating Costs (£/a)	Annuity (£/a)	Annual Costs (£/a)
Adsorption (heat regeneration)	2 938 980	681 507	736 086	1 417 594
Pervaporation and decanter (including recycling loop)	557 506	171 259	139 631	310 890
Hybrid process pervaporation and adsorption (heat regeneration)	404 326	93 525	101 266	194 791
Hybrid process pervaporation and adsorption (steam regeneration)	457 419	100 323	114 564	214 887

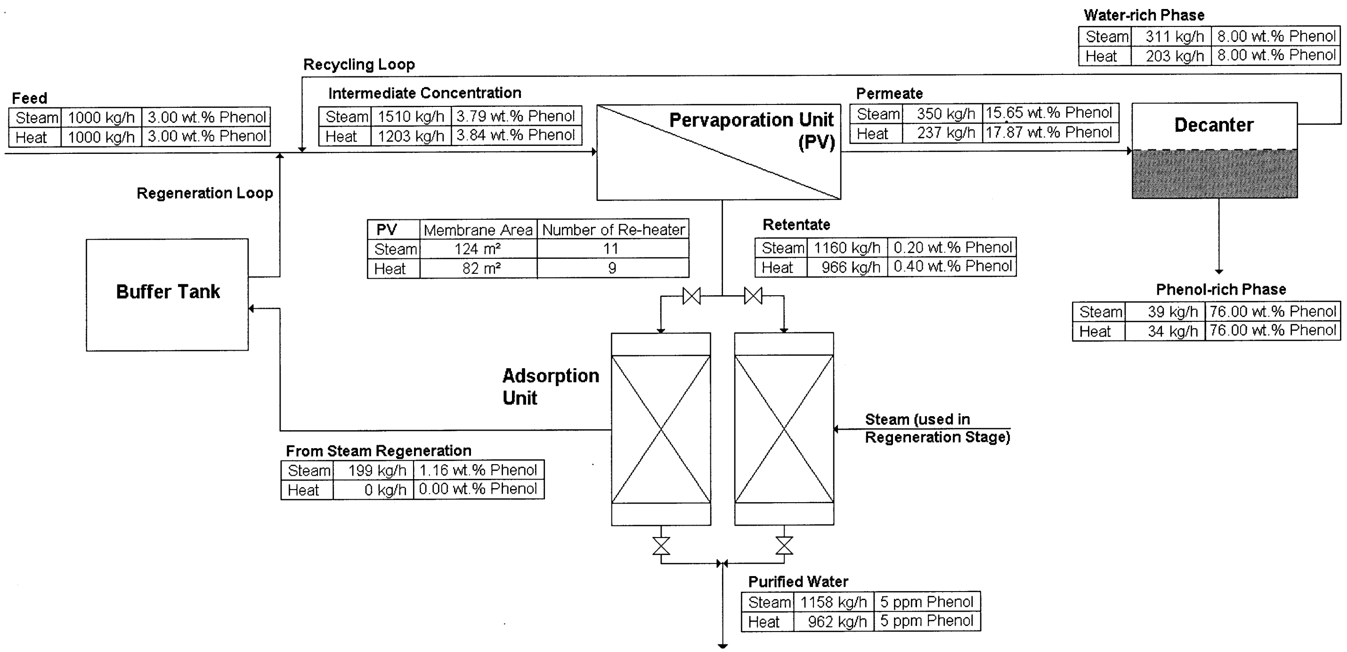


Figure 8. Schematic of hybrid process layout (without condenser and heat exchangers): pervaporation-adsorption with steam and heat regeneration.

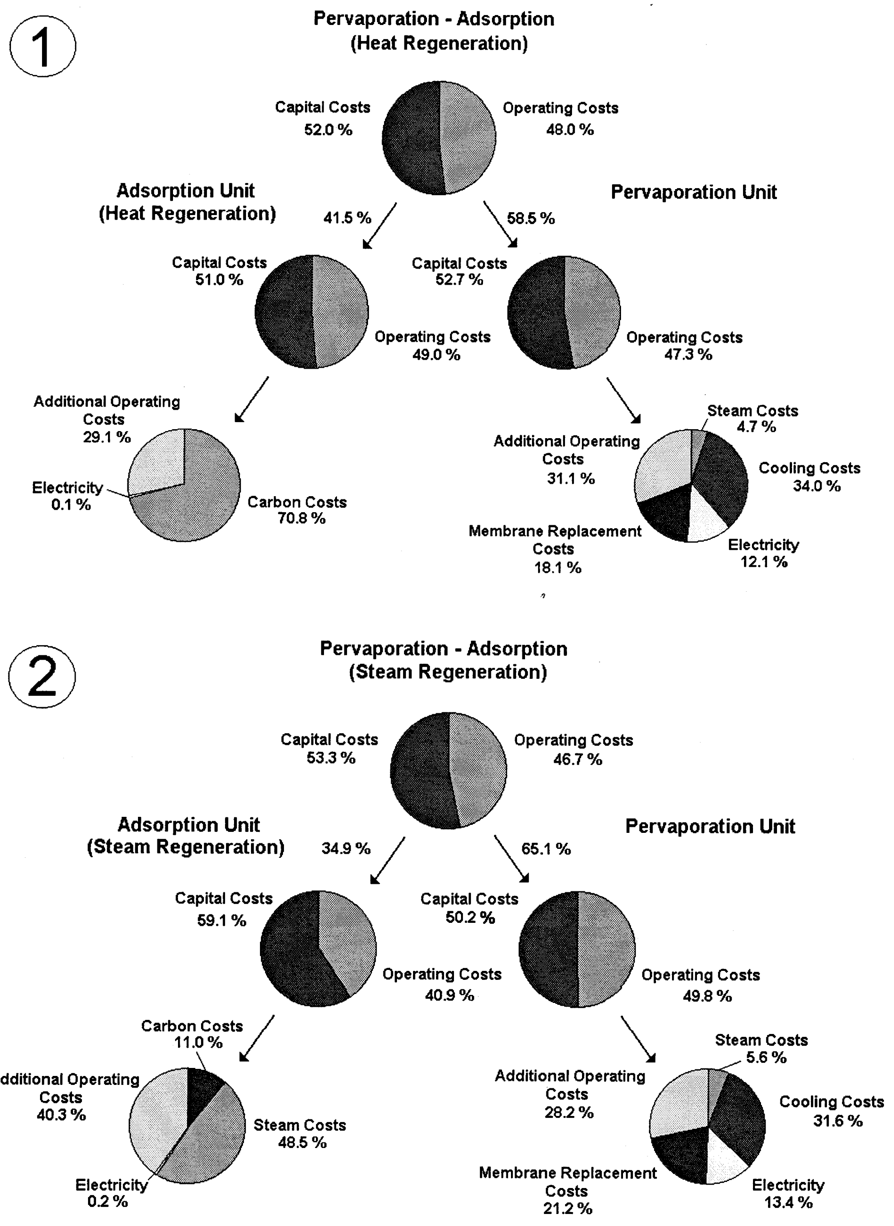


Figure 9. Cost analysis of hybrid processes: 1) pervaporation-adsorption with heat regeneration and 2) pervaporation-adsorption with steam regeneration.

sorption. The heat-regeneration costs are dominated by carbon costs (70.8 % of operating costs), while in steam regeneration, the steam costs (48.5 % of operating costs) take up the greatest share. The greatest share of operating costs in the case of pervaporation is related to the cooling requirement (34.0% and 31.6% of operating costs per process) to liquefy the permeate and thereby maintain the vacuum.

Process design and economic conditions for both hybrid processes are superior to the stand-alone units. Because both hybrid processes have either economic or ecological advantages over each other, and the costs of the processes are within the accuracy goals for this study (±20 to ±30 %), both process were studied further.

SENSITIVITY ANALYSIS

Based on the final designs of the hybrid processes, a sensitivity analysis was conducted to determine the stability of the results toward changes in selected economic boundaries. For the sensitivity analysis 2 key cost parameters were

1. membrane costs, and
2. membrane life cycle.

The annual costs were chosen for comparison because a change in membrane costs will affect both initial investment and operating costs as functions of membrane replacement costs.

Changing membrane costs have a relatively small effect on the annual cost (Fig. 10). A 25% change in membrane costs leads to a change of less than 5% in annual costs. This outcome may be the result of membrane costs accounting for only about 10% of the total investment costs, while membrane replacement costs account for less than 15% of the annual operating costs. The steam-regeneration hybrid process is more affected by a change in membrane costs because it requires a larger membrane area than does heat regeneration. The membrane life cycle is more important to the cost analysis than is membrane area. Changes in the membrane life cycle can lead to an exponential increase in annual costs (Fig. 10). Thus, a membrane replacement period in excess of 1 year is important. The steam-regeneration hybrid process is more affected by a change in membrane life cycle than is the hybrid process with steam regeneration. The dependency of the steam-regeneration hybrid on life cycle may be related to the relatively large required membrane area.

Overall, the sensitivity analysis revealed that the membrane costs are certainly important but the key membrane parameter is the life cycle of the membrane, which must be at least 1.5 years to reduce the impact upon annual costs by less than 5%. Furthermore, an increase in membrane life cycle from 1 to 2 years can justify an increase in membrane costs by up to 25%.

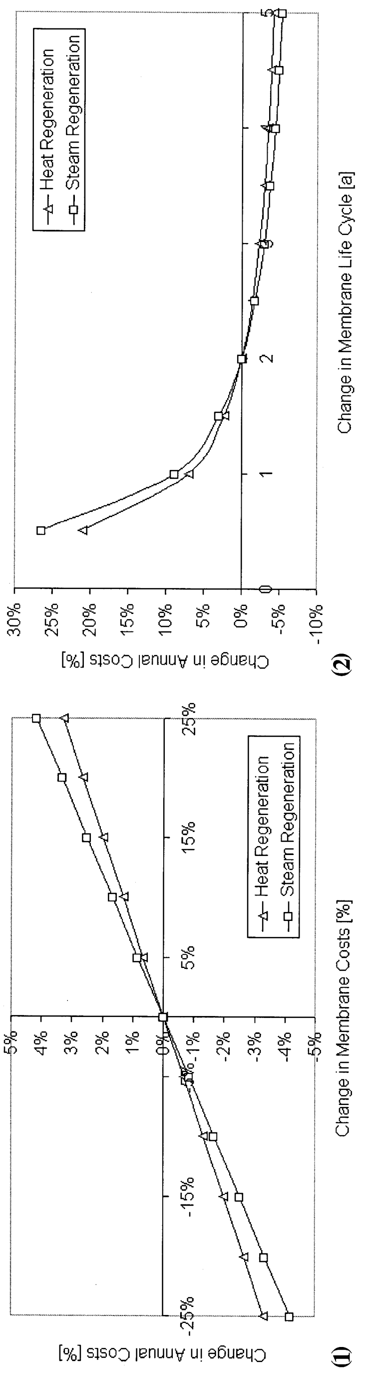


Figure 10. Sensitivity analysis of hybrid processes: 1) membrane costs and 2) membrane life cycle.

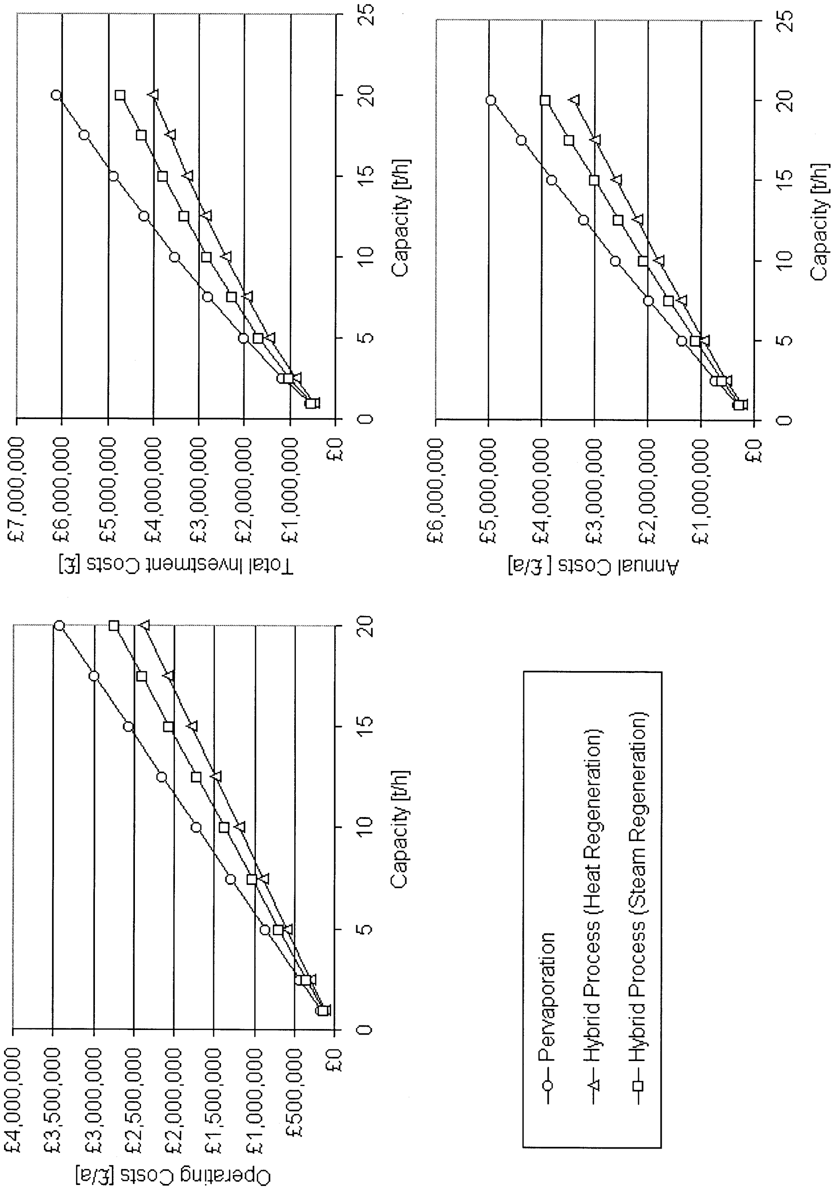


Figure 11. Scale-up of hybrid processes.

SCALE-UP OF THE HYBRID PROCESSES

For the scale-up of the hybrid process, the following method to estimate capital costs was used (20):

$$\frac{C_2}{C_1} = \left(\frac{S_2}{S_1}\right)^k \qquad (1)$$

For the scale-up of a standard plant, the six-tenths power rule ($k = 0.6$) can be applied; it typically provides the investment costs with an accuracy of ±30 % (32) and is therefore within the accuracy range of this study. However, the literature on the scale-up of membrane processes is very limited. For reverse osmosis (33) and ultrafiltration (34), some have suggested that the nonmembrane plant items and the membranes be scaled up independently.

Hence, due to their modular design, for nonmembrane plant items the factor n was set to 0.6 while the membrane costs were scaled-up with the factor n equal to 1.0.

Using the simulation tools and the cost assessment, 2 different scales of pervaporation and adsorption units (1000 kg/h and 10 000 kg/h) are designed and evaluated for different membranes and duties. This analysis revealed that for pervaporation the scale-up factor $n = 0.8$. Furthermore, with the cost data collected (25), a scale-up factor $n = 0.5$ was determined for adsorption. Based on the annual cost, different scales of the hybrid process were estimated (Fig. 11).

With an increasing capacity, the economic advantages of the hybrid processes also increase over those of the stand-alone pervaporation processes. In particular the heat-regeneration hybrid process has the increased advantage of higher capacities due to the lower scale-up factor of its adsorption unit. Overall, larger capacities increase the economic advantages of hybrid processes over the stand-alone pervaporation units, and therefore, the use of the higher-complexity units is justified.

CONCLUSIONS

This study, which compared stand-alone pervaporation and adsorption units with hybrid processes combining both processes, shows that hybrid processes are economically superior to the stand-alone units. Furthermore, the proposed hybrid processes produce a water stream for direct discharge in accordance with environmental standards. A decanter and a recycling loop in the process layout enable the hybrid processes to produce a concentrated phenolic stream for recycling. Both steam and heat regeneration are viable alternatives for housing adsorption units in hybrid processes. While heat regeneration is the more attractive economical process, steam regeneration seems to be more attractive on technical grounds because it offers a higher phenol recovery rate. Because the results of cost analysis of the regeneration alternatives are within the probable range of accuracy deemed appropriate for this study, no final ranking of the processes is given. A sensitivity analysis of the final hybrid process layouts revealed that the membrane life cycle is a very critical parameter for cost determinations of the processes, while the influence of the membrane costs is a less significant factor. Furthermore, the advantages of the hybrid processes increase with an increasing membrane capacity. Compared to previously described hybrid processes (10–18) and liquid-liquid extraction (16–18), the hybrid processes proposed in this study not only achieve a lower phenol concentration in the water but are also expected to be cheaper.

Overall, one can conclude that pervaporation-based hybrid processes that combine pervaporation, adsorption, and a decanter are potential alternatives to stand-alone units for the recovery of phenol from industrial wastewater streams.

NOMENCLATURE

Symbol

C	cost of unit/plant (£)
K	Freundlich constant (mg/g)
k	scale-up factor (–)
n	Freundlich constant (–)
P^*	permeability (kmol/m·s)
S	capacity of unit/plant (kmol/h), (kg/h)
x	weight fraction in liquid phase (–)
y	weight fraction in vapor phase (–)

Greek Letters

$\alpha_{o/w}$	selectivity $\left[\alpha_{o/w} = \frac{y_o x_w}{x_o y_w} = \frac{y_o(1 - x_o)}{x_o(1 - y_o)}\right]$

Subscript

o	organic compound (phenol)
w	water

REFERENCES

1. Paul, D. Clean Production with Membrane Technology. In *International Conference on Membrane Science and Technology*, Beijing, P.R. China, June 9–13, 1998; 11–12.

2. Use of Pervaporation-Bioreactor Hybrid Processes in Biotechnology. Chem. Eng. Technol. **2000,** *23* (7), 569–577.
3. Baudot, A.; Marin, M. Pervaporation of Aroma Compounds: Comparison of Membrane Performances with Vapor-Liquid Equilibria and Engineering Aspects of Process Improvement. Trans. IChemE Part C **1997,** *75* (2), 117–142.
4. Baker, R.W. Separation of VOCs from Water by Pervaporation. In *Euromembrane '97*, Twente, The Netherlands, 1997; 313.
5. Livingston, A.G. A Novel Membrane Bioreactor for Detoxifying Industrial Wastewater: I. Biodegradation of Phenol in a Synthetically Concocted Wastewater. Biotechnol. Bioeng. **1993,** *41* (10), 915–926.
6. Livingston, A.G. A Novel Membrane Bioreactor for Detoxifying Industrial Wastewater: II. Biodegradation of 3-Chloronitrobenzene in an Industrially Produced Wastewater. Biotechnol. Bioeng. **1993,** *41* (10), 927–936.
7. Livingstone, A.G.; Arcangeli, J.P.; Boam, A.T.; Zhang, S.; Marangon, S.; Freitas dos Santos, L.M. Extractive Membrane Bioreactors for Detoxification of Chemical Industry Wastes: Process Development. J. Membrane Sci. **1998,** *151* (1), 29–44.
8. Lipnizki, F.; Field, R.W.; Ten, P.K. Pervaporation-Based Hybrid Processes: A Review on Process Design, Applications and Economics. J. Membrane Sci. **1999,** *153* (2), 183–210.
9. Jordan, W.; van Barneveld, H.; Gerlich, O.; Kleine-Boymann, M.; Ullrich, J. *Phenol*. In *Ullmann's Encyclopedia of Industrial Chemistry*; Elves, B., Hawkins, S., Russey, W., Schulz, G., Eds.; VCH Publishers Inc: Weinheim, Germany, 1991; 492–496.
10. Böddeker, K.W. Pervaporation of Phenols. US Patent 4,806,245, 21 February, 1989.
11. Böddeker, K.W.; Bengtson, G. Phenolanreicherung durch Pervaporation. Erdöl und Kohle-Erdgas **1987,** *40* (10), 439–441.
12. Ray, R.; Wytcherley, R.W.; Newbold, D.; McCray, S.; Friesen D.; Brose, D. Synergistic Membrane-Based Hybrid Separation Systems. J. Memb. Sci. **1991,** *62,* 347–369.
13. Ray, R.; Friesen, D.; Wytcherley, R.W.; Schofield, R. Pervaporation-Based Hybrid System. In *Proc. 4th Int. Conf. Pervaporation Processes in the Chemical Industry;* Bakish Material Corp: Englewood, NJ, 1989; 200–214.
14. Schofield, R.W.; McCray, S.B.; Ray, R.J.; Newbold, D.D. Opportunities for Pervaporation in the Water-Treatment Industry. In *Proc. 5th Int. Conf. Pervaporation Processes in the Chemical Industry*. Bakish Material Corp: Englewood, NJ, 1991; 409–420.
15. Bemquerer-Costa, A. Pervaporation mit Hydrophoben Membranen—Einsatzperspektiven und Wirtschaftlichkeit. Ph.D. diss., University of Aachen, Germany, 1989. (in German)

16. Klatt, S. Zum Einsatz von Pervaporation im Umfeld der Chemischen Industrie. Ph.D. diss., University of Aachen, Germany, 1993. (in German)
17. Klatt, S. Pervaporationsmembrane zur Trennung und Abtrennung von Organika. Teil I: Abtrennung von Phenol aus wäβrigen Lösungen. IVT-Information **1991,** *21* (1)*,* 4–12.
18. Rautenbach, R.; Klatt, S. Treatment of Phenol-Contaminated Wastewater by a RO-PV Hybrid Process. In *Proc. 5th Int. Conf. Pervaporation Processes in the Chemical Industry*; Bakish Material Corp: Englewood, NJ, 1991; 392–408.
19. Lipnizki, F.; Field, R.W. Pervaporation-Based Hybrid Processes: Technical and Economic Aspects in Treating Phenolic Waste Water. In *Int. Congr. on Membranes and Membrane Processes ICOM ′99*, 1999; 49.
20. Institution of Chemical Engineers. *A Guide to Capital Cost Estimation*, 3rd Ed.; Author: Rugby, 1988; 14–19.
21. Gesellschaft für Umwelttechnologie mbH, Friedberg-Ockstadt, 1999.(in German)
22. Faust, D.; Aly, O.M. *Adsorption Processes for Water Treatment*; Butterworth Publishers: Stoneham, 1987; 156–158.
23. Börger, G.G. *Umweltschutz in der Chemischen Industrie;* University of Bochum, Germany, 1996. (in German)
24. Tennison, S. Personal Communication. MAST Carbon, 1998.
25. Environmental Science and Engineering, Inc. *Removal of Volatile Organic Chemicals from Potable Water. Technologies and Costs.* Noyes Data Corporation: Park Ridge; 1986.
26. Economic Indicators. *Chem. Eng.* **1999,** *106* (12), 150.
27. Lipnizki, F.; Field, R.W. Design and Optimisation of Pervaporation Processes to Recover Organic Compounds from Waste Water. *International Conference on Membrane Science and Technology*, 1998; 162–163.
28. Lipnizki, F.; Field, R.W. Simulation and Process Design of Pervaporation Plate-And-Frame Modules to Recover Organic Compounds from Waste Water. Trans. I Chem E Part A **1999,** *77* (3)*,* 231–240.
29. Bennett, M.; Brisdon, B.J.; England, R.; Field, R.W. Performance of PDMS and Organofunctionalised PDMS membranes for the Pervaporative Recovery of Organics from Aqueous Streams. J. Memb. Sci. **1997,** *131* (1)*,* 63–88.
30. Ji, W.; Hilaly, A.; Sikdar, S.K.; Hwang, S.T. Optimization of Multicomponent Pervaporation for Removal of Volatile Organic Compounds from Water. J. Memb. Sci. **1994,** *97* (1), 109–125.
31. Arnold, D. Optimierungsstrategie zur Einbindung von Pervaporationsanlagen bei der Entwässerung von Lösungsmitteln. Ph.D. diss., University of Aachen, Germany, 1995. (in German)
32. Vier, J. Pervaporation Azeotroper Wäβriger und rein Organischer Stoffgemische—Verfahrensentwicklung und Integration. Ph.D. diss., University of Aachen, Germany, 1995. (in German)

33. ASPEN Plus^{TM} Release 9.3-1, 1996.
34. Backhurst, J.R.; Harker, J.H. *Process Plant Design;* Heinemann Educational Books Ltd: London, 1973.
35. Perry, R.H.; Green, D.W. *Perry's Chemical Engineers' Handbook,* 7th Ed.; McGraw-Hill Co: New York, 1997; Section 22.
36. Owen, G.; Bandi, M.; Howell, J.A.; Churchhouse, S.J. Economic Assessment of Membrane Processes for Water and Waste Water Treatment. J. Memb. Sci. **1995,** *102,* 77–91.

Received August 2000
Revised January 2001

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Downloaded At: 10:40 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS100107905