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Composite polymeric membranes for process intensification: Enzymatic hydrolysis of oligodextrans

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ABSTRACT

Enzymatic membrane reactors based on a polymeric matrix and activated carbon loaded with dextranase were synthesized to separate and purify dextrans. The steps carried out were: (1) testing the activity of the enzyme with a 40 kDa commercial dextran to obtain oligomers with low degree of polymerization, avoiding the production of monomer, (2) adsorbing the enzyme by the activated carbon considering concentration and pH as variables, as well as testing the activity of the loaded activated carbon obtained, (3) synthesizing the enzymatic membrane reactors, (4) characterizing them by SEM and IFME® software and (5) testing their performance in a flat membrane module at ultrafiltration pressures. Results show a proper activity of the enzyme and the loaded activated carbon, and optimal conditions for the adsorption of enzyme by the activated carbon were found (pH 5). Related to the enzymatic membrane reactors, the larger activated carbon–enzyme loading, the closer porous structure was obtained. Since a very specific enzyme was used, changes in the loading of the activated carbon–enzyme leads to a change on the mean value of degree of polymerization of the produced compounds, but not on the amount of a specific-in-size product obtained. By using 4 wt.% of activated carbon–enzyme loading in the preparation of the enzymatic membrane reactor it is possible to obtain, as purified reaction products, oligomers from 200 Da.

1. Introduction

Enzymatic hydrolysis is commonly used for the production of oligosaccharides useful for different applications in the food and the pharmaceutical industry. Oligosaccharides with low degree of polymerization are normally used as ingredient in functional foods [1]. One of the most promising applications of these oligosaccharides is their use as prebiotics for the production of functional food [2]. For this specific application the oligosaccharides mixture has to have a determined composition and range of molecular weight, for which the enzymatic hydrolysis is much appropriate because of the specificity of the reaction process. One of the disadvantages of the use of enzymes is the difficulty in the separation of the products from the reaction mixture, simultaneously with their deactivation and washing. For this purpose, it will be interesting to develop a single unit which carries out two processes: separation and reaction, well known, nowadays, as process intensification. Process intensification through integration of reaction and separation steps into a single unit is one of the key concepts involved in the development of sustainable chemical processes. At the core of this concept are the new advances in membrane science and technology, which make possible the integration of the separation units into the reactor. This is well illustrated by the enzymatic membrane reactors (EMRs), which comprise a membrane that simultaneously holds the active enzyme that catalyzes the reaction, either by light or by strong bonding, and separates the desired product at high level of purity. The utilization of hybrid materials has been demonstrated to be an important approach in many fields of science, and particularly, in separation processes [3,4]. Considering membrane technology, they offer the potential to combine the simple utilization of polymers with the functional properties of carbon materials. Nevertheless, the incorporation of the activated carbon in polymeric-based membranes responds also to the aim of using it to adsorb enzymes in order to synthesize EMRs. Some intrinsic advantages of these systems are that the process is readily operated in continuous mode, that the enzyme is not lost and is re-used, and that by a correct design of the membrane, the permeate is free of enzyme and reactants [5,6]. Therefore, important benefits may be achieved by process intensification such as 60% reduction of capital cost, 99% reduction in impurity levels resulting in significantly more valuable product, 70% plus reduction in energy usage and hence substantial reduction in operating cost,

Abbreviations: LAC, loaded activated carbon with enzyme; EMR, enzymatic membrane reactor; SEM, scanning electron microscopy; PSf, polysulfone; DMF, dimethyl formamide; MWCO, molecular weight cut-off; IP, index of polydispersity; DP, degree of polymerization.

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99.8% reduction in reactor volume for a potentially hazardous process, leading to inherently safe operation [7]. Thus, in this project we have developed a novel EMR that has been used for the controlled depolymerization of high molar mass dextrans to obtain low molar mass oligosaccharides, avoiding the synthesis of monomer, which can be obtained by easier and cheaper methods like the acid hydrolysis [8].

2. Experimental

2.1. Materials

For membrane synthesis, the polymer used was polysulfone ($M_w \approx 35{,}000$, CAS number 25135-51-7, from Sigma–Aldrich, Spain), employing dimethyl formamide (DMF, PA-ACS-ISO, 99.8%, CAS number 68-12-2, from Panreac, Spain) as solvent and deionised water as non-solvent. The polymer concentration was 15 wt.% in all cases.

The activated carbon used was a commercial one from NORIT Americas Inc., product id. NORIT DARCO 12×40, with a measured surface area of $578 \pm 6\ m^2/g$ and micro-pore total volume of 0.14 mL/g. Before using, it was previously ground and sieved to obtain particles of sizes between 30 and 60 μm, by using a sonic sieving (Gilsonic Autosiever). After sieving, characteristic properties of activated carbon did not change significantly, measured superficial area was $584 \pm 5\ m^2/g$ and micro-pore total volume of 0.13 mL/g.

The enzyme used was a commercial dextranase (*dextranase from Chaetomium erraticum*, CAS number 9025-70-1, from Sigma–Aldrich, Spain).

To test the activity of the enzyme as well as to test the performance of the EMR, a commercial 40 kDa dextran ($M_r \approx 40{,}000$, CAS number 9004-54-0, from Fluka, Spain) was used.

2.2. Methods

2.2.1. Synthesis

The method used to obtain membranes was the Loeb–Sourirajan phase inversion process, specifically, immersion precipitation. This method, which is well described in Ref. [9], consists in obtaining a homogeneous mixture between the polymer and the solvent, cast a film and immerse it in a coagulation bath containing the non-solvent, in order to precipitate the polymer and obtain the membrane.

To obtain the EMR, activated carbon was used to adsorb the enzyme, and the pair was immobilized into the polymeric membrane precursor. The adsorption of the enzyme by the activated carbon was performed in batch experiments by mixing 50 mg of the activated carbon with 10 mL of the solution containing the liquid enzyme (after diluting it in deionised water) in agitated Erlenmeyer flasks and considering two variables: the enzyme concentration (0.1, 0.2, 0.3, 0.4 and 0.5 mg/mL) and pH (3, 5 and 7).

Two types of EMR were synthesized: a mono-layered one and a two-layered one (Fig. 1); the difference among them is the location of the pair activated carbon–enzyme. In both systems, a basic polymeric membrane was used in the same conditions and methods. Related to the mono-layered one, a homogeneous mixture between the polymer, the solvent and the pair activated carbon–enzyme (LAC) was obtained; afterwards, the polymeric film was cast over a glass support and the EMR was precipitated inside the coagulation bath. Several LAC loadings were considered in the polymeric solution: 0.35 wt.%, 0.90 wt.%, 1.50 wt.% and 4.00 wt.%. Related to the two-layered one, a mixture of the polymer and the solvent was prepared; the polymeric film was cast over a glass support, and the LAC was added over the surface of the film before immersing it into the coagulation bath.

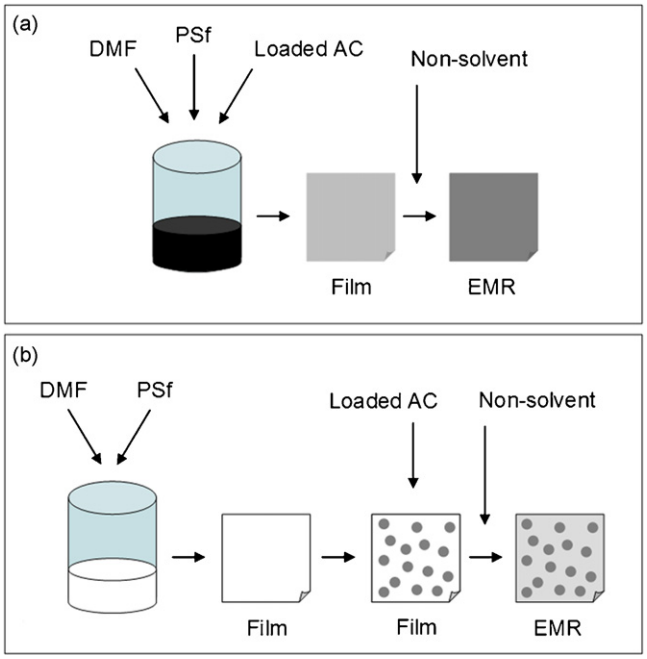

Fig. 1. Schemes of the two types of EMR synthesized: (a) mono-layered one and (b) two-layered one.

In order to achieve a desired molecular weight cut-off (MWCO) of the membrane, a commercial membrane (Osmonics GE Series, MWCO = 8 kDa) was also used as second layer with the synthesized EMR. Future work will consist of casting a thin layer over the obtained EMR in order to obtain it with a specific and desired MWCO.

2.2.2. Enzyme activity

The activity of the enzyme as well as the activity of the LAC were also tested before obtaining the EMR in batch experiments at 50 °C (optimal temperature for the enzyme activity) and using a 40 kDa commercial dextran solution with a concentration of 1.5 g/L as substrate. Concerning to the activity of the enzyme, several enzyme concentrations were tested (0.1, 0.2, 0.5, 2.0 and 10.0 mL/L) and samples of the reaction products, at several times, were extracted and analysed by gel permeation chromatography (5 and 30 min, 1, 3, 5 and 24 h). Concerning the activity of the LAC, experiments with the different LAC produced were carried out with two different LAC amounts (2 and 10 mg) in 100 mL of dextran solution.

2.2.3. Enzymatic membrane reactors performance

The synthesized EMRs were used for the purification and separation of dextrans. Thus, a dextran solution with a concentration of 1.5 g/L in deionised water was used as a feed stream. In all cases, trans-membrane pressure was set to 4 bar and the temperature of the feed vessel was maintained constant at 50 °C, the optimum temperature for the enzyme activity.

2.2.4. Membrane morphological characterization

The morphology of the membranes was studied by using two complementary techniques: the scanning electron microscopy (JEOL JSM-6400 Scanning Microscopy Series, with a working voltage of 15 kV) to obtain cross-section or surface micrographs of the membranes, and the IFME® software [10,11] to quantify the results obtained with the SEM and obtain the main morphological parameters (pore size and distribution, porosity, symmetry and regularity).

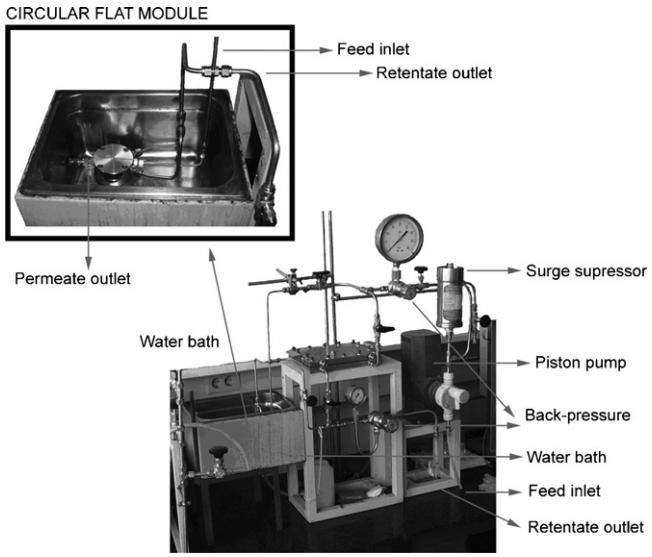

Fig. 2. Experimental set-up.

2.2.5. Analysis

The method used to quantify the adsorption of enzyme by the activated carbon was the organic elemental analysis as usual procedure by using a Carlo Erba-ThermoQuest Model 1108 elemental analyser. Activated carbon before and after the adsorption of the enzyme in the batch experiments was used as sample. For the quantification of the enzyme, the reference element chosen was nitrogen, the original activated carbon contains only traces of this element but its concentration increases when it adsorbs the enzyme. In all the analysis, 50 mg of solid was employed in the measurements and at least, by duplicate.

The method used to determine the molar mass distribution of the dextrans mixture was Gel Permeation Chromatography using a Toso-Haas G3000PwXL column calibrated with xylose, glucose and low polydispersity standards of malto-oligosaccharides and dextrans (Fluka). The degree of polymerization (DP) was calculated as the following equation. In this calculation, the molecular weight of water is subtracted from the molecular weight of glucose considering that a water molecule is lost during the ester binding:

$$\mathrm{DP} = \frac{\bar{M}_{\mathrm{w}}}{M_{\mathrm{w,glucose}} - M_{\mathrm{w,water}}} \quad (1)$$

2.3. Equipment

The system used to perform experimental tests with the EMRs, as well as the membrane module used is explained next. All of them were designed, optimized and manufactured in our laboratories.

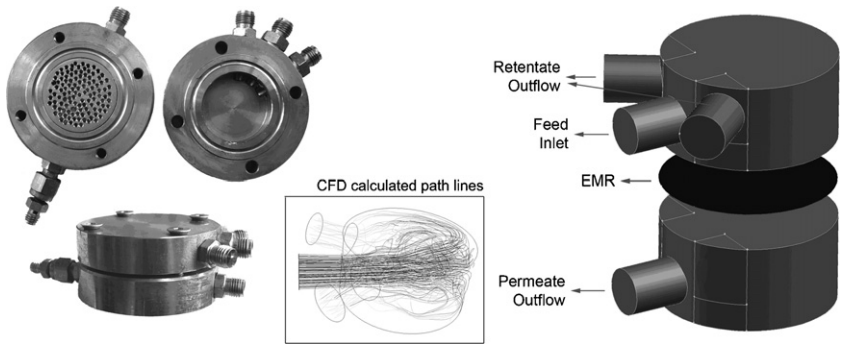

Fig. 3. Membrane module and inside path lines obtained by CFD.

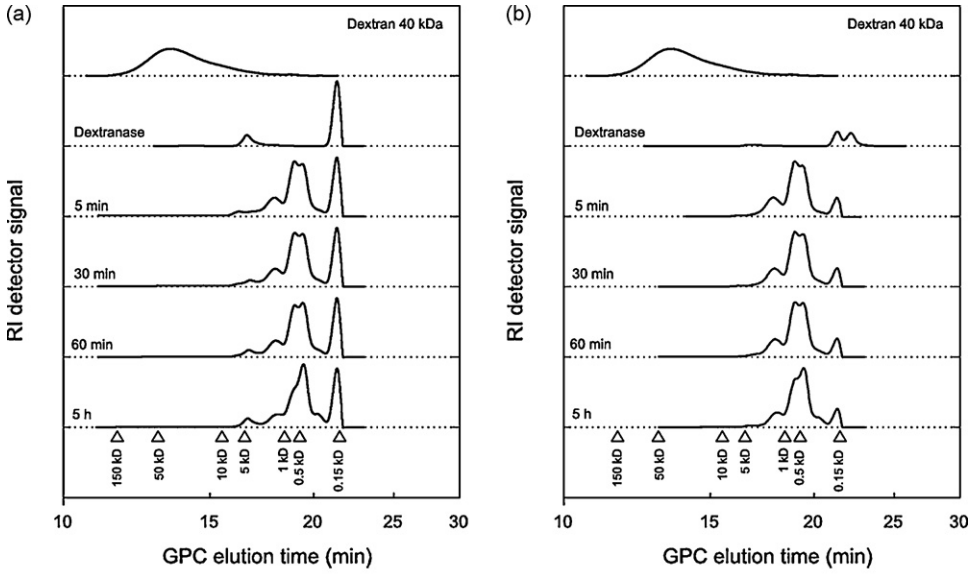

Fig. 4. Activity of dextranase tested with a 40 kDa dextran as function of time and enzyme concentration: (a) 2.0 mL/L and (b) 0.5 mL/L.

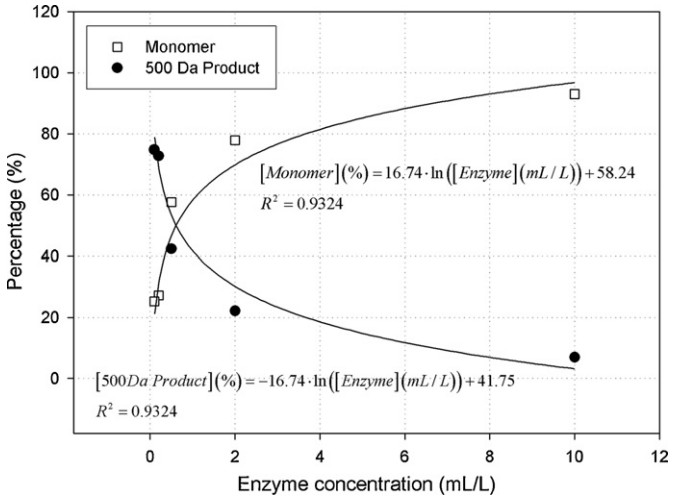

Fig. 5. Comparison between the production of monomer and 500 Da product as function of enzyme concentration, evaluated at a reaction time of 1 h.

The experimental set-up (Fig. 2) consists in a piston pump (used in all the experiments with a volumetric flow rate of 28 L/h) followed by a surge suppressor in order to minimize the pulse effects. Two back-pressure controllers are used to maintain the pressure regular and constant during the experiments. Finally, a water bath is also used to maintain the temperature of the module and thus, the EMR, constant at 50 °C (optimum temperature for the performance of the enzyme).

A stainless steel flat membrane module is used in the set-up. This module is able to house a circular flat membrane of 15 cm^2 (total area). The module was optimized by computational fluid dynamics and includes one inlet and two outlets, approximately, 5° on the right and 5° on the left from the inlet, in order to increase the shear stress on the membrane, perform unsteady flow and eliminate stagnant flow over the membrane (Fig. 3). All these characteristics facilitate the minimization of fouling effects.

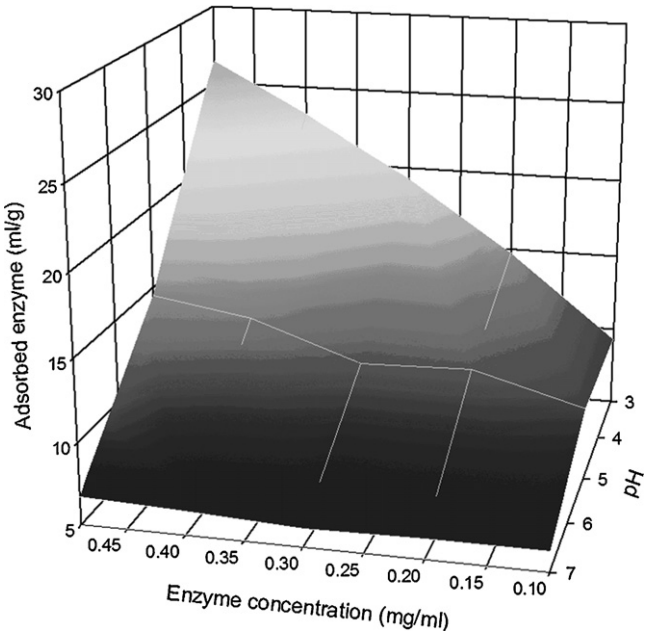

Fig. 6. Enzyme adsorbed in the activated carbon as function of the enzyme concentration and pH.

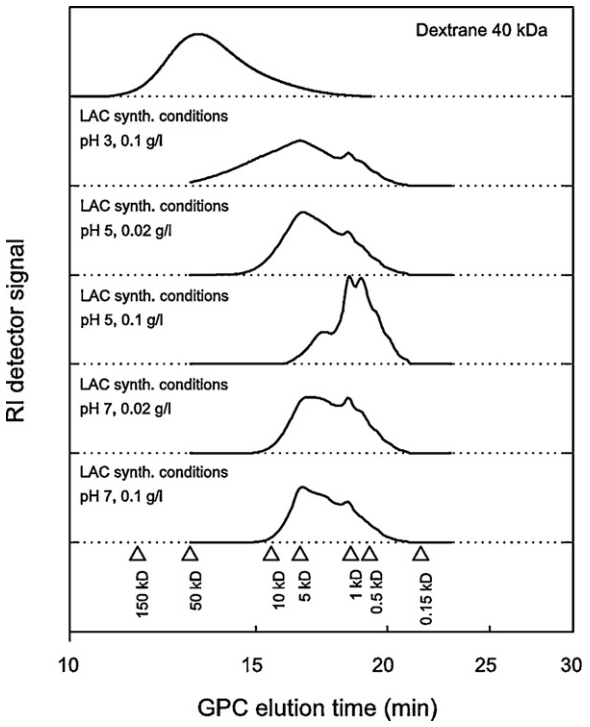

Fig. 7. Activity of the activated carbon–enzyme pair as function of the pH used to adsorb the enzyme and the amount of LAC used; 1 h reaction time at 50 °C.

3. Results and discussion

3.1. Activity of the enzyme

Fig. 4(a) and (b) shows the activity of the enzyme at two different concentrations (2.0 and 0.5 mL/L) and for several reaction times (5, 30, 60 min and 5 h). As the dextranase is very specific for the solute used, very low amounts of enzyme are needed to consume all the 40 kDa dextran in a short period of time (in both concentrations). When a very high conversion is achieved in the reaction, the initial oligosaccharides are consumed and the final product obtained is the monomer, which is not of our interest in this case. It can be seen from the figures and in both concentrations that the entire initial product is consumed yielding intermediate MW products. Nevertheless, in the case of high concentration of enzyme (Fig. 4(a)), there is a high amount of monomer. A correlation between the amounts of monomer produced and the 500 Da product was found as function of the enzyme concentration (Fig. 5), at a given reaction time. A logarithmic fit was encountered, which indicates the rapid consumption of the solute by the enzyme.

3.2. Adsorption of enzyme by the activated carbon

Two variables were considered for the study of the adsorption of enzyme by the activated carbon: the enzyme concentration and the

Table 1
Mean molecular size (number and weight), index of polydispersity (IP) and degree of polymerization (DP) of the reaction products, for each experimental condition and from the activity of the LAC tests

	$\bar{M}_n$	$\bar{M}_w$	IP ($\bar{M}_w/\bar{M}_n$)	DP
Dextran 40 kDa	5600	26,000	4.64	160
pH 3, 10 mg	1700	7,900	4.65	49
pH 5, 2 mg	1400	5,000	3.57	31
pH 5, 10 mg	590	1,100	1.86	7
pH 7, 2 mg	1000	2,600	2.60	16
pH 7, 10 mg	1300	3,000	2.31	19

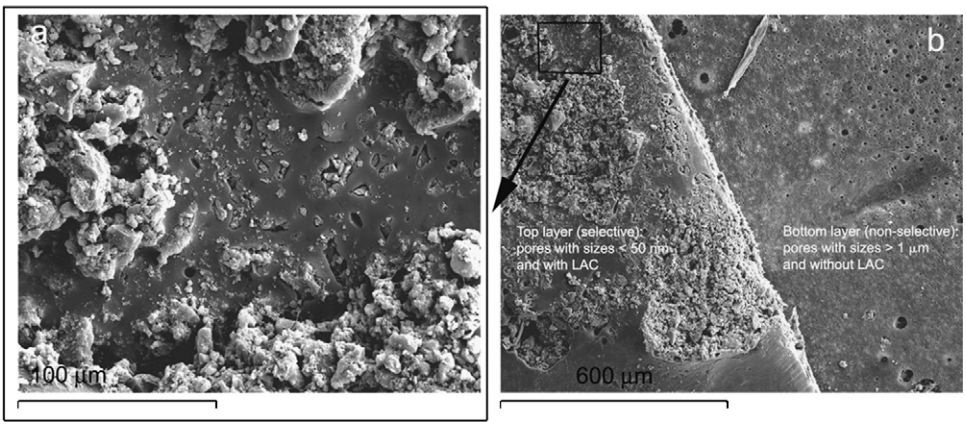

Fig. 8. SEM micrographs from the top and bottom surface of a two-layered enzymatic membrane reactor. Top surface contains activated carbon–enzyme particles, while bottom is surface free. (a) is a magnification of (b) as indicated by the arrow.

pH. Results show that pH is the key variable and limits the variation of the results as function of the concentration.

The initial concentration of nitrogen in the activated carbon was 0.53 wt.%. The highest amount of nitrogen adsorbed was obtained at the lowest pH (3); using an enzyme concentration of 0.5 mL/mL, a value of 4.35 wt.% was obtained, while with 0.3 mL/mL a value of 3.29 wt.% was achieved. As the pH was increased, the results obtained showed a clear decrement of the adsorbed enzyme, at pH 7 and with a concentration of 0.5 mL/mL only 1.50 wt.% was achieved, while at 0.3 mL/mL, 1.46 wt.% was measured. Therefore, it indicates that when low adsorptions are achieved, mainly by the increment of the pH, low effects from the concentration variations are obtained. The high influence of the pH is explained considering the chemical structure of components, as the pH is being modified, the amino and the acid groups also change, and thus the polarity and the linkage capability. More information related to the influence of the pH in the adsorption capability of the activated carbon can be found elsewhere [12].

Fig. 6 shows a 3D surface contour with the variation of the absorbed enzyme as function of the pH and enzyme concentration. Therefore, the mass balance was carried out considering the measured results which correspond to the concentration of nitrogen (in wt.%) in the solid sample (LAC), the initial concentration of nitrogen in the enzyme (0.14%) and in the activated carbon (0.53%) and considering the amounts used.

The activity of the enzyme was tested after its adsorption onto the activated carbon. Fig. 7 shows the results as function of the variables. It can be observed that the largest activity is obtained at

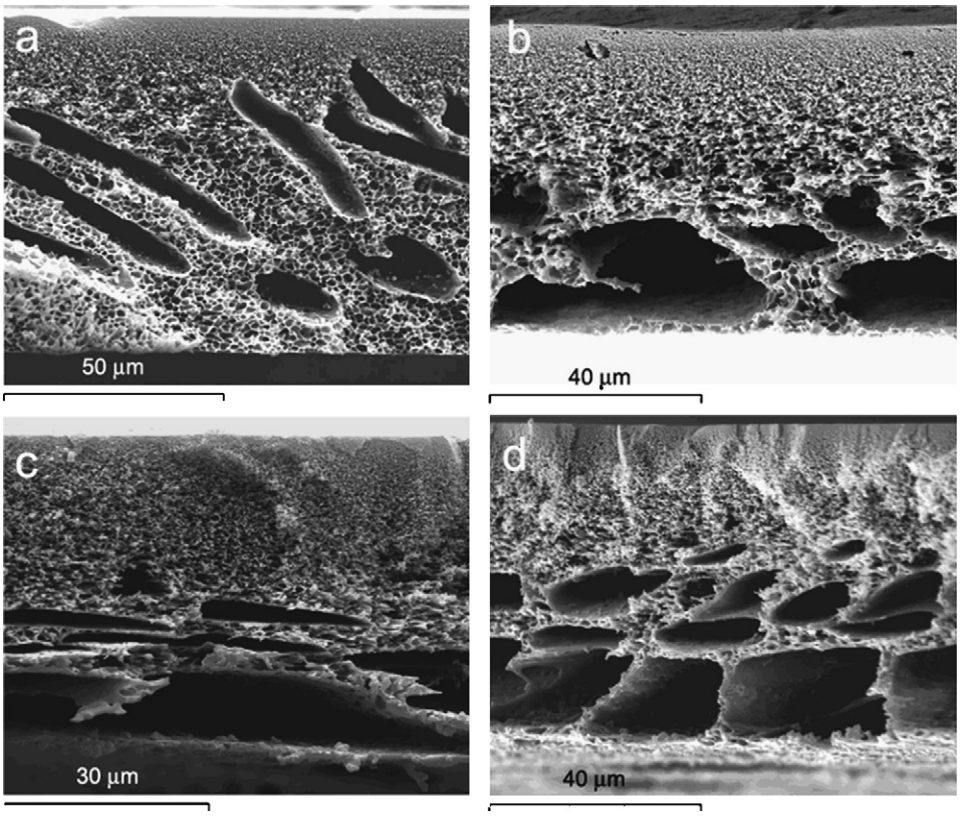

Fig. 9. SEM cross-section micrographs of EMR. Different activated carbon–enzyme loadings: (a) 4.00 wt.%, (b) 1.50 wt.%, (c) 0.90 wt.% and (d) 0.35 wt.% The percentage is referred to the amount of activated carbon–enzyme within the polymeric solution.

Table 2
Numerical results of morphological parameters from cross-section SEM micrographs of four EMR with different LAC loadings obtained by IFME® software

	LAC loading (%)			
	0.35	0.90	1.50	4.00
Porosity, p (μm^2)	0.0685	0.1417	0.2566	0.1546
Mean pore size (μm)	2.53	1.64	1.22	1.61
Largest pore size (μm)	14.63	17.13	13.07	9.40
Standard deviation	0.45	0.46	0.17	0.14
Asymmetry (%)	15	18	16	13
Irregularity	0.0019	0.0029	0.0031	0.0007

pH 5. Nevertheless, results at pH 7 show higher activity than at pH 3. Therefore, LAC obtained at pH 3 shows the worst results, although it was the one that adsorbed more enzyme. This can be explained by the fact that two phenomena occurred. As the pH was decreased more enzyme was adsorbed, but at the same time, more enzyme deactivation occurred.

Table 1 shows the mean molecular size (number and weight), the index of polydispersity (IP) and the degree of polymerization (DP) of the reaction products, for each experimental condition. In the optimal condition (pH 5 and 10 mg), the mean molecular size is the lowest and also the IP, which means that purer substances are obtained. In this case, the DP is 7, a close value to the monomer. At pH 3, the mean molecular size is the one closer to the initial dextran (the lowest activity) and also the one which has the closer DP value to the dextran. There is a large parallelism between the IP and the DP.

Considering the two effects found, pH 5 was taken as the optimum one, and for the following EMRs synthesized, this pH was considered. It should be noted that this pH corresponds to the suggested one by the enzyme manufacturer (for using the enzyme alone) for general applications.

3.3. Synthesis, characterization and performance of EMR

3.3.1. Enzymatic membrane reactor morphology

As introduced in the experimental part, two types of EMRs were obtained: a mono-layered and a two-layered EMR.

Concerning to the two-layered EMR, Fig. 8 presents a surface SEM micrograph where the bottom surface without LAC and the top one with the LAC dispersed can be observed. In this case, there is a low interaction between the solvent and the LAC particles, and therefore, after their immobilization over the surface, they preserve the initial shape, as can be seen in the micrographs.

Concerning to the mono-layered EMR, Fig. 9 shows the cross-section SEM micrograph of the four types of EMR. It can be seen that as the LAC loading increases, the porous structure becomes closer and the size and number of macro-voids are reduced. The consequences of this effect in terms of flux and cut-off are explained somewhere else in Ref. [13]. The mentioned micrographs were interpreted by IFME® software [10,11] in order to obtain quantitative results of the main morphological parameters (Table 2). Results show that as LAC loading increases, the mean size of the macro-voids decreases, and their position within the membrane as well as their shape changes. The position of the macro-voids has an effect

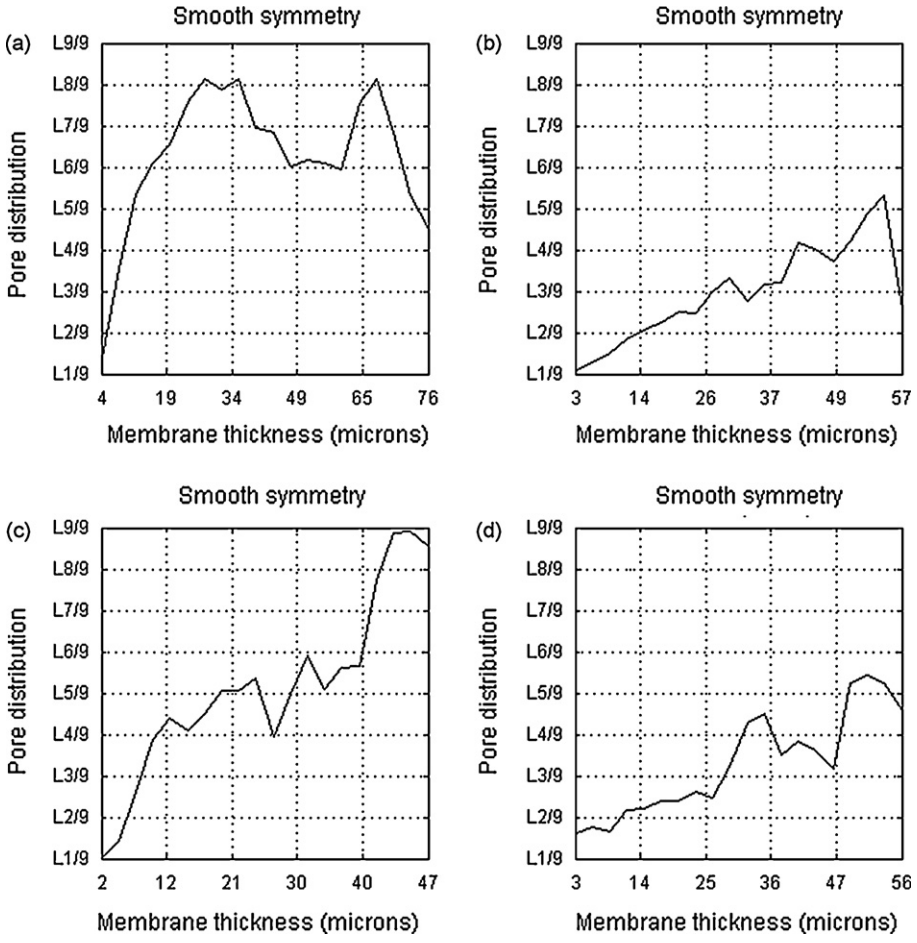

Fig. 10. Symmetry profiles from the SEM cross-section micrographs obtained with IFME®. Different activated carbon–enzyme loadings: (a) 4.00 wt.%, (b) 1.50 wt.%, (c) 0.90 wt.% and (d) 0.35 wt.%.

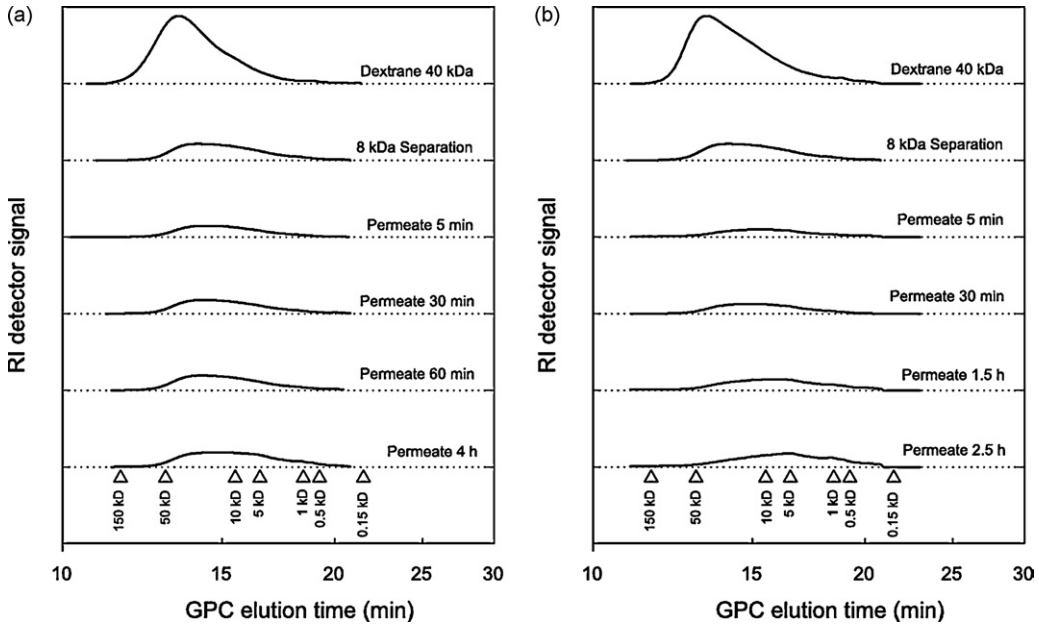

Fig. 11. Chromatographic results of the performance of two types of mono-layered EMR obtained with different LAC loadings: (a) 1.5 wt.% and (b) 4.0 wt.%, including in both the separation results obtained by using alone the 8 kDa membrane.

on the symmetry of the membrane (Fig. 10 shows the symmetry profiles), but it can also be observed that there are no important changes in the micro-porous structure.

3.3.2. Enzymatic membrane reactor performance

The performance of the two types of EMR in terms of type of reaction products and separation showed similar results, in contrast with past experiments [14].

The permeabilities obtained in all cases had an order of magnitude of 10 L/(m^2 h bar) usual values for this type of commercial membranes, which are the limiting ones, since typical permeability of synthesized EMR is 300 L/(m^2 h bar). The consequence of this permeability is a low residence time of the solute inside the EMR, which implies several hours of experiments to achieve reaction products. This means a non-optimum correspondence between the reaction and separation. In previous works [14], in which synthesized membranes with nominal permeability of 0.04 L/(m^2 h bar) were used, minor operation times were needed (better correspondence), although low amount of product was obtained. Because in this type of membrane some hours of experiments are needed, there was no significant difference between the performance of the mono-layered and the two-layered EMR; this was not the case in our previous works [14] due to low time experiments.

Fig. 11 shows the chromatograms corresponding to the performance of two mono-layered EMRs obtained with different loadings of LAC. Also the performance of an 8 kDa membrane without enzyme (only separation) is showed in order to facilitate the understanding of the reaction contribution in the hybrid operation. It can be seen that in both cases the maximum molecular weight of the components which are in the permeate agrees with the MWCO of the membrane (there are chains in the permeate with MW higher than 10 kDa, but with an amount equal or less than 10% from the total amount that exists in the feed), but there are significant differences on the mean molecular size of the products obtained. When using EMR with a LAC loading of 1.5 wt.%, components with a mean molecular weight of 12 kDa were obtained, from 500 Da to 40 kDa, and when using a LAC loading of 4.0 wt.%, components with a mean molecular weigh of 5 kDa were detected in the permeate, from 200 Da to 40 kDa.

4. Conclusions

In this work, the viability in terms of performance of a novel EMR based on polysulfone and LAC with dextranase was demonstrated.

Activated carbon has a good capability to adsorb the dextranase, especially at low pH. Nevertheless, the decrement of the pH also causes an enzyme deactivation, and therefore, an optimum value can be found, which corresponds to a compromise between the two effects.

The porous morphology of a loaded membrane with activated carbon–enzyme (mono-layered) does not change significantly from a non-loaded one. Only when high amounts of LAC are used, macrovoids are reduced in number and size, as well as its location changes. The interaction between the solvent and the activated carbon–enzyme is very high, and thus, the morphology of the particles changes completely. Nevertheless, the resulting EMR preserves the activity. It does not take place with the two-layered EMR, whose morphology of the particles does not change significantly.

In terms of performance, several hours of experiment are needed to achieve acceptable conversions, because of the non-optimized ratio between the separation and reaction processes. For the same reason, there are no significant differences between the mono-layered and the two-layered EMR. Therefore, the mono-layered one is the best one, since it corresponds to the most compact system and can be used in diffusion processes. In all cases, products with a molecular size behind the monomer and up to the initial compound can be obtained by adjusting the LAC loading.

Future work will consider the synthesis of a thin layer over the obtained EMR in order to give it the desired molecular weight cut-off and also to limit the permeability of the membrane. The objective is to let a residence time inside the membrane to achieve the desired reaction conversion.

Acknowledgements

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