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A multi-objective mathematical programming framework for a sustainability analysis of wastewater treatment processes

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Abstract: Industrial processes are gradually becoming more efficient as new designs consider the effect on costs and environmental impacts and costs. However, decisions on operating costs might not always be in hand with lower environmental impacts. Therefore, innovative approaches are needed to better understand and recognise the economic and environmental effects of industrial processes. This paper presents a multi-objective mathematical programming framework for a sustainability analysis of two wastewater treatment processes: pervaporation (PERV) and steam stripping (SS). The framework comprises mass and energy balances, design specifications, equipment size and utilities consumption. In addition, the framework makes use of life cycle approaches to quantify the environmental impact of the process under a holistic perspective. As a result, optimal operating conditions, at which environmental impact and treatment cost are minimised, have been identified. The multi-objective operating curves developed as part of this paper serve as a basis for decision making geared towards sustainable process designs.

Keywords: multi-objective mathematical programming; treatment technologies minimum environmental impact; life cycle assessment; LCA.

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1 Introduction

The rapid development of operations and processes has given rise to multiple environmental problems and challenges in the sense that firms face increasingly competitive environments (Roy and Vezina, 2001; Azapagic et al., 2004). Therefore, industries search for multiple criteria (economic, maintenance, reliability, environmental) that would assist them in determining optimal operating conditions or the most adequate technology to incorporate into their processes (Jimenez and Lorente, 2001). Among these criteria, sustainability concerns are becoming a relevant issue for both customers and legislators (Romero-Hernandez et al., 1998). As such, computational methods usually devoted to artificial intelligence and operational research problems solution have been introduced into the areas of environmental engineering (El-Din et al., 2004).

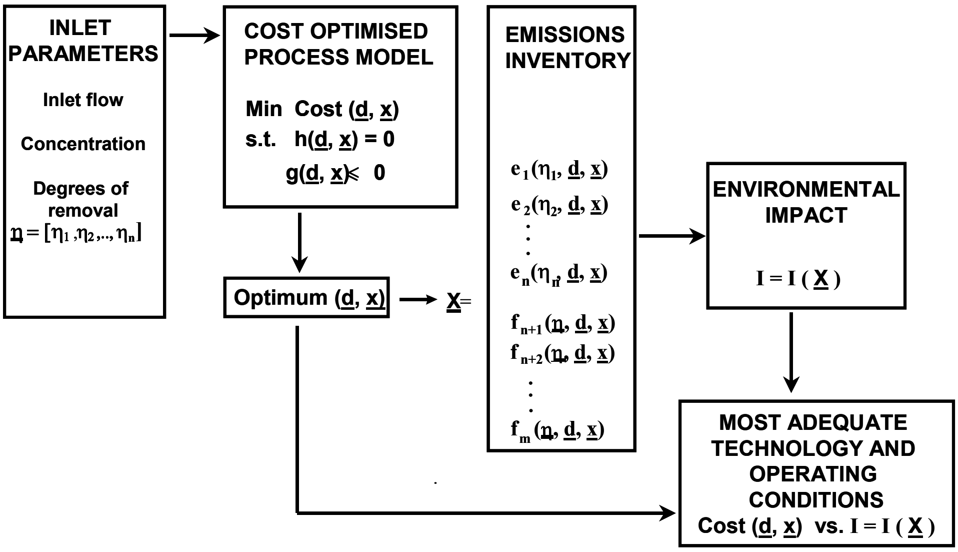
There are different interests and concerns influencing the implementation of environmental initiatives into process design and operation (Pereira, 1999). In particular, those concerned with avoiding (or reducing) emissions into the environment. Furthermore, treatment technologies that reduce the concentration of pollutants from waste streams (which result from producing a specific good) before being discharged into the environment exist (Bourgeois et al., 2004), but are still in development stages and not directly applicable for industrial aims.

This paper presents a framework devised in order to define two objectives of interest for the industry, i.e., treatment cost and environmental impact. The approach is illustrated with a case study which includes the analysis of steam stripping (SS) and pervaporation (PERV). A mathematical non-linear programming formulation is proposed for each treatment process, allowing the numerical evaluation of both criteria.

The framework is applied under two different methodologies: the first one is a mono-objective optimisation problem that considers the minimisation of the treatment cost, subject to emission restrictions in the discharge stream (Romero-Hernandez, 2005). The resulting environmental impact is then computed in a second step. The analytical non-linear formulation allows the application of exact optimisation procedures available in the widely used generalised algebraic modelling system (Brooke et al., 1998).

However, the consideration of the only economic objective in the above-mentioned optimisation step is not entirely satisfactory. The development, in the operations research area, of a great diversity of multi-objective optimisation techniques actually proved that focusing on only one criterion provides a limited view of the actual situation. The dominance concept, introduced by Pareto, highlights that between the mono-objective optima; a set of good compromise solutions can usually be identified. The second proposed methodology is a bi-criteria optimisation step that considers the minimisation of both economic and environmental criteria.

Figure 1 Representation of the integrated mono-objective approach



2 Framework

The main steps to be performed for the mono-objective strategy are presented below, while a schematic representation of the integrated approach is presented in Figure 1.

1 *Characterise the flowrate and the concentration of the pollutants in the wastewater.*

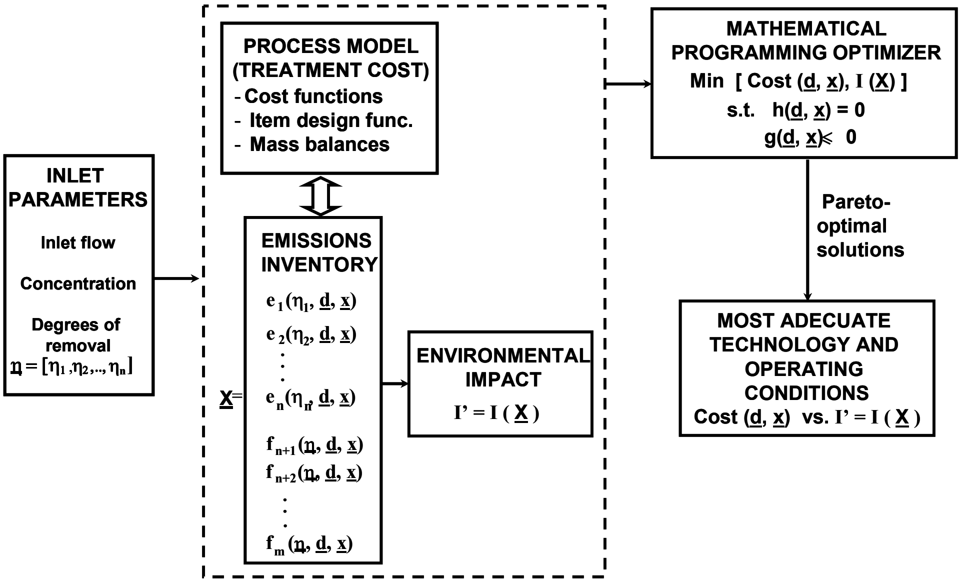
2 *Develop cost optimised models* for PERV and SS treatment technologies at the cost optimal point (depending on the discharge constraint).

3 *Generate an inventory of pollutants* including both emissions arising due to incomplete abatement and discharges associated with process inputs. This should be based on a life cycle assessment (LCA) approach. This activity helps to compare the environmental performance of each wastewater treatment technology, based on the relationship between emissions associated to *outputs* (waste streams arriving from the process) and *inputs* (i.e., emissions generated from the production of electricity, steam, steel, etc., which are required in order to operate the process).

4 *Assess the environmental impact of the entire system* using appropriate environmental metrics. This will help to identify the optimal degrees of pollution abatement (ODPAs) at which environmental impact is minimised. Moreover, it shall assist in the identification of the most adequate technology.

As shown in Figure 1 for mono-objective approach, when entry flows are determined, just one criteria is minimised, generally the economic cost. Mass and energy balance restrictions limit this optimisation. Thus, the environmental results are established. The emissions of different pollutants are stored in an $\underline{X}$ vector. This is related with the environmental impact through parameters according to the impact that will be measured. This procedure is explained in Section 6.

Figure 2 Representation of the integrated multi-objective approach



The bi-criteria nature of the problem lead directly to a simultaneous optimisation approach, in which both criteria, cost and environmental impact, are optimised. Moreover, both objectives tend to show inverse relationships between them, it means they are 'antagonic'. This argument justifies the fact that better solutions might be found using multi-objective methodologies to solve the problem.

3 Mathematical model

The first part of the integrated approach consists in defining the inlet parameters (flow and concentration) and the maximum amount of pollutant that can be discharged without posing significant risk to the environment. These values provide an indication of the minimum amount of pollutant that needs to be removed by the treatment technologies. The second part of this approach deals with the design and evaluation of the processes. PERV and SS technologies are represented by a set of mathematical equations that describe the properties of the inlet waste stream, equipment specifications, cost functions and the degree of pollutant removal. The concept of *removal efficiency* is incorporated into the model as a parameter describing the amount of pollutant removed in relation to its initial concentration. The system assumes *n* number of pollutant species regulated by emission limits and *m* number of pollutant species associated with inputs generation. The set of removal efficiencies is defined by $\underline{\eta}$, which is a vector with *n* number of removal efficiencies applied to each pollutant specie, $\underline{\eta} = [\eta_1, \eta_2, \ldots, \eta_n]$. Therefore, the mathematical model consists of a series of specified parameters, such as the inlet flowrate and the initial concentration of pollutant in the wastewater stream (assumed to be fixed by the production process) and removal efficiencies (which are directly related to the emission limits imposed by legislation). These parameters are incorporated into a cost optimisation program.

This optimisation identifies the process design that may minimise one or several objectives, such as the cost of abatement or the environmental impact, subject to a set of discharge limits, $\underline{\eta}$ and equality and inequality constraints, $h(\underline{d}, \underline{x}) = 0$ and $g(\underline{d}, \underline{x}) \leq 0$, which represent design specifications, mass and energy balances. Index $\underline{d}$ denotes the potential existence of equipment units while $\underline{x}$ corresponds to design variables and operating conditions.

Two outputs emerge from the optimisation program:

1 The minimum cost and the optimum design and operating conditions required to achieve the specified emission limits, $Cost\ (\underline{d}, \underline{x})$.

2 A vector of total emissions, $\underline{X}$, determined at the cost optimal configuration. It comprises both emission of pollutants from the wastewater stream, also called *outputs*, $e_{i\ (i=1,\ldots,n)}$ and emission of pollutants associated with *inputs*, $f_{i\ (i=n+1,\ldots,m)}$:

$$\underline{X} = [e_1, e_2, \ldots, e_n, f_{n+1}, f_{n+2}, \ldots, f_m] \quad (1)$$

The environmental impact of the system is then related to $\underline{X}$ through an environmental function, $I = I(\underline{X})$. Any type of environmental impact [i.e., global warming, ozone depletion, ozone creation, critical air volumes (CAV), etc.] can be incorporated into this function, usually with the use of environmental indices, *EI*, for each pollutant species, *i*.

Given that each index describes a specific environmental impact per unit of mass of pollutant species, it allows all emissions from different compounds to be lumped together into a single number, which then represents the specific impact. Thus, the environmental function is expressed as the sum of environmental impacts generated by both *outputs* and *inputs* from each pollutant species, *i* and can be described as follows:

$$I(\underline{X}) = \sum_{i=1}^{n} e_i(\eta_i, X)EI_i + \sum_{i=n+1}^{m} f_i(\eta_i, X)EI_i \tag{2}$$

This mathematical model considers the environmental impact of the process. An iterative process can be carried out by varying the emission limits until the optimal conditions, at which the minimum environmental impact occurs, are identified. Therefore, the main outputs that emerge from this approach are the maximum load of pollutants that can be discharged into the environment; the optimal operating conditions and configuration for PERV and SS, which incurs in minimum treatment cost < and the minimum environmental impact that can be achieved due to the treatment of wastewater discharges.

4 Case study

PERV processes are not new. In fact, these types of processes have been widely used and modelled for industrial applications (Hickey, 1994a, 1994b, 1994c). Readers interested in economic implication of PERV processes should revise Hickey (1994c), where he presents a chemical and physical concern about PERV focusing on the process characteristics. In this paper, operating results are taken and integrated into a framework that includes costs. However, the paper does not address the environmental implications related to these designs nor a multi-objective approach that provides insight on the economic-environmental trade-offs. These limitations are tackled in the following case study.

In order to illustrate and validate the correctness of this integrated approach, a case study was performed. Hence, a system composed by PERV and SS and a wastewater discharge containing Benzene, which is a volatile organic compound (VOC) typically discharged in production processes, has been modelled and studied.

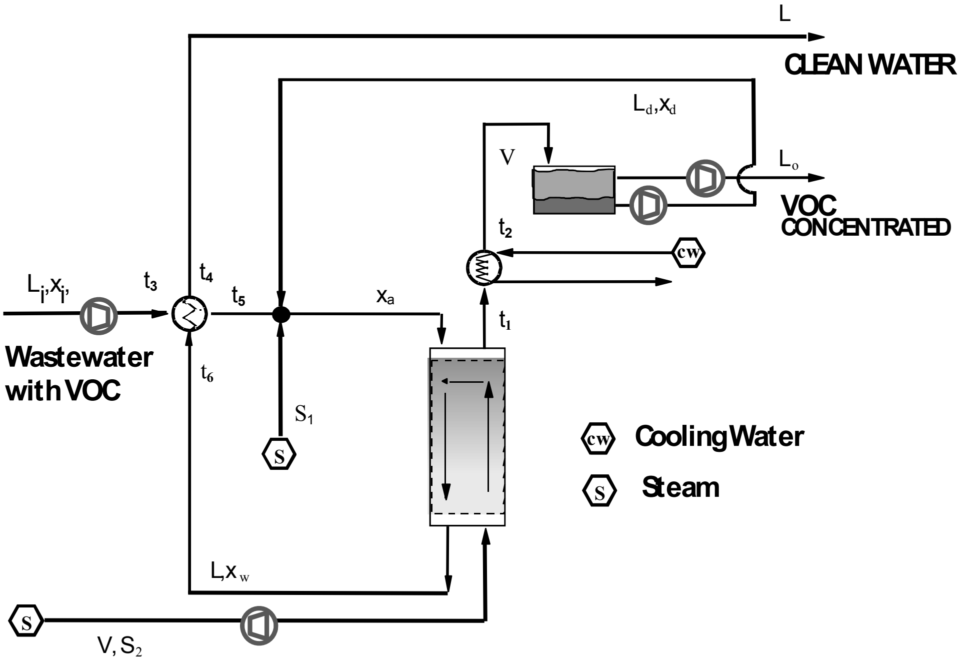
Appendix A presents the mathematical model used to analyse the PERV process.

4.1 Pervaporation

A wastewater contaminated with dilute quantities of VOC, is mixed together with two recycle streams before being pumped through a bank of membrane modules aligned in series and parallel (Figure 3). The retentate leaving the membrane bank is treated water. The vapour phase permeated from each module is collected into a common stream and enters the downstream part of the plant where condensation of the VOC to a pure organic stream takes place. The permeate vapour is passed through a rotary blower to increase the pressure. The permeate is subsequently transported into an intercondenser where it is cooled and the majority of the water is condensed. The vapour stream exiting the intercondenser passes through a dry vacuum pump where the pressure is raised again. It is then sent to an aftercondenser where all the remaining permeate stream is condensed.

The downstream separation steps were designed following the framework proposed in previous work (Hickey and Gooding 1994a, 1994b, 1994c).

Figure 3 Pervaporation

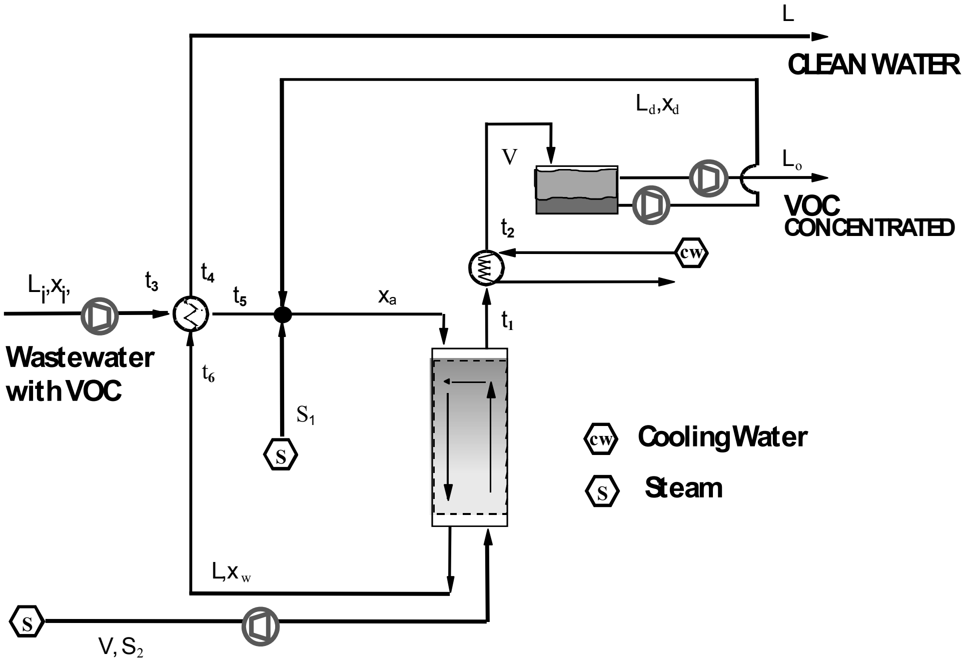


The concentration of VOC in the aftercondenser is higher than its solubility limit in water. Thus, the condensate can be separated into a pure organic phase and a VOC saturated water stream in the decanter. The water phases from both condensers are recycled to the system feed. The volume of the final pure-VOC stream that leaves the process is a small fraction of the original volume of contaminated water. The PERV process was modelled by a resistance in series model composed of a liquid film resistance and a membrane resistance (Lipski and Côté, 1990). The model consists of two degrees of freedom (membrane thickness and inlet pressure).

4.2 Steam stripping

A liquid stream containing a VOC is fed into a stripping column where the VOC is removed as shown in Figure 4. The end products are a water stream that is almost devoid of pollutant and a low-volume organic stream which contains the majority of the VOC. Low pressure steam is fed at the bottom of the column carrying the organic material out as it leaves the top of the column. The organic material is then condensed and sent to a decanter, where most of the pollutant exits as an almost pure organic stream. The water layer, with a low concentration of VOC is recycled. The model was developed following ideas of the open literature (Bravo, 1994; Hwang, 1992). The process model has four degrees of freedom (liquid loading, temperature of treated water, steam flowrate for heating and steam flowrate for stripping).

Figure 4 Steam stripping



4.3 Computation strategy

A set of equations representing mass and energy balances including equipment design constraints, capital and operating costs, as well as environmental impacts, was developed for the previously mentioned processes.

Life cycle inventory techniques were used to determine the emissions inventory of both processes. Emissions produced through electricity generation, steam generation, steel production for the major equipment items and untreated pollutant, were all considered. Pollutant species involved within the system were: Benzene which is removed from the wastewater stream (*outputs*) and SO_2, Hydrocarbons (HC), NO_2, N_2O, CO, CO_2, associated with *inputs* generation.

In order to illustrate the environmental assessment of PERV and SS, a commonly referred environmental impact category was incorporated into the environmental function: global warming potential (GWP). GWP estimates the relative contribution of each pollutant compared to carbon dioxide, to heat up the atmosphere (greenhouse effect). Nonetheless, it may be possible to incorporate any other environmental category such as photochemical ozone creation (POC), CAV, ozone depletion potential (ODP), abiotic depletion (AD). A detailed description of these categories can be found in the international standard ISO 14040.

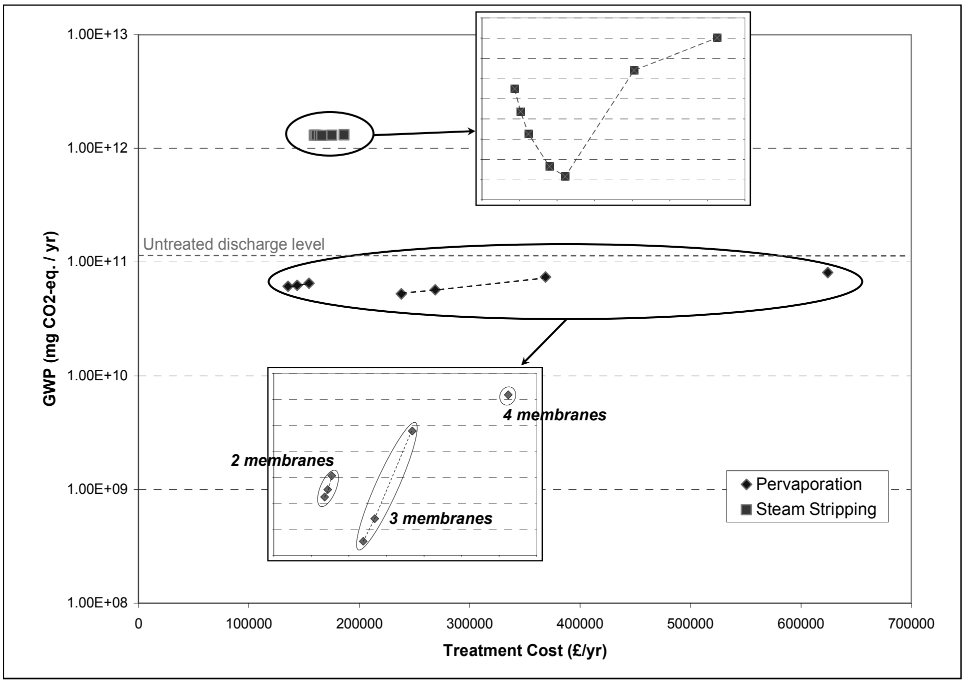
The modelling and optimisation software general algebraic modelling systems (GAMS) allow to model linear systems and non-linear systems. It also incorporates real variables, discrete and mix (which combine both) to solve mono-objective problems (Rosenthal, 2008). This type of systems is particularly useful to find solutions in high complex problems or in long extension models.

GAMS also presents a reasonably friendly interface. In the same way, the utilised commands are accessible enough for people that are not familiar with programming languages. The model structures in GAMS consist of: *constant variable assignment*, *variables declaration and positive variables declaration*, *equations, parameters*, *limits and initial point values.* GAMS offers a set of 'solvers' (solution methods) that can be chosen according to the model. For this paper, the GRG method was selected and implemented from the solution module CONOPT3 (developed by ARKI Consulting & Development). The algorithm, details can be found at Drud (1985) and in Brooke et al. (1998).

5 Mono-objective optimisation approach

Figure 5 presents the results, measured as GWP impacts, obtained using the aforementioned framework in order to treat a wastewater stream with a flowrate of 10 m^3/hr containing 1000 g/m^3 of Benzene.

Figure 5 Treatment cost vs. GWP impacts, measured for various degrees of pollution abatement and two different technologies



Criteria to rank the relative performance of both technologies should favour the cost of treatment over the environmental impact. The reason for this is that so far, previous results have shown that most of the time, the environmental impacts presented do not vary in more than one order of magnitude among different technologies while treatment cost are always a significant factor to consider. In this case study, treatment costs ranged from 135,000 to almost 700,000 pounds per year, depending on the technology. *PERV* *appeared to be the best single option for the removal of* a wastewater flow of 10 m^3/hr containing 1000 g/m^3 of *Benzene*. In both cases, this technology proved to be one of the cheapest options and also as the most environmentally friendly.

Capital costs played an important role on the selection of the cheapest wastewater treatment technology. The cost of equipment for PERV is ca. 80 % of the total cost. There is an inverse relationship between capital cost and environmental impact. Technologies analysed in this case study showed that PERV created the lowest environmental impacts, while demanding in most of cases the highest capital investment. The reason being is that pollution generated for the production of steel or membranes (the main raw materials for the capital equipment) is negligible, compared to the pollution created by electricity and steam generation. Utilities are the main source of pollution, so a rule of thumb for the analysis of technologies at a first stage is that the most environmentally friendly treatment technology demands the lowest amount of utilities. Furthermore, the only important issue regarding emissions associated with capital equipment should be to guarantee that none of the (usually low) emissions are heavily toxic.

Moreover, analysis on SS performance showed that this *treatment technology may in some cases create higher environmental impacts than those caused by an untreated discharge*. The ODPAs, at which total environmental impacts are minimised, appeared at high values of removal efficiency since it is on this region that the amount of inputs required for the process increases significantly. As such, the environmental impact caused by the wastewater discharge is outweighed by the environmental impacts of a significantly increased amount of inputs.

6 Multi-objective optimisation approach

The previous computations were performed in two steps: first, the water treatment process costs were optimised (mono-objective strategy) and then the resulting environmental impact was computed. However, the bi-criteria nature of the problem naturally leads towards optimisation procedures simultaneously accounting for both economic and environmental objectives. Moreover, the two objectives are likely to show antagonist behaviours. This latter point justifies the fact that a multi-criteria approach might provide some interesting compromise solutions.

Mathematically, the optimisation area in the multi-objective problem might be defined as:

$$\begin{aligned} Min\, f(x) = \left[f_1(x), f_2(x), \ldots, f_K(x)\right] \\ \text{s.t.} \quad g(x) \le 0 \\ h(x) = 0 \\ x \in X \end{aligned}$$

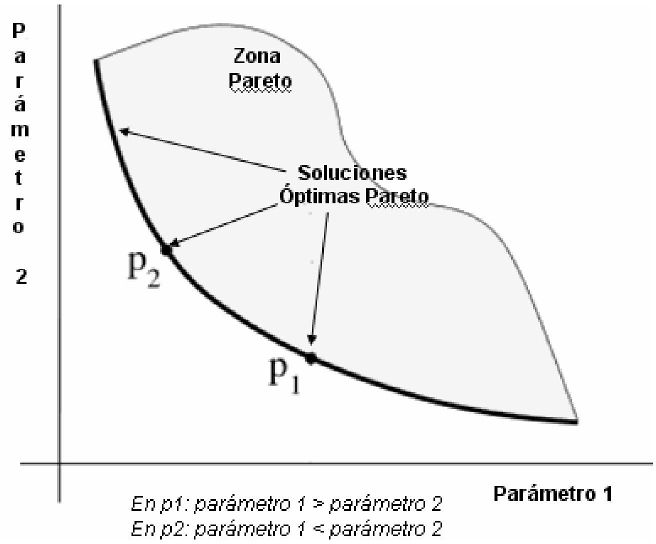
where $X \subset \mathrm{IR}^n$ is the definition set for the x vector (with n variables), g represents the inequality-restriction matrix, h is the equality-restriction matrix and f_k ($k = 1,\ldots,K$) are the problem objectives.

In the latest 1800s, economist W. Pareto formulated the concept of Pareto's optimum that established the origins for the multi-objective optimisation area. Considering F the set of feasible solutions of the problem, delimitated by the g and h restrictions, it is considered that x^* is a Pareto optimum if, for each $x \in F$, exists at least one k ($k \in \{1,\ldots,K\}$) for which: $f_k(x^*) < f_k(x)$.

It means, x^* is a Pareto optimum if there is no other feasible x vector that decreases one of the objectives without increasing each other simultaneously.

In most cases Pareto optimum is not a unique solution but a set of solutions named by Pareto's curve.

Figure 6 Pareto zone and Pareto optimum



Several methods have been developed and published in the devoted literature to convert a multi-objective problem into a mono-objective problem. A commonly used method is presented below:

- *K aggregated and weighted objectives*. In this method, both criteria are merged into a single new criterion to be optimised. This criterion is defined as:

  $$Min\ f_{eq} = \Sigma_{k=1,\ldots,K}\left[w_k\ f_k\left(x\right)\right].w_k$$

  where w_k represents the weight assigned to each objective (it might include a normalisation factor to make comparable the objectives in the added function).

  This methodology is equivalent to searching within the feasible solutions region previously defined, the function minimum in the hyper-plane, built in accordance to w_k in the objective space. Hence, changing the weights w_k (with $\Sigma_{k=1,\ldots,K}[w_k] = 1$), lead to a Pareto's curve described with a set of non-dominated discrete solutions.

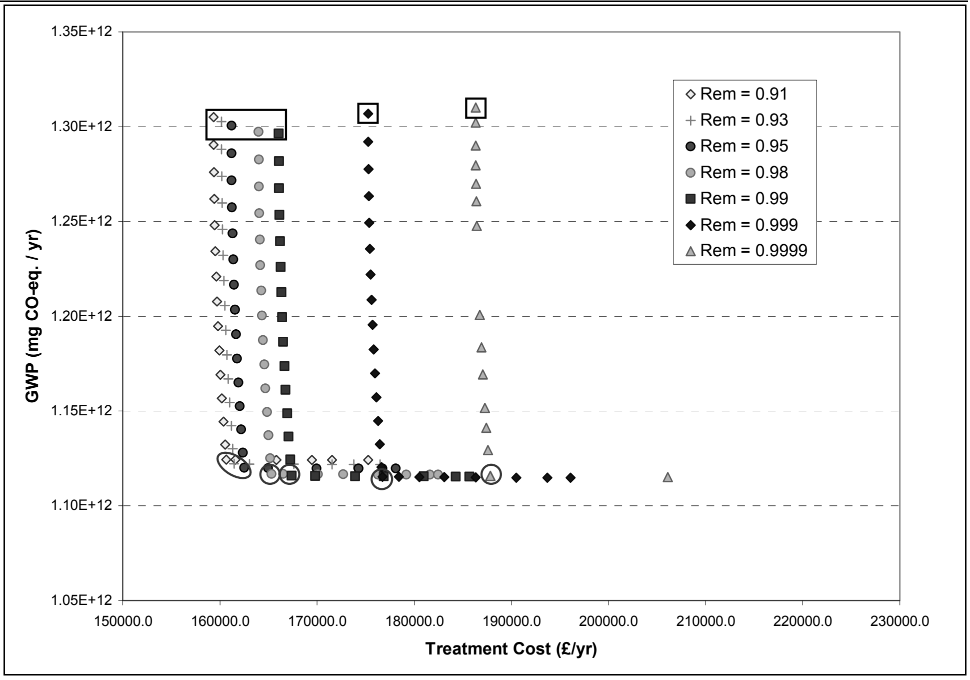
Thus, the environmental impact calculations were integrated into the optimisation step by assigning some weights to both (economic and environmental) criteria and combining them within a single objective function such as:

$$New\_Objective = \left(w_1\right)Treatment\_Cost + \left(w_2\right)Environmental\_Impact \qquad (3)$$

By then varying the relative weight values w_1 and w_2, a set of results was obtained, which described an approximation of the so-called Pareto zone. These solutions are those that dominate the other ones for at least one criterion: if solution j is dominated by (i.e., is worse than) solution k for the cost criterion, then k is dominated by j for the environmental criterion (or reversely).

This multi-objective strategy was illustrated for both considered treatment technologies, but only in the case of the GWP category impact. For each considered removal value of the pollutant, a Pareto zone is determined by changing w_1 and w_2.

Figure 7 Cost vs. GWP Pareto zones for the SS process

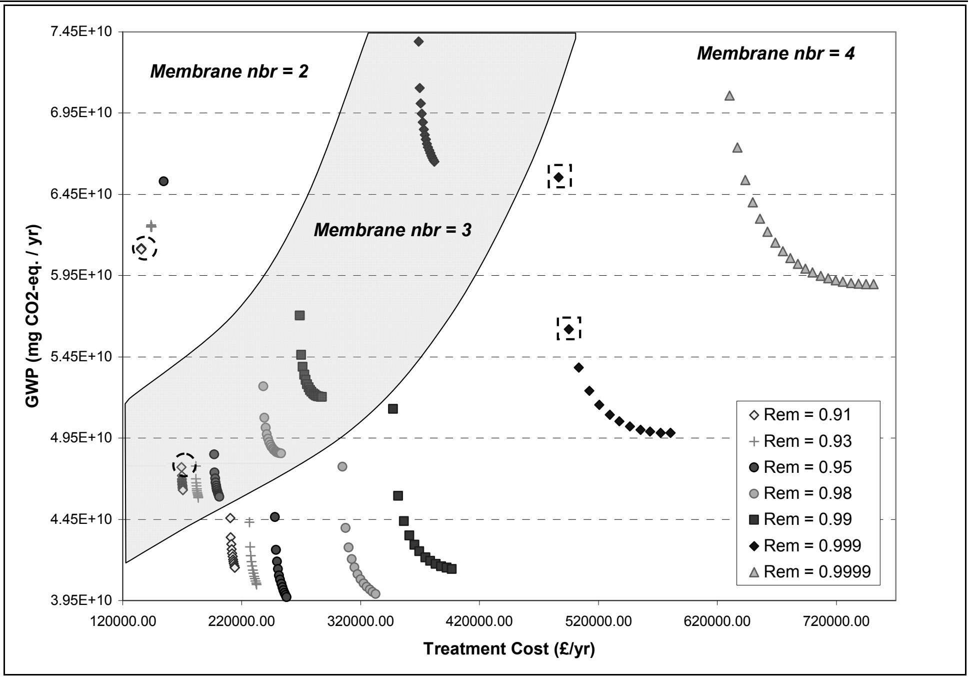


6.1 SS process

Figure 7 shows the set of Pareto zones obtained for the tested removal efficiencies. For each zone, the leftmost point corresponds to the treatment cost optimisation only (the weight for GWP, w_2, is equal to zero): this point is the same as that represented in Figure 5. The rightmost point is associated to the GWP optimisation only ($w_1 = 0$). Intermediate points correspond to compromise solutions with both nonzero weight factors. It is to note that all the Pareto zones show 'parallel' trends, i.e., from one removal efficiency to another, the treatment cost increases while the GWP impact remains almost identical.

For all removal cases, the Pareto zone first shows a decreasing trend (for lower GWP weights), but the curve stabilises to a stage for which the GWP remains almost steady while the treatment cost continuously increases. Therefore, the lowest point of each mentioned stage (highlighted by square frames in Figure 7) constitutes a better option than the leftmost (circled) point, obtained with the mono-objective strategy: while the treatment cost only increases in about 0.8% (in all cases), the GWP falls of about 13% in all removal cases. The gain for the environmental impact can thus be significant without involving much higher costs: the advantage of the multi-objective approach is, in this case, obvious.

Figure 8 Cost vs. GWP Pareto zones for the PERV process



6.2 PERV process

With regard to the PERV technology, the same computational strategy is adopted. Results are presented in Figure 8 as a set of Pareto zone was obtained for each tested removal efficiency. First, recall that, like for the mono-objective computations, the global results divide into three sections, according to the used membrane number. However, in this multi-objective framework, it is worth noting that for specific removal efficiency, it is not possible to make preferences between two solutions with two or three membranes respectively. For instance, considering the two circled points in Figure 8 (91% removal, leftmost points for the two-membrane and three-membrane regions), the treatment cost increases of about 25% while the environmental impact decreases of 22%: both options are non-dominated, i.e., valid to a decision maker, who might be able to give priority to the 'economic option' or, reversely, to the 'environmental' option. That is why solutions for membrane number higher than the minimum needed number are also presented in Figure 8.

It should be noted that the GWP impact variation between the leftmost and rightmost points in each zone is much gentler than in the SS case, especially for the lowest removal cases. Thus, even compromise solutions with higher costs will not be able to bring significant improvement for CAV impact.

Moreover, the detailed analysis of the Pareto regions proves that these zones show similar trends and no steady stage. With the exception of some removal cases, it turns out to be more difficult to determine the 'best' compromise solution, like for the SS process. Nevertheless, the set of compromise solutions still provides very interesting information for the decision maker, who might either consider other criteria, or define an 'upper acceptable' cost in order to choose among the possible configurations.

Finally, despite the regularity of Pareto zone trends, it is possible in some cases to identify good compromise solutions that enable improved environmental criterion without involving high cost increases: for instance, between the two points highlighted by squares in Figure 8 (99.9% removal), the cost increase is equal to 1.75% while the GWP impact decreases of more than 14%. The leftmost option is thus preferable.

7 Conclusions

The integrated approach presented in this article can assist in environmental decision making towards sustainable development. It provides criteria regarding:

1 cost of treatment

2 environmental impacts and the optimal degree of pollution abatement.

These two factors are case specific and depend on the type of emissions, the characteristics of the receiving environment and the treatment technology. In addition, several uncertainties and subjective judgment seem to be part of all evaluation methods. Therefore, they all must be put into perspective when conducting an analysis of wastewater discharges and treatment options.

The multi-criteria strategy proved its efficiency on the GWP case. For the SS process, it provided compromise solutions that enable a great decrease in the environmental impact without affecting the treatment cost that much. Concerning the PERV treatment technology, even if the lack of steady stage does allow to draw satisfactory conclusions, relevant sets of Pareto solutions could be identified, enabling the decision maker to choose among a set of good compromise configurations. This approach might then be extended to the other environmental impact factors.

The integrated approach presented in this paper aggregates state-of-the-art knowledge into multi-decision criteria. This approach is robust enough to be used by companies or legislators in order to identify the most cost-effective technology for treatment of wastewater discharges and as a basis to rationally determine emissions limits. Furthermore, the framework can be applied in order to study other operations (not only treatment plants), technologies or more complex systems under a wider-basis such as whole industrial process.

Two perspectives are part of the scope of future work. First, with concern to the multi-objective treatment of the problem and secondly, the bi-criteria solutions provided in this study highlight the possibility to consider simultaneously more than two objectives: for instance, the treatment cost combined with several environmental impacts (GWP, CAV, POC, etc.). Moreover, the presented study is completely deterministic, but considering uncertainty in the numerical models might lead to design robust configurations, which adapt easily to parameter fluctuations (for instance, here, variation of the VOC concentration in the wastewater stream).

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References

Azapagic, A., Perdan, S. and Clift, R. (2004) *Sustainable Development in Practice: Case studies for Engineers and Scientists*, John Wiley and Sons, West Sussex, England.

Bourgeois, J.C., Walsh, M.E. and Gagnon, G.A. (2004) 'Comparison of process options for treatment of water treatment residual streams', *Journal of Environmental Engineering and Science*, Vol. 3, pp.477–484.

Bravo, J.L. (1994) 'Design steam strippers for water treatment', *Chemical Engineering Progress*, Vol. 90, pp.56–63.

Brooke, A., Kendrick, D., Meeraus, A. and Raman, R. (1998) *GAMS Users Guide*, GAMS Development Corporation.

Douglas, J.M. (1988) *Conceptual Design of Chemical Process*, McGraw Hill, Singapore.

Drud, A. (1985) 'A GRG code for large sparse dynamic nonlinear optimization problems', *Mathematical Programming*, Vol. 31, pp.153–191.

El-Din, A.G., Smith, D.W. and El-Din, G. (2004) 'Application of artificial neural networks in wastewater treatment', *Journal of Environmental Engineering and Science*, Vol. 3, pp.S81–S95.

Henley, E.J. and Seader, J.D. (1981) *Separation Process Principles*, John Wiley and Sons, USA.

Hickey, P.J. and Gooding, C.H. (1994a) 'Modelling spiral wound modules for the pervaporative removal of VOC's from wastewater', *Journal of Membrane Science*, Vol. 88, pp.47–68.

Hickey, P.J. and Gooding, C.H. (1994b) 'Mass transfer in spiral wound pervaporation modules', *Journal of Membrane Science*, Vol. 92, pp.59–74.

Hickey, P.J. and Gooding, C.H. (1994c) 'The economic optimization of spiral wound membrane modules for the pervaporative removal of VOCs from water', *Journal of Membrane Science*, Vol. 97, pp.53–70.

Hwang, Y.L. (1992) 'Steam stripping for removal of organic pollutants from water', *Industrial Engineering and Chemistry Research*, Vol. 31, pp.1753–1768.

Jimenez, J.d.B. and Lorente, J.J.C. (2001) 'Environmental performance as an operations objective', *International Journal of Operations and Production Management*, Vol. 21, pp.1553–1572.

Lipski, C. and Côté, P. (1990) 'The Use of pervaporation for the removal of organic contaminants from water', *Environmental Progress*, Vol. 9, pp.254–261.

Pereira, C.J. (1999) 'Environmentally friendly processes', *Chemical Engineering Science*, Vol. 54, pp.1959–1973.

Perry, R.H. (1984) *Chemical Engineer's Handbook*, McGraw Hill, USA.

Peters, M.S. and Timmerhaus, K.D. (1980) *Plant Design and Economics for Chemical Engineers*, McGraw Hill, USA.

Romero-Hernandez, O. (2005) 'Applying life cycle tools and process engineering to determine the most adequate treatment process conditions. A tool in environmental policy', *International Journal of LCA*, Vol. 10, pp.355–363.

Romero-Hernandez, O., Pistikopoulos, E.N. and Livingston, A.G. (1998) 'Waste treatment and optimal degree of pollution abatement', *Environmental Progress*, Vol. 17, pp.270–277.

Rosenthal, R. (2008) *GAMS – A User's Guide*, GAMS Development Corporation, USA.

Roy, M.J. and Vezina, R. (2001) 'Environmental performance as a bass for competitive strategy: opportunities and threats', *Corporate Environmental Strategy*, Vol. 8, pp.339–347.

Wijmans, J.G., Kaschmekat, J. and Davidson, J.E. (1990) 'Treatment of organic-contaminated wastewater streams by pervaporation', *Environmental Progress*, Vol. 9, No. 4, pp.262–268.

Appendix A Mathematical programming model: pervaporation

Due to space limitation, a more detailed description of both treatment models as well as the corresponding programming files is available upon request.

Determination of the main equipment size

Variables involved in the development of the mathematical pervaporation model are defined at the end of this section. Calculations performed with this model consider the membrane module described in the following table:

Table A1 Spiral wound module

Module:	Length: 1 m
	Inner diameter: 0.1 m
	Diameter permeate collection tube: 0.0254 m
	Number of membrane leaves: 4
	Specific membrane area: 4.4 m^2 per module
Membrane:	Dow Corning Silastic (silicon rubber membrane)
Feed spacer:	Spacer strand diameter: 0.725 mm (Naltex Ultraflo)
Permeate spacer:	TP22 as described by Hickey and Gooding (1994b)
	Permeate channel height: 2.03 mm

Membrane area and module arrangement: the model used to predict the required membrane area has been proposed by Lipski and Côte (1990). The average flux of the organic compound across the membrane was computed as the product of an overall mass transfer coefficient and an average driving force. The mass transfer coefficient was calculated based on a resistance-in-series model accounting for the liquid film resistance and the membrane resistance. The liquid film resistance was calculated as a function of the superficial velocity, while the membrane resistance was expressed as a function of the membrane thickness, the permeability of the organic compound through the membrane and the Henry's law coefficient.

In order to determine the driving force, a low partial pressure on the vacuum side (400Pa) was assumed with a compensation factor of $\frac{1}{0.85}$ (Hickey and Gooding, 1994c). Finally, bearing in mind that the concentration of the treated water leaving the membrane train should reach a value of $(1-\delta).x_i$, the membrane area can be determined as function of the flowrate, the overall mass transfer resistance and the degree of removal:

$$A_m = \frac{1}{0.85} \cdot \upsilon_w \cdot L_\alpha \cdot \left(\frac{1}{k_l} + \frac{L_m}{K^* \cdot P_o} \right) \cdot \ln \left[\frac{x_\alpha}{(1-\delta) \cdot x_i} \right] \qquad \text{(A1)}$$

The mass transfer coefficient is correlated directly with the superficial velocity.

$$k_l = (8.422).10^{-5}.v^{0.379} \tag{A2}$$

The superficial velocity is hence a function of the inlet flowrate of the module bank divided by the cross sectional area of the modules available for feed flow. The latter is determined as the product of the number of modules in parallel, the height of the feed channel and half the module specific membrane area divided by the length of one module.

$$v = L_\alpha \cdot \upsilon_w \cdot \frac{2 \cdot L}{n_p \cdot h \cdot sA_m} \tag{A3}$$

Condensers: due to the high cost of refrigeration, a low approach temperature is chosen for the condenser (Douglas, 1988). Therefore, ΔT is fixed to 10°C for both condensers.

$$A_{ic} = \frac{Q_{ic}}{\Delta T_{ic} \cdot U_{ic}} \tag{A4}$$

$$A_{ac} = \frac{Q_{ac}}{\Delta T_{ac} \cdot U_{ac}} \tag{A5}$$

The heat duty calculation for the intercondenser takes into account the latent heat of condensing water and the sensible heat of both vapours. The value for the heat of vaporisation was calculated for a pressure of 2,500 Pa; changes for different pressures are insignificant. The temperature for both, intercondenser and aftercondenser, t_3, was fixed to 20°C.

$$Q_{ic} = (t_2 - t_3) \cdot (V_{w1} \cdot cp_w + V_{o1} \cdot cp_o) + V_{w1} \cdot \Delta H_{w1} \tag{A6}$$

For the aftercondenser, the duty was calculated allowing for the latent and sensible heat of the whole stream.

$$Q_{ac} = V_2 \cdot \left[(t_4 - t_3)\left(cp_w + y_2 \cdot (cp_o - cp_w)\right) + \Delta H_{w2} + y_2 (\Delta H_{o2} - \Delta H_{w2}) \right] \tag{A7}$$

Feed and vacuum pumps: Hickey and Gooding (1994c) provide a simple expression, which correlates the pressure drop per length of module directly with the superficial velocity. In addition, the maximum allowable pressure drop along the module train was set to 1.5 Bar, in order to avoid membrane burst.

$$\Delta p_1 = 268000 \cdot (v)^{1.611} \cdot L \cdot \frac{A_m}{n_p \cdot sA_m} \tag{A8}$$

The energy consumption of the feed pump is a linear function of the volumetric flowrate entering the module bank, the pressure drop along the modules and the pump efficiency respectively.

$$W_{fp} = \frac{1}{\varepsilon_{fp}} \cdot L_\alpha \cdot \upsilon_w \cdot \Delta p_1 \tag{A9}$$

Changes in efficiency produced by varying flowrates should be significant and a correlation for ε_{fp} was derived from a chart taken from a publication by the IFP (1976).

$$\varepsilon_{fp} = 0.3054.\log_{10}[3600.L_{\alpha}.\upsilon_w] + 0.1366 \tag{A10}$$

The volumetric flowrate entering the rotary blower can be computed, as shown in equation (A9). For small fluxes across the membrane and predominantly organic compounds with small values for the heat of vaporisation in the permeate, the temperature difference between feed and permeate is negligible. Temperature of the permeate was set to equal the feed inlet temperature of 20°C.

$$q_{rb} = \frac{R \cdot t_1}{p_p} \cdot (V_{o1} + V_{w1}) \tag{A11}$$

The energy required by the vacuum pumps to compress the vapour can be estimated from the ideal adiabatic compression energy, assuming a permeate pressure of 400 Pa and a pressure in the intercondenser of 8,000 Pa. This pressure was considered to give a reasonable blower efficiency ε_{rb} of 70% as well as feasible intercondenser conditions.

$$W_{rb} = \frac{1}{\varepsilon_{rb}} \cdot \frac{1}{\gamma_1} \cdot (V_{o1} + V_{w1}) \cdot R \cdot t_1 \cdot \left[\left(\frac{p_2}{p_p} \right)^{\gamma_1} - 1 \right] \tag{A12}$$

The dry vacuum pump is used to raise the pressure of stream V_2 exiting the intercondenser to a pressure slightly higher than the sum of the component vapour pressures, which guarantees that all vapour is condensed. Thus, the pressure in the aftercondenser was fixed to 12,000 Pa.

$$W_{dvp} = \frac{1}{\varepsilon_{dvp}} \cdot \frac{1}{\gamma_2} \cdot V_2 \cdot R \cdot t_3 \cdot \left[\left(\frac{p_3}{p_2} \right)^{\gamma_2} - 1 \right] \tag{A13}$$

When the vapour is compressed adiabatically there is a temperature rise. The discharge temperature from the pumps can be calculated as follows:

$$t_2 = t_1 \cdot \left(\frac{p_2}{p_p} \right)^{\gamma_1} \tag{A14}$$

$$t_4 = t_3 \cdot \left(\frac{p_3}{p_2} \right)^{\gamma_2} \tag{A15}$$

Values for γ_1 and γ_2 are a function of the composition of the two streams entering the compressors:

$$\gamma_1 = \frac{V_{w1} \cdot \gamma_w + V_{o1} \cdot \gamma_o}{V_{w1} + V_{o1}} \tag{A16}$$

$$\gamma_2 = \gamma_w + y_2(\gamma_o - \gamma_w) \tag{A17}$$

Mass and energy balances

The amount and the composition of the stream entering the membrane modules are determined by the wastewater entering the plant and the two recycle streams collected from the condensers:

$$L_\alpha = L_{in} + L_{r1} + L_{r2} \tag{A18}$$

$$x_\alpha = \frac{L_{in} \cdot x_i + L_{r1} \cdot x_{r1} + L_{r2} \cdot x_{r2}}{L_\alpha} \tag{A19}$$

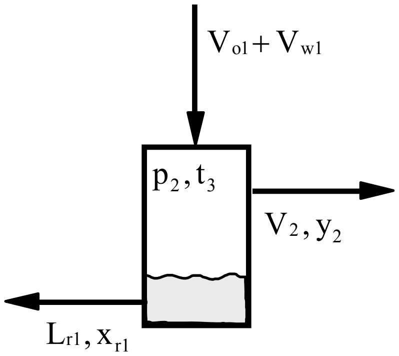
Under the assumption of a constant permeate pressure, p_p, equal to 400 Pa and for fixed values of water permeability and vapour pressure, the amount of water crossing the membrane is only a function of the membrane area and thickness.

$$V_{o1} = L_{in} \cdot x_i \cdot \delta \tag{A20}$$

$$V_{w1} = \frac{A_m}{L_m} \cdot P_w \cdot \left(p_{sw} - p_p\right) \tag{A21}$$

$$\Psi = \frac{V_2}{V_{o1} + V_{w1}} \tag{A22}$$

Figure A1 Schematic diagram of the process intercondenser



The intercondenser works like a flash drum. The equations for isothermal flash calculations are based in the Rachford-Rice procedure, as given in Henley and Seader (1981). Water with only dilute quantities of organics justify the use of Raoult's law and Henry's law for the equilibrium relations of water and the organic, respectively. Equilibrium equations are:

$$\frac{V_{o1} \cdot (1 - K/p_2)}{1 + \Psi(K/p_2 - 1)} + \frac{V_{w1} \cdot (1 - p_{sw}/p_2)}{1 + \Psi(p_{sw}/p_2 - 1)} = 0 \tag{A23}$$

$$V_2 = \Psi \cdot (V_{o1} + V_{w1}) \tag{A24}$$

$$L_{r1} = (1 - \Psi) \cdot (V_{o1} + V_{w1}) \tag{A25}$$

$$x_{r1} = \frac{V_{o1}}{V_{o1} + V_{w1}} \cdot \frac{1}{1 + \Psi(K/p_2 - 1)} \tag{A26}$$

$$y_2 = \frac{K}{p_2} \cdot x_{r1} \tag{A27}$$

The streams leaving the decanter were assumed to be a pure organic stream and a water stream with a concentration of VOC at its solubility limit. Flowrate of the second recycle stream can be determined as follows:

$$L_{r2} = V_2 \cdot \frac{1 - y_2}{1 - x_{r2}} \tag{A28}$$

Costs equations

The total treatment costs for this abatement technology are made up by operating and capital costs.

$$C_t = C_o + C_c \tag{A29}$$

Operating cost: electricity and the replacement of the membranes contribute to the operating cost. It is assumed that the membranes and modules have a lifetime of three years (Wijmans et al., 1990).

$$C_o = C_{el} + \tfrac{1}{3} \cdot C_m \tag{A30}$$

The main sources of electricity consumption are the feed pump, the rotary blower, the dry vacuum pump and the refrigeration unit. For refrigeration cycles the transferred heat load is usually bigger than the electrical power uptake (Peters and Timmerhaus, 1980). Thus, a value of two was introduced for the ratio of the cooling duties in the two condensers to the electricity requirements.

$$C_{el} = wh \cdot sc_{el} 0.001[1.25(W_{fp} + W_{rb} + W_{dvp}) + 0.5(Q_{ic} + Q_{ac})] \tag{A31}$$

Capital cost: the equipment contributing to the capital cost consists of a feed pump, membranes and modules, rotary blower, one vacuum pump, two condensers, a refrigeration unit and three smaller pumps moving small liquid streams through low pressure differences. The flash drums and the decanter were considered to play only a negligible role.

$$C_c = bm \cdot dep \cdot (C_{fp} + C_m + C_{rb} + C_{dvp} + C_{ic} + C_{ac} + C_{ref} + C_{pu}) \tag{A32}$$

The costs for the small pumps were assumed to be constant over the whole range of wastewater inlet flowrates, as was done in the steam stripping cost model. Due to the pressure drop along the train of membrane modules and therefore the higher duty of the feed pump, a correlation with flowrate and pressure drop as parameters was applied.

$$C_{fp} = r \cdot \frac{MS_{95}}{MS_{68}} 15(0.0414 L_i \cdot \Delta p_1)^{0.52} 1.93 \tag{A33}$$

Similar cost correlations (Douglas, 1988) were used to determine the cost for the dry vacuum pump, the intercondenser and the aftercondenser.

The cost of the silicone rubber membrane (£130 m^{-2}) is a linear function of the total membrane area.

$$C_m = 130 \cdot A_m \tag{A34}$$

The cost for the refrigeration unit was determined using the exponential method as explained in Perry (1984) and using the values given in the same source. The cost is correlated to the refrigeration duty, which is equal to the aggregated heat duties of the two condensers:

$$C_{ref} = r \cdot 133000 \cdot \left(\frac{Q_{ic} + Q_{ac}}{351700} \right)^{0.73} \tag{A35}$$

The calculation for the cost of the rotary blower was estimated from Peters and Timmerhaus (1991). The cost is a direct function of the volumetric flowrate entering the rotary blower:

$$C_{rb} = r \cdot \frac{MS_{95}}{MS_{90}} \cdot 29411 (q_{rb})^{0.747} \tag{A36}$$

Nomenclature

A_{ac}	Area aftercondenser	m^2
A_{ic}	Area intercondenser	m^2
A_m	Membrane area	m^2
bm	Bare module factor	-
C_{ac}	Cost of aftercondenser	£
C_c	Capital cost	£/year
C_{dvp}	Cost of dry vacuum pump	£
C_{el}	Electricity cost	£/year
C_{fp}	Cost of feed pump	£
C_{ic}	Cost of intercondenser	£
C_m	Cost of membranes installed in modules	£
C_o	Operating cost	£/year
cp_o	Specific ideal gas heat capacity VOC at t = 20°C	J/(kmol.K)
C_{pu}	Cost for three smaller pumps	£
cp_w	Specific heat capacity for steam at t = 22°C	J/(kmol.K)
C_{rb}	Cost of rotary blower	£
C_{ref}	Cost of refrigeration system	£
C_t	Total cost	£/year
dep	Capital charge factor	$year^{-1}$
dp_1	Pressure drop along module train	Pa

Nomenclature (continued)

h	Height of feed channel in membrane module	m
η	Removal efficiency	-
K	Henry's law coefficient for VOC	Pa
K^*	Henry's law coefficient for VOC	(Pa.m^3)/mol
k_l	Mass transfer coefficient in liquid	m/s
L	Length of module	m
L_α	Flowrate of wastewater entering the membrane bank	kmol/s
L_{in}	Flowrate of wastewater entering the plant	kmol/s
L_m	Thickness of membrane	m
L_{r1}	Flowrate recycle stream from intercondenser	kmol/s
L_{r2}	Flowrate recycle stream from decanter	kmol/s
MS_{68}	Marshall and Swift Index value 1968	-
MS_{90}	Marshall and Swift Index value 1990	-
MS_{95}	Marshall and Swift Index value 1995	-
n_p	Number of membrane modules in parallel	-
p_2	Pressure in intercondenser	Pa
p_3	Pressure in aftercondenser	Pa
P_o	Permeability of VOC as vapour through the membrane	mol/(m.s.Pa)
p_p	Permeate pressure	Pa
p_{sw}	Vapour pressure for water at t = 20°	Pa
P_w	Permeability of water as vapour through the membrane	kmol/(m.s.Pa)
Q_{ac}	heat duty aftercondenser	W
Q_{ic}	heat duty intercondenser	W
q_{rb}	Volumetric flowrate of rotary blower inlet	m^3/s
r	Pound to dollar ratio	£/$
R	Ideal gas law constant	J/(kmol.K)
sA_m	Calculated membrane area per module	m^2
sc_{el}	Specific electrical power cost	£/kW.hr
t_1	Temperature on permeate side of the membrane	K
t_2	Temperature after compression by rotary blower	K
t_3	Temperature in intercondenser	K
t_4	Temperature after compression by dry vacuum pump	K
U_{ac}	Heat transfer coefficient aftercondenser	J/(m^2.K)
U_{ic}	Heat transfer coefficient intercondenser	J/(m^2.K)
v	Superficial feed velocity	m/s
V_2	Molar vapour flowrate leaving intercondenser	kmol/s
V_{o1}	Molar organic permeate flowrate	kmol/s
V_{w1}	Molar flowrate of permeating steam	kmol/s
W_{dvp}	Energy required to operate the dry vacuum pump	W

Nomenclature (continued)

W_{fp}	Energy required to operate the feed pump	W
wh	Annual working hours	hours/year
W_{rb}	Energy required to operate the rotary blower	W
x_α	Concentration of VOC in water entering the module train	mol_{VOC}/mol_{water}
x_i	Concentration of VOC in wastewater inlet stream	mol_{VOC}/mol_{water}
x_{r1}	Concentration of VOC in first recycle stream	mol_{VOC}/mol_{water}
x_{r2}	Concentration of VOC in decanted water	mol_{VOC}/mol_{water}
y_2	Concentration of VOC in vapour leaving intercondenser	mol_{VOC}/mol_{water}
ψ	Ratio of $vapour_{out}/vapour_{in}$ intercondenser	-
δ	Grade of removal	-
γ_1	Coefficient used for r-blower estimation	-
γ_2	Coefficient used for v-pump estimation	-
ε_{dvp}	Compressor efficiency for dry vacuum pump	-
ε_{fp}	Feed pump efficiency	-
ΔH_{o2}	Vaporisation heat of VOC at p = 10kPa	J/kmol
ΔH_{w1}	Vaporisation heat of water at p = 2.5kPa	J/kmol
ΔH_{w2}	Vaporisation heat of water at p = 10kPa	J/kmol
γ_o	R/c_p as given by Douglas	-
ε_{rb}	Rotary blower efficiency	-
ΔT_{ac}	Mean temperature difference in aftercondenser	K
ΔT_{ic}	Mean temperature difference in intercondenser	K
γ_w	$(c_p/c_v-1)/(c_p/c_v)$	-
υ_w	Liquid molar volume of water	$m^3/kmol$