Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 5, Part 1
ISSN 1313-2539, Published at: http://www.science-journals.eu

PERVAPORATION IN THE CONTEXT OF WASTEWATER TREATEMENT

Madlena P. Lazarova
Bulgarian Academy of Sciences, Institute of Chemical Engineering, 1113 Sofia, Bulgaria

Abstract

Membrane technologies represent one of the most effective and energy-saving alternative separation processes. In this paper the emerging process of pervaporation is introduced together with other membrane processes relevant to environmental applications, in particular to wastewater treatment. The basic process layouts of pervaporation are given; the mass transport is described by a three-step process and the selection criteria for membranes are included. Brief description of commercial pervaporation modules is given and the coupling of pervaporation with other separation techniques for better performance and process optimization is considered.

Key words*: pervaporation, wastewater treatment, module design, hybrid process*

1. INTRODUCTION

Industrial companies today have to constantly improve its production performance by investing into new technologies. Membrane separation processes offer advantages over the conventional techniques such as higher selectivity, lower energy consumption and compact modular design (Chapman et al., 2008). The membrane processes microfiltration, ultrafiltration, electrodialysis, gas separation and reverse osmosis have shown to be successful alternatives for environmental applications to the existing adsorption, absorption and extraction. For example, the use of electrodialysis for the removal of metals from wastewater effluents, or the use of reverse osmosis for the production of potable water by desalination.

Pervaporation is a relatively new membrane technique. It has found its main applications in dehydration of organic solvents, removal of dilute organics from aqueous streams and separation of organic-organic mixtures, which are putting pervaporation into practice also for environmental applications (Lazarova and Friedl, 2010).

Membrane processes relevant to environmental management are listed in Table 1. In case of pervaporation, hydrophobic pervaporation has the highest potential for environmental applications by removal of organic compounds from diluted wastewater streams, thus its performance and prospects are discussed in this paper.

2. PERVAPORATION PROCESS LAYOUT

In pervaporation the mass transfer of components is realized through a dense membrane combined with a phase change from liquid to vapor. A liquid mixture comes in contact with the upstream side of the membrane and the permeating through it product is removed as vapor at the downstream side. The driving force for transport across the membrane is the gradient of chemical potential based on a partial pressure difference (Lipnizki, 2004). Usually partial pressure difference is generated by a vacuum pump, maintaining a low vapor pressure on the downstream side (Fig.1.1.), or an inert sweep gas can be used on the permeate side (Fig.1.2).

Table 1. Membrane processes for environmental applications

Membrane process	Applications
Microfiltration	Separation of oil-water emulsions; removal of colloids from wastewater; removal of dust particles from air
Ultrafiltration	Separation of oil-water emulsions; recovery of proteins from whey and milk
Nanofiltration	Treatment of electroplating rinse water
Gas separation	Removal of CO_2 and H_2S from landfill gas; removal of condensable solvents
Reverse osmosis	Treatment of leachate from landfill sites; removal of nitrate from ground water
Vapor permeation	Removal of condensable solvents from air
Pervaporation	Dehydration of solvents; removal of organics from wastewater
Membrane distillation	Desalination of brine
Electrodialysis	Removal of metals from wastewater; acid recycle from 'pickling' baths; desalination of brackish water
Liquid membranes	Recovery of plating chemicals; removal of acid gases from air

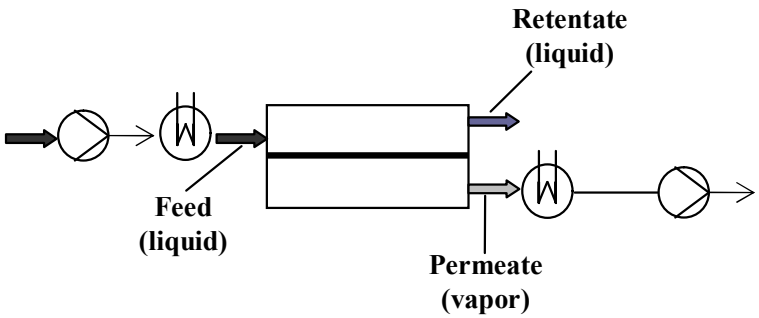


Fig. 1.1. Pervaporation process layout – vacuum pervaporation

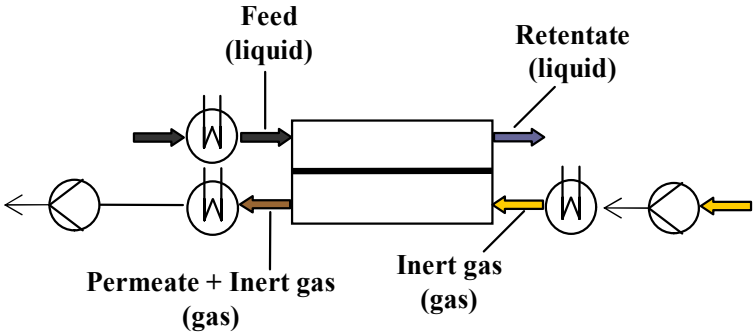


Fig. 1.2. Pervaporation process layout – sweep gas pervaporation

Commonly vacuum pervaporation is used in industry and the main process units are feed mixture, feed pump, heater, membrane module, condenser and vacuum pump. For successful implementation a good understanding of mass transfer in pervaporation is required.

3. MASS TRANSPORT IN PERVAPORATION AND MEMBRANE SELECTION

Knowledge of mass transport mechanism in pervaporation enables the improvement of membranes and membrane modules. The components in the feed stream partition into the membrane, permeate through the membrane and evaporate into the vapor phase. The species in the feed have different membrane affinities and different diffusion rates through the membrane, so separation is based upon selective solution and diffusion. Thus, pervaporation transport is widely described by the solution-diffusion theory. According to it the overall mass transfer mechanism consists of three steps: sorption of the components into the upstream side of the membrane, diffusion of the permeants through the membrane and desorption at the downstream side of the membrane (Khayet et al., 2008).

As mentioned above, the driving force for transport across the membrane is the concentration gradient as representation of the chemical potential difference of a species *i* between the bulk feed and the bulk permeate phases. The flux through the membrane is proportional to the concentration gradient and inversely proportional to the overall mass transfer resistance. The latter is a sum of the resistance in the liquid boundary layer on the feed side of the membrane, R_i^L, the resistance of the membrane, R_i^M, and the resistance in the vapor boundary layer on the permeate side of the membrane, R_i^V:

$$J_i = \frac{1}{R_i} \times \Delta C_i = \frac{1}{\left(R_i^L + R_i^M + R_i^V\right)} \times \left(C_i^L - C_i^V\right) \quad (1)$$

The mass transfer through both liquid boundary layer and membrane is assumed to be dominating and the resistance in the vapor boundary layer is considered small (Vane, 2005).

In addition to flux, the performance of a pervaporation membrane is based on its ability to separate different feed components and to deliver permeate highly enriched in the desired component. Usually, the separation factor of species *i* relative to species j, α_{ij}, is given as a measure for separation quality:

$$\alpha_{ij} = \frac{C_i^V \times C_j^L}{C_i^L \times C_j^V} \quad (2)$$

where C is the respective concentration.

Thus, the main selection criteria for a suitable pervaporation membrane are to achieve a significant permeate flux together with a high separation performance.

For the recovery of organic compounds from wastewater effluents, hydrophobic membranes are needed. Different materials have been studied for this purpose. From the hydrophobic polymers those with leading properties are silicone rubbers (polydimethylsiloxane, tetramethyldisiloxane, polyoctylmethylsiloxane), polytrimethylsilyl propyne, polyvinylidenefluoride and polytetrafluoroethylene. Along with polymeric materials, inorganic and mixed matrix materials have been tested. Still, the most widely applied membranes for organic compounds recovery from wastewaters by pervaporation are the polydimethylsiloxane (PDMS) membranes. Some examples for the selectivity of PDMS are given in table 2.

Table 2. Pervaporation separation factors of PDMS membranes for recovery of organic compounds from wastewaters (Böddeker and Bengtson, 1989; Raghunath and Hwang, 1992; Athayde et al., 1997)

Target compound	**Separation factor**
Ethanol, methanol	5-20
Propanol, butanol, aniline	20-200
Phenol	27
Acetone	50
Benzene, toluene, chloroform	200-1000
Acetaldehyde	48
n-Hexane	1300
Acetic acid, ethylene glycol	1-5

4. COMMERCIAL PERVAPORATION MODULES

Membranes have to be incorporated into modules in order to be used in the process. Therefore, the development of a suitable module design together with the choice of membrane greatly influence the successful application of pervaporation. The membrane module configurations commercially available today are shown in figures 2.1 to 2.4 (after Xu, 2001; Lipnizki, 1999). The main module designs are the plate-and-frame and the spiral-wound systems which are based on flat membranes, as well as the hollow fiber modules, based on tubular membrane configurations (Scott, 1995).

ISSN 1313-2539, Published at: http://www.science-journals.eu

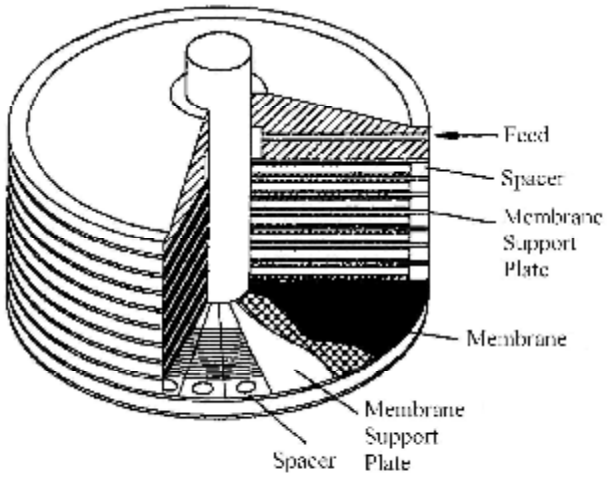


Fig. 2.2. Commercial pervaporation modules – plate-and-frame design

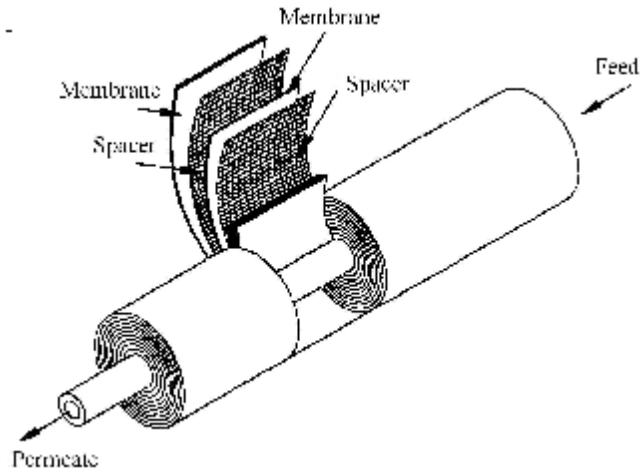


Fig. 2.2. Commercial pervaporation modules – spiral-wound design

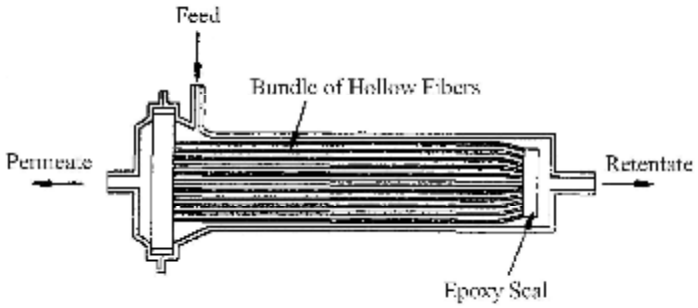


Fig. 2.3.1. Commercial pervaporation modules – hollow fiber design, shell side feed

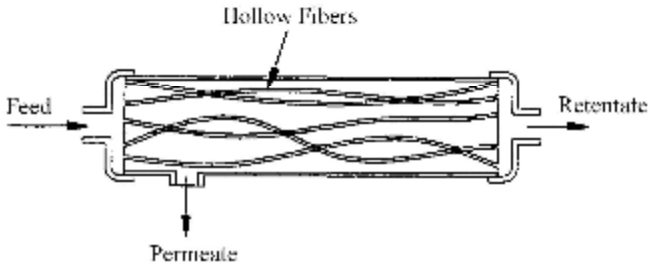


Fig. 2.3.2. Commercial pervaporation modules – hollow fiber design, tube side feed

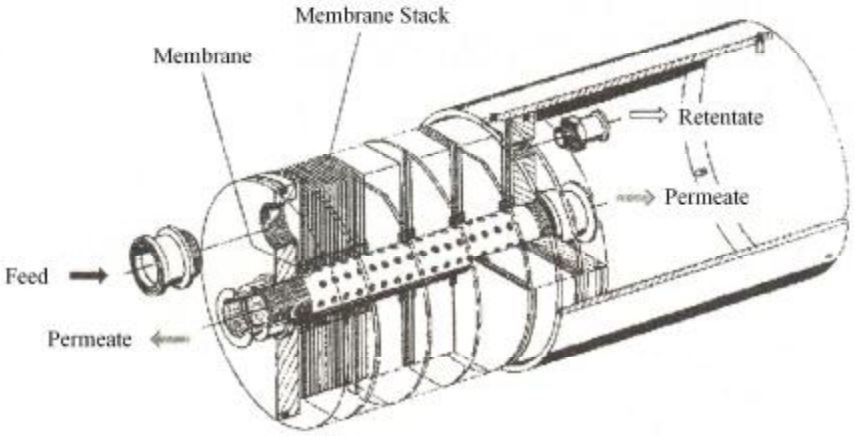


Fig. 2.4. Commercial pervaporation modules – pocket design

In the plate-and-frame modules the membranes are supported by stainless steel perforated plates and spacers, which form permeate channels. These channels are open to all sides and ensure easy removal of the permeate. The plate-and-frame modules have good resistance to fouling.

The spiral-wound modules consist of a membrane envelope wound around a perforated central collection tube and the assembly is fitted inside an appropriate tubular housing. The feed is circulated axially down the module across the membrane, permeate spirals towards the centre and exits via the collection tube. The spiral-wound modules are not suitable for high pressure operation.

Hollow fiber modules are formed in two basic geometries in which the feed flows on the shell side of the fibers or into the fibers (tube side feed). The first is the closed-end design where compounds pass through the fiber wall from outside in and permeate exits via the open fiber ends. This design allows very large membrane area to be contained in an economical system. In the second hollow fiber design the feed flows through the fibers which often have larger diameters than those used in closed-end design.

A novel design, the so called pocket module (Fig.2.4) from GKSS (Germany), gives good mass transfer on the feed side and a low permeate pressure drop (Lipnizki, 1999).

Although several companies produce different types of commercial pervaporation modules, the market leader is Sulzer Chemtech Membrantechnik AG (Germany).

5. RECOVERY/REMOVAL OF ORGANICS FROM WASTEWATERS BY PERVAPORATION

The level of organic compounds allowed in wastewater effluents is lowered every few years. When the target organics are valuable (see Table 2), they are recovered and reused/recycled. In case of organic contaminants such as petroleum hydrocarbons and chlorinated hydrocarbons – trichloroethylene and carbon tetrachloride, they need to be removed and safely disposed. Compared to conventional technologies, hydrophobic pervaporation can be used to effectively recover and concentrate organics from water to a standard that both organics and water can be reused without further processing and no additives are required.

There are considerations for pervaporation restrictions due to exponential increase of membrane area when recovering low organic concentrations, as well as limited membrane selectivity which might provide sufficiently pure permeate. Thus, coupling of pervaporation with other separation techniques for better performance and process optimization can be applied. Successful applications so far are process combinations of bioreactor and pervaporation unit or hydrophobic pervaporation with hydrophilic pervaporation (Lipnizki et al., 1999).

4. CONCLUSIONS

The emerging membrane technique pervaporation shows to be a successful alternative for environmental applications to the conventional processes. Its main environmental application is in recovery of organics from industrial wastewater streams. For this purpose, the most widely used hydrophobic membranes are rubbery polymers such as polydimethylsiloxane. A number of companies produce commercial membranes suitable for organic removal from water which are utilised at pilot and industrial scales. From an economical aspect, when low organic concentrations are targeted, pervaporation can be coupled with another separation process to achieve better performance and/or process optimisation.

ACKNOWLEDGEMENTS

M. L. wishes to acknowledge the financial support received from Human Resources Development Operational Programme 2007-2013, contract №BG051PO001-3.3.04/30/28.08.2009, for the participation in the Scientific Events 2011, 13th International Symposium Materials, Methods & Technologies.

REFERENCES

1. Chapman PD, Oliveira T, Livingston AG, Li K. Membranes for the dehydration of solvents by pervaporation, J Membr Sci 2008; 318: 5–37.
2. Lazarova M., Friedl A Implementation of pervaporation in bioethanol production from Lignocellulosic Materials, J International Scientific Publication: Materials, Methods& Technologies 2010; 4: 422-429.

3. Lipnizki F, Hausmanns S, Field R. Influence of impermeable components on the permeation of aqueous 1-propanol mixtures in hydrophobic pervaporation. J Membr Sci 2004; 228: 129–138.
4. Khayet M, Cojocaru C, Zakrzewska-Trznadel G. Studies on pervaporation separation of acetone, acetonitrile and ethanol from aqueous solutions. Sep Purif Technol 2008; 63: 303–310.
5. Vane L. A review of pervaporation for product recovery from biomass fermentation processes. J Chem Technol Biotechnol 2005; 80:603-629.
6. Böddeker KW, Bengtson G. in: R.Y.M. Huang (Ed.), Pervaporation: Membrane Separation Processes, Elsevier Science Publisher, Amsterdam, 1989; 437-460.
7. Raghunath B, Hwang ST. Effect of boundary layer mass transfer in the pervaporation of dilute aqueous organics. J Membr Sci 1992; 65:147-161.
8. Athayde AL, Baker RW, Daniels R, Le MH, Ly JH. Pervaporation for wastewater treatment. Chemtech 1997; 27:34-39.
9. Xu W. Design and development of a pervaporation membrane separation module. Master thesis, University of Toronto, 2001; 1-145.
10. Lipnizki F, Hausmanns S, Ten P-K, Field RW, Laufenberg G. Organophilic pervaporation:prospects and performance. Chem Eng J 1999; 73: 113-129.
11. Scott K. Separation of liquid mixtures/pervaporation, in: K. Scott (Ed.), Handbook of Industrial Membranes, Elsevier, Oxford, 1995; 331-354.
12. Lipnizki F, Field R W, Ten P-K. Pervaporation-based hybrid process: a review of process design, applications and economics, J Membr Sci 1999; 153: 183-210.