Green Synthesis of Vanillin: Pervaporation and Dialysis for Process Intensification in a Membrane Reactor

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In the present work, two different membrane processes (pervaporation and dialysis) are compared in view of their utilization in a membrane reactor, where vanillin, which is probably the most important aroma of the food industry, is synthesized in a green and sustainable way. The utilized precursor (ferulic acid, which is possibly a natural product from agricultural wastes) is partially oxidized (photocatalytically or biologically) and the product is continuously recovered from the reacting solution by the membrane process to avoid its degradation. It is observed that pervaporation is much more selective towards vanillin than dialysis, but the permeate flux of dialysis is much higher. Furthermore, dialysis can work also at lower temperatures and can be used to continuously restore the consumed substrate into the reacting mixture. A mathematical model of the integrated process (reaction combined with membrane separation) reproduces quite satisfactorily the experimental results and can be used for the analysis and the design of the process.

1. Introduction

The utilization of vanillin (4-hydroxy-3-methoxybenzaldehyde) in the food and cosmetic industries is continuously increasing due to its pleasant flavor and to its nutraceutical and healthy properties, which are really appreciated by consumers (Havkin-Frenkel and Belanger, 2011). In view of the fact that the production of this aroma from the cultivated plants cannot satisfy the demand of the industry and is particularly costly, some methods of chemical synthesis have been developed, that utilizes mainly by-products from the petrochemical (guaiacol) and wood (lignin) industries as raw materials. However, these chemical routes are not eco-friendly, so that, in order to meet the preferences of the consumers towards more "natural" products (Bomgardner, 2016), the research on new green processes has grown in the last years. On the other hand, nowadays, many food industries are willing to pay a higher cost for a green product. Biotechnological and photocatalytic syntheses have been proposed to satisfy the need of greener and sustainable processes. In both methods, the produced vanillin is an intermediate product, which is further oxidized and degraded in the reacting solution. Moreover, the presence of vanillin hinders the rate of production. In order to avoid these problems, it is worth recovering vanillin from the reactor while it is produced. Some membrane separation processes appear very promising to accomplish this task, because they can be easily integrated with the reactive process in a so-called "membrane reactor". Böddeker et al. (1997) was probably the first who investigated pervaporation as an effective tool to selectively extract vanillin from a hypothetical fermentation broth. Camera-Roda et al. (2013) used pervaporation for the coupling with the photocatalytic synthesis of vanillin. The present work analyses and compare the capabilities of pervaporation and dialysis to recover vanillin from the reacting solution.

2. Materials and methods

All the chemicals (alcohols, vanillin, trans-ferulic acid, and standards for caffeic acid, vanillylmandelic acid, homovanillic acid, vanillic acid) were purchased from Sigma–Aldrich with a purity >99%.

The membranes in polyether block amide (PEBA) were prepared by the solvent casting method. PEBAX® 2533 by Arkema was dissolved in n-butyl alcohol and isopropyl alcohol (PEBAX 8.7 w%, n-butyl alcohol 22.8 w %, isopropyl alcohol 68.5 w%) and the solution was cast onto a glass plate by a doctor blade with adjustable clearance. Then the solvents are evaporated for 1 day at 70 °C. The clearance of the doctor blade was regulated to obtain non-porous ("dense") membranes with a final thickness of 45 μm. The same type of membranes was used during the pervaporation and dialysis tests.

In some experiments, the membrane process was coupled with the production of vanillin, which was obtained by the partial oxidation of ferulic acid in a photocatalytic annular reactor (inner diameter= 2.4 cm; outer diameter = 3.4 cm, length = 26.5 cm, V=121 mL) according to the procedure described by Camera-Roda et al. (2013). The photocatalyst was titanium dioxide (Merck TiO_2, 100 % anatase) in the form of fine powders suspended in the reacting solution. The integration of the membrane process was achieved by continuously recirculating the reacting solution through the reactor and the membrane module. The flow rate of the recirculated stream was sufficiently high to obtain very low values of the Damköhler number and of the reciprocal of the Péclet number. In this way, the two separate apparatuses (reactor and membrane module) work in differential conditions and the coupling of the membrane separation and the reaction is almost perfect (Camera-Roda et al., 2018). Since the objective was the recovery of vanillin from the reacting solution, a diluted aqueous solution of vanillin (about 1.6 mM) was generally adopted. In pervaporation, the following operating conditions assured compatibility with the photocatalytic process: vanillin concentration upstream the membrane=1.6 mM, temperature=60 °C, permeate pressure=2 mbar. The description of the pervaporation apparatus can be found in Camera-Roda et al. (2014). The dialysis apparatus is shown in Figure1.
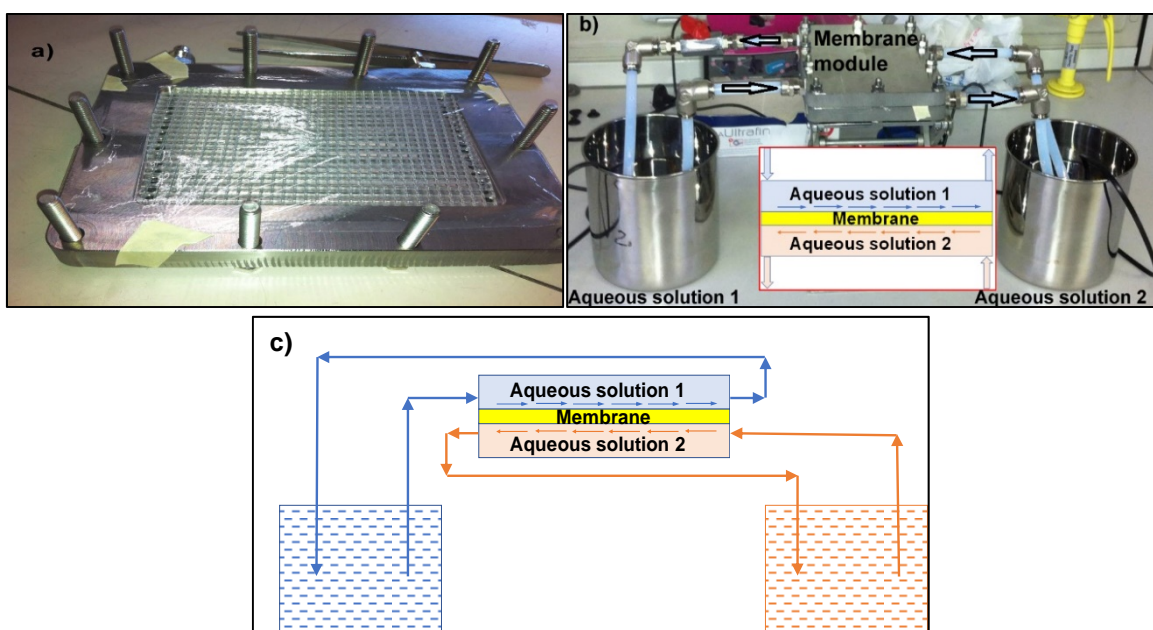

Figure 1. a) Picture of the dialysis module with the membrane inside. b) Picture of the dialysis system. c) Scheme of the dialysis system.

The active membrane area in dialysis is 96 cm^2 and the two aqueous solutions (1 and 2 in Figure 1b) flow in countercurrent as schematically shown in Figure1c.

3. Results

Preliminary pervaporation and dialysis experiments were carried out to evaluate the separation capabilities. Successively, the photocatalysis-pervaporation and photocatalysis-dialysis integrated processes were studied to compare the two integrated processes.

3.1 Pervaporation

In the adopted operating conditions the permeate fluxes of water and vanillin were 560 and 0.66 g/(h m^2), respectively. Therefore, the enrichment factor of vanillin, i.e. the ratio of its concentration upstream the

membrane to the one in the condensate downstream the membrane, was 4.84. The values of the flux and of the enrichment factor are relatively low, but they can be adequate to effectively recover most of the produced vanillin if the membrane area is sufficiently high (Camera-Roda et al 2014).

The driving force for permeation is given by the difference of the partial pressure of vanillin, ΔP_{van}, between the two sides of the membrane. So, in pervaporation, it is $\Delta P_{van} = P^*_{van}(T)\,\gamma_{van}\,x_{van} - P_D\,y_{van}$ where $P^*_{van}(T)$ is the vapor pressure of vanillin at temperature T, γ_{van} the activity coefficient, x_{van} the molar fraction in the liquid upstream the membrane, P_D the pressure downstream the membrane and y_{van} the molar fraction in the permeate vapor phase. Actually, the vapor pressure of vanillin is much lower than the one of water and, consequently, the relative volatility with respect to water is low (Camera-Roda et al 2014). At the adopted operating temperature (60 °C) the partial pressure of vanillin upstream the membrane is nonnegligible just thanks to the high activity coefficient of vanillin in aqueous solution (γ_{van}>100 at infinite dilution). Despite of the low volatility of vanillin, the permeate is enriched in vanillin because the solubility of water in the PEBAX membrane is some orders of magnitude lower than vanillin solubility and therefore the membrane acts as a barrier (Böddeker, 2008) towards the passage of water, even though water diffusivity is higher than vanillin diffusivity. In fact, adsorption tests showed that the partition coefficients, defined as the ratio of the mass concentration of the given substance in the membrane at equilibrium to its partial pressure in the liquid solution, are 42000 and 0.01 kg/(m^3 mbar) for vanillin and water, respectively. A solution-diffusion model was developed taking also into account viscous transport and Knudsen diffusion to describe the transport through the porous support of the membrane. This model was able to reproduce accurately the experimental results. Moreover, the model shows that the permeation of vanillin, in accordance with the experimental evidence (Böddeker and Bengston, 1990; Böddeker, 1997), takes place in presence of an almost negligible variation of its partial pressure across the membrane. In practice, ΔP_{van} accounts just for 1 % of the one that would be obtained if it were possible to keep close to 0 the vanillin partial pressure downstream the membrane.

3.2 Membrane reactor (pervaporation coupled with photocatalysis)

When the photocatalytic reaction is integrated with pervaporation, many chemicals are present in the aqueous reacting solution: TiO_2 powders, the substrate (cis and trans ferulic acid), the main product (vanillin) and other by-products of the reaction. The powders cannot pass through the dense membrane and does not give fouling. The HPLC chromatograms of the reacting solution and of the permeate obtained after 2 h are shown in Figure 2.
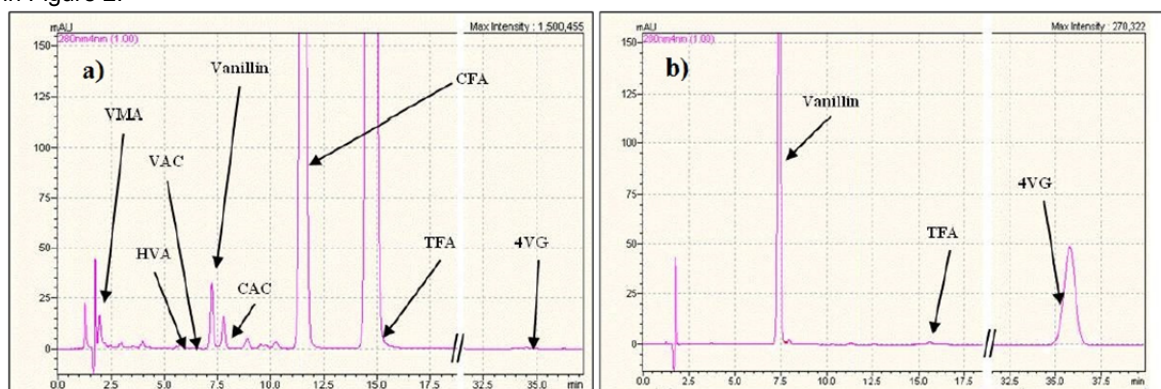

Figure 2. HPLC chromatograms after 2 h of reaction: a) in the reacting solution; b) in the permeate. VMA: Vanillylmandelic acid; HVA: Homovanillic acid; VAC: Vanillic acid; CAC: Caffeic acid; CFA: Cis-ferulic acid; TFA: Trans-ferulic acid; 4-VG: 4-vynil guaiacol; other peaks are unknown.

Despite the numerous chromatogram peaks in Figure 2a denote the presence of many compounds in the reacting solution, only the peaks related to vanillin and 4-VG are present in the permeate. The enrichment factors are about 4.84 and 150 for vanillin and 4-VG, respectively. The selective permeation of vanillin allows for a substantial improvement of the yield because if vanillin is recovered from the reactor it cannot inhibit the reaction and it does not undergo degradation. Moreover, the high rejection towards the substrate allows working with a higher conversion of ferulic acid (Camera-Roda et al., 2014). Brazinha et al. (2011) speculated that the retention of FA is due to phenomena related to the dissociation of the molecules in the aqueous solution at the working pH (around 3.5-4). However, the practical effects of the dissociation are limited (Camera-Roda et al., 2014), whereas the actual reason for the poor permeation is the low volatility of most of the compounds. Accordingly, in Figure3 a correlation is evident between the boiling point of the different

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compounds and their permeability. Only the compounds with a low boiling point (vanillin and 4-VG), i.e. with high volatility, can permeate at a non-negligible extent.
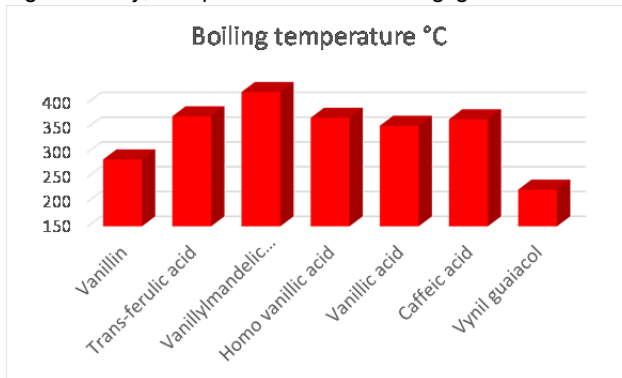

Figure 3. Boiling points of some compounds that are present in the reacting solution.

3.3 Dialysis

When the same membranes are used in dialysis, the transport mechanism through the membrane is the same that is effective in pervaporation (solution-diffusion) (Camera-Roda et al., 2018), but the permeate does not evaporate and the volatility of the permeating species is unimportant. Therefore, the problems encountered during the pervaporation of vanillin (low volatility and difficulties in exploiting the potential driving force) are not present in dialysis. The driving force in dialysis for the permeation of a given compound is the difference of its activity between the two liquid phases at the opposite sides of the membrane. In diluted aqueous solutions, the values of the activity coefficients of the organic permeants in the two liquid phases are very similar and the driving force can be expressed simply by its concentration difference. In fact, Figure 4 shows that the flux of vanillin increases linearly with the concentration difference, ΔC_{van}, between upstream and downstream the membrane.
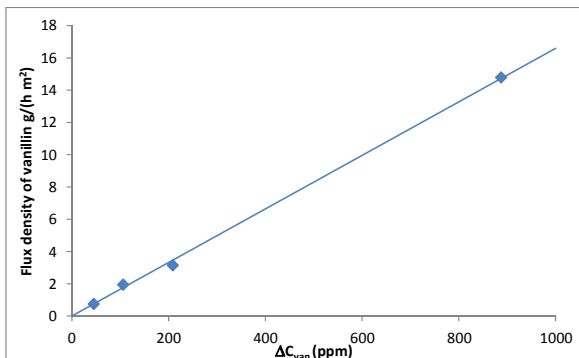

Figure 4. The flux of vanillin in dialysis vs. ΔC_{van}, Temperature=25 °C.

It is worth noting that the vanillin flux obtained in dialysis at ambient temperature is at least one order of magnitude higher than the one obtained at 60 °C in pervaporation. A mathematical model has been developed to describe the permeation of vanillin in dialysis. The model takes into account:

- the mass balance for vanillin in phase 1 (aqueous solution 1 of Figure 1b):

$$-\frac{dC_1}{dt} = \frac{A_m}{V_1} k_1 \left[C_1 - \frac{C_m|_{x=0}}{K} \right]$$

where C_1 is the vanillin concentration in phase 1, t the time, A_m the membrane area, V_1 the volume of phase 1, k_1 the mass transfer coefficient in phase 1, $C_m|_{x=0}$ the vanillin concentration inside the membrane at x=0, K the vanillin partition coefficient;

- the mass balance for vanillin inside the membrane:

$$\frac{\partial C}{\partial t} - \frac{\partial}{\partial x} \left[D_0 \exp(g\,C) \frac{\partial C}{\partial x} \right] = 0$$

where C is the vanillin concentration in the membrane, x the spatial coordinate (x=0 at the phase 1-membrane interface), D_0 the vanillin diffusivity in the membrane at C→0 and g the plasticization factor;

- the mass balance for vanillin in phase 1 (aqueous solution 1 of Figure 1b):

$$\frac{dC_2}{dt} = \frac{A_m}{V_2} k_2 \left[\frac{C_m\big|_{x=\delta}}{K} - C_2 \right]$$ where C_2 is the vanillin concentration in phase 2, V_2 the volume of phase 2, k_2 the

mass transfer coefficient in phase 2 and $C_m\big|_{x=\delta}$ the vanillin concentration inside the membrane at $x=\delta$.

The mass transfer coefficients k_1 and k_2 were predicted by the well-known analogy: $Sh=1.62\times(Re\times Sc\times d_h/\delta)^{1/3}$ with d_h the hydraulic diameter of the channel, Sh, Re, Sc the Sherwood, Reynolds, Schmidt numbers, respectively. The model has been solved numerically by the finite volume method with a Crank-Nicolson time integration scheme. All the parameters were obtained by independent measurements with the exceptions of D_0 and g, that have been evaluated by fitting the concentration-time experimental data obtained in 4 runs carried out at different initial concentrations of vanillin ($0.3< C_1\big|_{t=0} <15$ mM, $C_2\big|_{t=0} =0$). Figure 5 compares the output of the mathematical model with the experimental points obtained in one of these experiments.
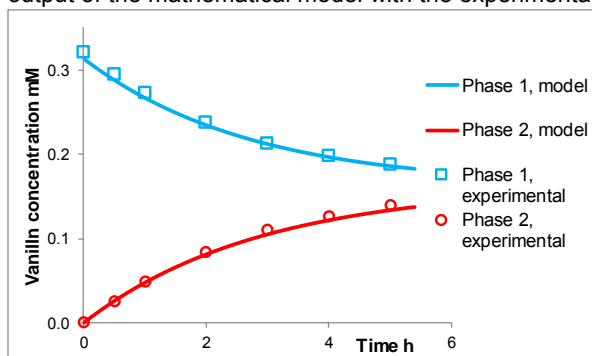

Figure 5. Vanillin concentration in phase 1 and phase 2 vs. time.

The best fitting was obtained with $D_0 = 9\times10^{-11}$ m^2/s and $g=0$. The relatively high value of the diffusivity and the high partition coefficient demonstrate that the polymer is highly permeable to vanillin.

The model has been used also to evaluate the importance of concentration polarization. In Figure 6 it is apparent that most of the mass transfer resistance is in the two liquid phases, whereas mass transfer resistance across the membrane is minor. Of course, concentration polarization can be reduced by increasing the flow rates through the membrane module thus intensifying the tangential velocity of the fluid.
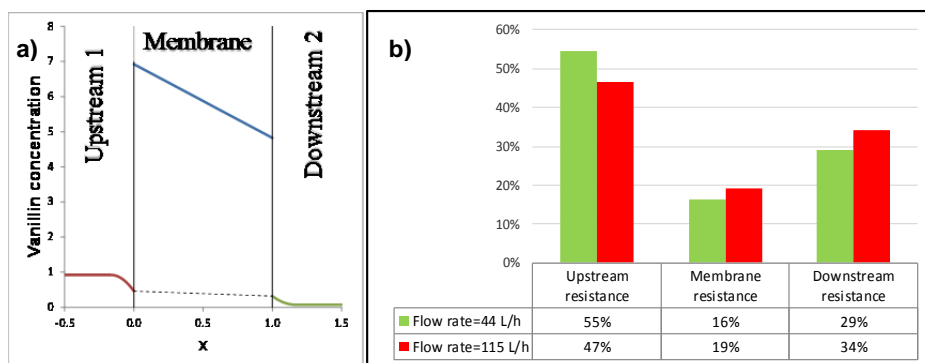

Figure 6. Concentration polarization in dialysis at 3.5 min. a) concentration profiles of vanillin; b) the contributions (in percentage) of upstream, downstream and membrane resistances to overall resistance at two different flow rates (44 and 115 L/h) in phase 1. Flow rate in phase 2 =75 L/h, $C_1\big|_{t=0}$ =0.31 mM.

3.4 Membrane reactor (dialysis coupled with photocatalysis)

In view of the fact that volatility does not limit the permeation of the organic compounds, almost all the organic compounds are not retained in dialysis, so that vanillin is easily recovered but also the substrate (trans-ferulic acid) permeates easily. In order to avoid the depletion of the substrate in the reactor by its permeation, it is advisable to start with a relatively high concentration of ferulic acid in the liquid phase at the opposite side of the reacting solution. In this way, permeation of the substrate takes place towards the reactor and it is continuously supplied to the reactor while it is consumed by the reaction. The HPLC chromatograms obtained operating in this way are reported in Figure 7.
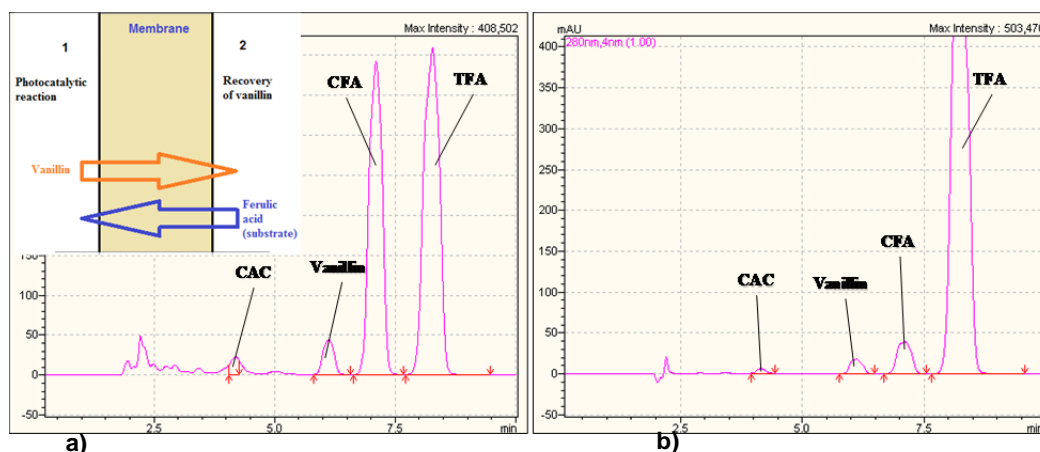
Figure 7. Figure 2. HPLC chromatograms after 2 h of reaction: a) reacting solution; b) liquid phase 2.

It is evident that vanillin together with the other organic products, which are produced in the reactor, is removed from the reacting solution, while trans-ferulic acid is continuously fed to the reactor.

4. Conclusions

It has been observed that PEBAX membranes may be suitable for the recovery of vanillin in photocatalytic membrane reactors or membrane bioreactors to avoid problems that reduce the production yield. The possible membrane processes are pervaporation and dialysis. In pervaporation, the enrichment factor of vanillin and the rejection of the original substrate are very satisfactory. However, due to the low volatility of vanillin, acceptable values of the flux can be obtained only at relatively high temperatures. This requirement limits the convenience of pervaporation in particular in coupling with a bioreactor where microorganisms cannot withstand the required high temperatures. On the contrary in dialysis, volatility is largely irrelevant and, consequently, the vanillin flux at ambient temperature is at least one order of magnitude higher than in pervaporation at 60 °C. However, the higher flux has the potential to give rise to concentration polarization, thus, it is advisable to operate in conditions that reduce this negative phenomenon. Moreover, almost all of the organics easily permeate during dialysis, so that it is no longer possible to retain in the reactor the substrate (ferulic acid) for the vanillin production. However, the high permeability of the substrate can be utilized to continuously restore in the reactor the substrate, which is consumed by the photocatalytic reaction, simply by starting with a high substrate concentration of ferulic acid in the second liquid phase (i.e. at the opposite side of the reacting solution).

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