



Development of polymeric hollow fiber membranes containing catalytic metal nanoparticles

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ABSTRACT

Metal nanoparticles (MNPs) have unique physico-chemical properties advantageous for catalytic applications which differ from bulk material. However, the main drawback of MNPs is their insufficient stability due to a high trend for aggregation. To cope with this inconvenience, the stabilization of MNPs in polymeric matrices has been tested. This procedure is a promising strategy to maintain catalytic properties.

The aim of this work is the synthesis of polymer-stabilized MNPs inside functionalized polymeric membranes in order to build catalytic membrane reactors. First, the polymeric support must have functional groups capable to retain nanoparticle precursors (i.e. sulfonic), then, nanoparticles can grow inside the polymeric matrix by chemical reduction of metal ions.

Two different strategies have been used in this work. Firstly, polyethersulfone microfiltration hollow fibers have been modified by applying polyelectrolyte multilayers. Secondly, polysulfone ultrafiltration membranes were modified by UV-photografting using sodium p-styrene sulfonate as a vinyl monomer. The catalytic performance of developed hollow fibers has been evaluated by using the reduction of nitrophenol to aminophenol by sodium borohydride. Hollow fiber modules with Pd MNPs have been tested in dead-end and cross-flow filtration. Complete nitrophenol degradation is possible depending on operation parameters such as applied pressure and permeate flux.

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1. Introduction

The rejection of synthetic chemicals by man during decades has led to water pollution. Some of these polluting molecules with low molecular weight (pesticides, endocrine disruptor, antibiotics, ...) are hardly removed by the conventional water treatment processes [1,2]. Either the oxidation or the reduction of these chemicals by means of soft catalytic reactions might allow the treatment of some polluted water if the derived compounds are more easily removable. Furthermore, the combination of catalysis and membrane processes may change and separate pollutants through a single step [3].

Metal nanoparticles have unique physical and chemical properties which differ from bulk metal and isolated atoms [4–7]. Catalysis provides a natural application for nanoparticles because their large surface area-to-volume ratio allows effective utilization of expen-

sive metals such as Platinum Group Metals [8]. Without a suitable support, however, metal particles aggregate, reducing their effective surface area and increasing the average particle size which is the key parameter that controls many of the special properties of nanomaterials [9–11]. To overcome this problem, catalytic nanoparticles have been immobilized on solid supports, e.g., carbon, metal oxides, and zeolites, or stabilized by capping ligands that range from small organic molecules to large polymers [4]. From the above strategies, encapsulation by polymers seems advantageous because in addition to stabilizing and protecting the particles, polymers offer unique possibilities for modifying both the environment around catalytic sites and the access to these sites [12]. Hence, the protective polymer not only influences particle size and morphology but can also have a tremendous influence on catalytic activity and/or selectivity. Thus, including nanoparticles inside polymeric membrane would yield to a useful material for process intensification [3,13,14].

Catalytic polymeric membranes reactor are promising devices for their aptitude to separate the reagents and the products [13,15].

Among the different existing membrane configurations, hollow fibers (tubular membranes of a few millimeters in diameter, with micrometric walls) present the main advantage of having a very

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high-volume area, which allows the manufacture of modules with a large filter surface but with a reduced volume [16]. Hollow fibers properties can be tailored by surface modification which can be carried out through different techniques such as photochemical modification (photografting), modification by plasma, or coated with polymers or polyelectrolyte [17,18].

For instance, the UV photografting [19–21] technique, based on free radical polymerisation initiated from the membrane, permits to obtain various types of grafted polymeric chains. This kind of grafting is very stable due to the covalent bond existing between the grafted polymer and the membrane and it can be very useful for adding chemical functionality at the surface of the membrane. This method was initially used for decreasing membrane molecular weight cut-off by adding charged sites using charged monomers such as acrylic acid (AA) or styrene sulfonate (SS) [18]. As a result, the filtration properties of the membrane were enhanced.

Besides, another surface modification involves sequential deposition of polyelectrolyte multilayers (PEMs), originally described by Decher [22]. These multilayers are prepared by sequential deposition (layer-by-layer deposition) of low molecular weight polymers with ionic charges (e.g. sulphonic groups, amine groups...) allowing the presence of either cationic or anionic sites on the external surface of the membrane or in the inside pores [22–24]. The layers formed by polyelectrolytes of opposite charge are attracted to each other by electrostatic interactions, thus creating dense layers. At first, PEMs were used for the modification of membranes and their application in improved filtration processes, filtered solutes interacting differently with the filtering surface as a function of its electric charge [25].

In the present work, we have loaded the charged groups on the membrane with metal ions and subsequently reduce these ions to obtain metal nanoparticles (MNPs) by inter-matrix synthesis technique [5,11,26]. This method for preparing nanoparticles has already been successfully tested for the development of new electrochemical sensors [27,28]. Therefore, using polymer grafting or polyelectrolyte deposition, highly active catalytic nanoparticles can be included inside hollow fiber membranes to obtain a catalytic membrane reactor [12,29,30]. Characterization of the catalytic effect of the fibers was performed using a reaction model widely used in the evaluation of new catalysts for reactions in aqueous phase, the reduction of p-nitrophenol in presence of sodium borohydride and metallic catalyst [23].

2. Experimental

2.1. Photografting set-up

A complete photografting set-up was described in a previous article [20]. Ultrafiltration polysulfone hollow fibers (PS-UF-HF) provided by Polymem SA (Fourquevaux, France) were initially wet by water, dipped in an aqueous monomer solution, and degassed using N₂. N,N'-methylene-bis-acrylamide (crosslinker), sodium p-styrene sulfonate, and 4-hydroxybenzophenone (photoinitiator) were purchased from Aldrich and used as received without further purification.

The fiber was passed through two UV polychromatic lamps with closed elliptical reflectors (model FOZFR 250, $\lambda > 295$ nm, $I_0 = 338$ mW cm⁻² for UVB, Hoenle UV France, Lyon, France). The operating rate can be adjusted between 5 and 20 m min⁻¹. After irradiation, hollow fibers were carefully washed with reverse osmosis treated water.

As a consequence of this procedure, the chemical modification only occurs on the hollow fiber outer surface (outside modified PS-UF-HF).

2.2. Layer-by-layer adsorption of polyelectrolyte

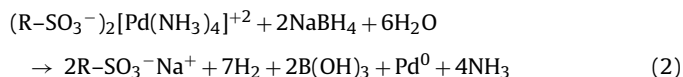
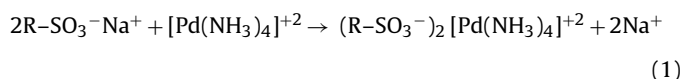
Polyethersulfone microfiltration hollow fibers (PES-MF-HF) were purchased from MEMBRANA GmbH, Germany (MicroPES TF10) and were modified by the polyelectrolyte multilayer technique, as described previously [22].

A first layer of polyanion (polystyrene sulfonate, PSS) was deposited by submerging the PES-MF-HF into an appropriate solution (PSS 20 mM and NaCl 0.5 M). The linking proceeds by a π - π interaction due to aromatic rings. A second layer of polycation (polyallylamine, PAH 20 mM and NaCl 0.5 M) was deposited after rinsing. In this case, hollow fibers are just modified on the surface because the polyelectrolytes cannot diffuse to the fiber interior (outside modified PES-MF-HF).

Alternatively, the inner part of the fiber can also be modified by pumping the polyelectrolyte through the membrane (inside/outside modified PES-MS-HF).

2.3. Metal loading

The synthesis of MNPs in the grafted polymeric layer of the membrane was carried out *in situ* by a two-step procedure [28]. First, fibers were dipped in a [Pd(NH₃)₄]⁺² 0.01 M solution what yields to ion loading in the membrane surface by an ion-exchange reaction (Eq. (1)). Secondly, metal ions load on fibers undergo a reduction with 0.1 M aqueous NaBH₄ solution (Eq. (2)). It is noteworthy that this modification was done directly on the fibers which were already in filtration modules. Afterwards, fibers were rinsed with pure water.



Determination of metal concentrations in aqueous solutions was carried out either by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Iris Intrepid II XSP spectrometer (Thermo Electron Co.) or by ICP mass spectrometry (ICP-MS) using a ThermoElemental ICP-MS, model PQExcell. In all cases, average uncertainty was <2%.

Fibers were also modified by deposition of gold nanoparticles prepared *ex situ* using the citrate method, in which sodium citrate serves as both reducing agent and stabilizer [31].

2.4. Test filtration

Modified PES-MS-HF were tested in a dead-end filtration set-up using a single-fiber module whereas modified PS-UF-HF were tested in a tangential filtration set-up using a laboratory made module of 5 fibers. Fig. 1 shows the module conception for both filtration procedures. In dead-end filtration set-up, the solution was passed through the membrane at constant pressure and permeated through the membrane. In this case, the solutes which are unable to pass through the membrane increase its concentration in solution which may encourage the membrane fouling. In the case of tangential filtration, passage through the membrane is in the perpendicular direction to the flow of solution to be filtered. This will get two effluents: permeate (which crosses the membrane) and retentate (which is retained). The solution tank is driven by a pump and passes through the membrane module (permeate) while the other can be recycled back to the tank. This type of configuration is more interesting to reduce the fouling but needs more energy.

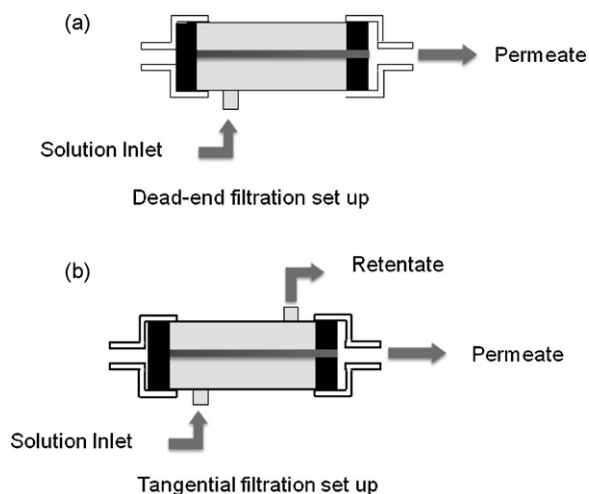


Fig. 1. Experimental filtration set-up.

2.5. Catalytic reduction of 4-nitrophenol

The catalytic performance of modified hollow fibers has been evaluated by a model reaction, reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride (Fig. 2).

This reaction is quite simple to follow by UV spectroscopy as the solution of 4-nitrophenol is yellow and has a maximum absorption between 330 and 400 nm (depending on the pH). The decrease in the intensity of this peak is directly connected with the transformation of 4-nitrophenol compound which absorbs below 300 nm and therefore is colourless. Furthermore, this reaction does not take place in the absence of catalyst [23,32–35].

3. Results

3.1. MNPs content in the membrane

The white hollow fibers turned grey after Pd reduction or pink after Au reduction, which was a good qualitative test of nanoparticle formation. ICP-AES and ICP-MS confirmed that the metal loading was about $1.87 \mu\text{g Pd}/\text{cm}^2$ for the modified outside PS-UF-HF membranes, $0.82 \mu\text{g}/\text{cm}^2$ for the outside modified PES-MF-HF

and $155 \mu\text{g Au}/\text{cm}^2$ for the inside/outside modified PES-MF-HF (surface area refers to the surface of the external hollow fiber skin). These data are in agreement with expected results since the modification of membrane inner part with polyelectrolytes allows a higher incorporation of metal nanoparticles inside the membrane compared with the surface modification.

3.2. Catalytic reduction of 4-nitrophenol

UV spectra of solutions of pure 4-nitrophenol, with or without reducing agent and with or without bare fiber did not significantly change after 24 h at room temperature (Fig. 3). On the contrary, the analysis of the UV spectra of a nitrophenol solution with reducing agent and a fiber with nanoparticles inside (catalytic surface = 1.6 cm^2) demonstrate the catalytic activity of our system because the 4-nitrophenol UV absorption peak clearly disappeared after 24 h and we obtained a spectra similar to a solution of 4-aminophenol. Thus, the catalytic activity of modified fibers containing nanoparticles was proved implying that catalytic sites are accessible to the reagents.

3.3. Catalytic activity test of PSS/PAH/Au inside coated fiber in frontal filtration mode

Since, microfiltration membranes allow higher fluxes than ultrafiltration membranes, modified PES-MS-HF were tested in dead-end filtration configuration. In this case, fibers were coated using the LBL technique and nanoparticles were deposited both on the outside and the inside of the fiber. Results of 4-nitrophenol degradation and specific flux over a 2-h reaction time are plotted respectively in Figs. 4 and 5. As it can be seen, a constant yield of more than 95% of 4-nitrophenol was obtained during the first hour but the effectivity decreased gradually to about 80% until the end of the experiment. Fig. 5 shows the evolution of the specific flux during the experiment and, although the trend is not clear, it looks like the flux slightly increased with the time.

3.4. Catalytic activity test of PSS/PAH/Pd outside coated fiber in dead-end filtration mode.

Outside modified PES-MF-HF containing *in situ* prepared Pd nanoparticles were also tested in a dead-end filtration set-up using

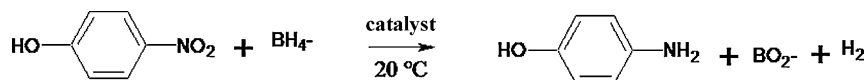


Fig. 2. Catalytic reduction of 4-nitrophenol.

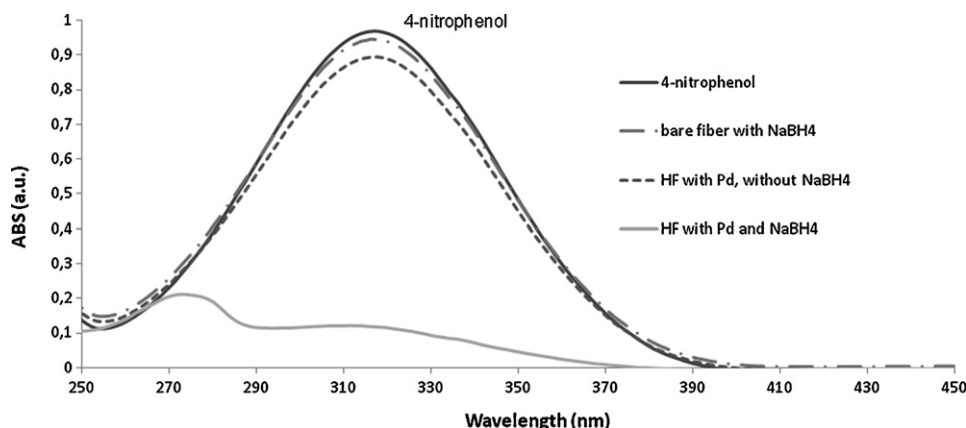


Fig. 3. UV monitoring of nitrophenol reduction in presence of PS-UF-HF/Pd, [4-nitrophenol] = 0.2 mM, [NaBH₄] = 100 mM, 24 h.

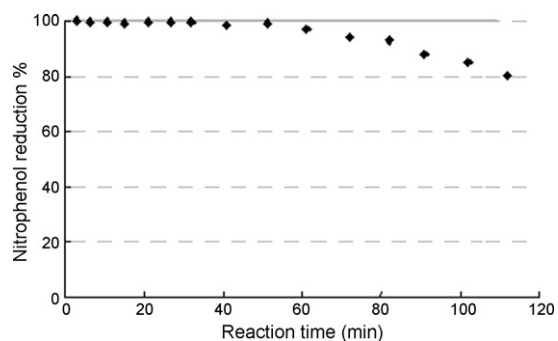


Fig. 4. Conversion of nitrophenol vs. reaction time in dead-end filtration using PSS/PAH/Au inside modified fiber, [4-nitrophenol] = 0.5 mM, [NaBH₄] = 50 mM.

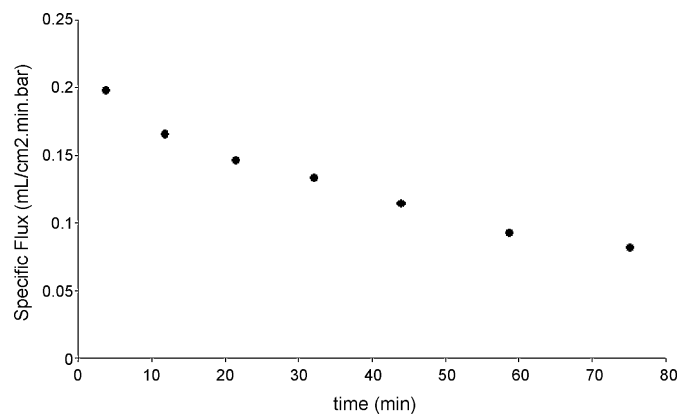


Fig. 7. Evolution of the specific flux with the time in dead-end filtration using an outside modified PES-MF-HF, [4-nitrophenol] = 0.5 mM, [NaBH₄] = 50 mM.

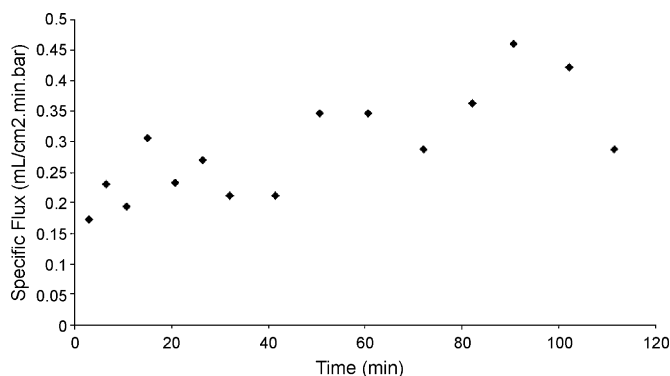


Fig. 5. Specific flux vs. reaction time of nitrophenol in dead-end filtration using PSS/PAH/Au inside modified fiber, [4-nitrophenol] = 0.5 mM, [NaBH₄] = 50 mM.

a single-fiber module. In this case, it is possible to reduce the initial concentration of 4-nitrophenol to less than 5% (95% efficiency) by a single passage through the catalytic membrane (Fig. 6). However, in order to achieve this value it was necessary to wait for about 1 h and catalytic filtration before this time was less successful. By the way, we observed that the catalytic efficiency increased with filtration time when flux decreased (Fig. 7).

3.5. Catalytic activity test of PSS/Pd outside coated PS-UF-HF in tangential filtration mode

In the tangential flow set-up, it was possible to reach a conversion of up to 90% in the permeate solution compared with the

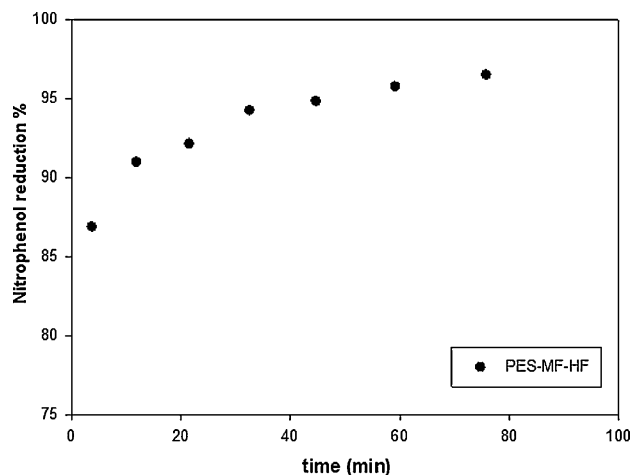


Fig. 6. Evolution of the reduction efficiency with the time in dead-end filtration using a outside modified PES-MF-HF, [4-nitrophenol] = 0.5 mM, [NaBH₄] = 50 mM.

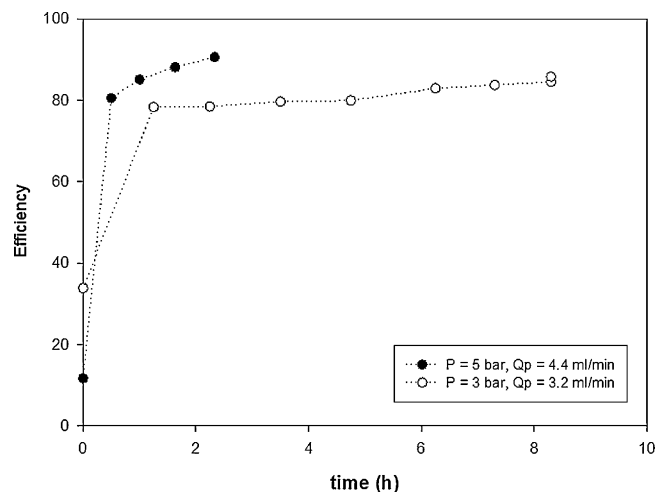


Fig. 8. Evolution of the reduction efficiency with the time in tangential filtration using a PS-UF-HF/Pd [4-nitrophenol] = 0.5 mM, [NaBH₄] = 50 mM.

initial concentration in the tank, demonstrating the catalytic activity of these membranes in an operation mode closer to a real water treatment (Fig. 8). The permeate flow rate in this case was quite low (e.g. 0.7 mmol⁻¹ min⁻¹ m⁻² at 5 bar) and it was found to be constant after 1 h of operation, this is why a plateau was observed for every applied pressure.

4. Discussion

The observed reduction rates in the tangential or dead-end set-up demonstrate the catalytic properties of the synthesized membranes. These rates are quite important given the relatively low metal loading of the membrane. These results can be explained by the important catalytic surface due to the absence of aggregation between nanoparticles stabilised by the polymeric matrix and the easy access of nitrophenol to catalytic nanoparticles located at the surface of the membrane which occur here by convection instead of diffusion.

First experiments were carried out with the PES-MF-HF coated inside and outside because we expected high conversion due to the high exchange surface. Although the high conversion obtained (100%) demonstrated the good efficiency of this set-up, the fast decrease observed was not expected. We account for a possible poisoning of the catalyst due to the by-products of nitrophenol reduction reaction which can interfere with the membrane surface. Indeed, although this reaction has been often used as a model for

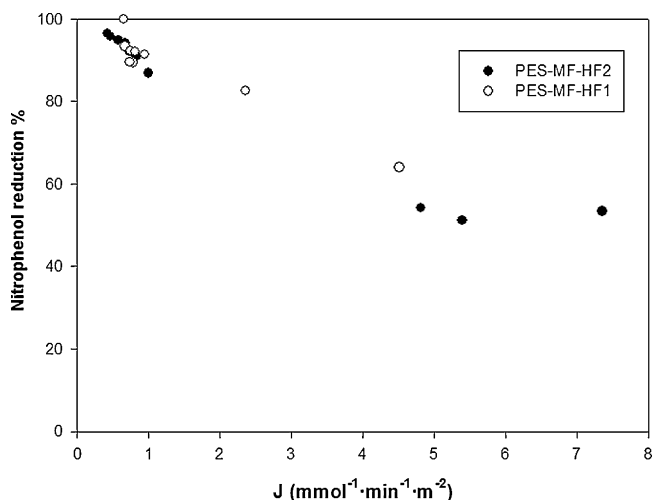
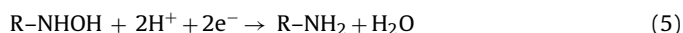
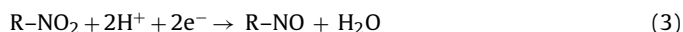
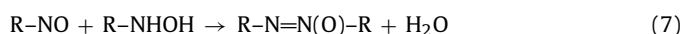


Fig. 9. Evolution of the reduction efficiency with the permeate flux in dead-end filtration using a PES-MF-HF/Pd [4-nitrophenol] = 0.5 mM, [NaBH₄] = 50 mM.

catalytic test due to its simplicity [23,29], the reaction is actually the result of a series of steps [37] (Eqs. (3)–(5)):



The reaction intermediates can interact among themselves leading to unwanted polyaromatic species (Eqs. (6) and (7)) which might have an affinity to polysulfone or polyethersulfone membranes, yielding to an undesirable absorption.



In this scenario, the higher the conversion, the higher the catalyst poisoning. For this reason, we chose to test a PES-MF-HF only modified in the surface and so less charged in catalyst. The obtained conversion is not so high as in the case of the inside/outside modified PES-MF-HF but superior to 80%. The evolution of this conversion is totally different as we observed an increase of the conversion with the time and a decrease of the flux at the same time. The decrease of the flux with time suggests a pore blockage. This blockage can be due to hydrogen produced during the reduction because hydrogen bubbles from NaBH₄ evolved onto the catalyst surface can possibly block pore and, as a consequence, dry some part of the membrane. Thus, aqueous solutions could not penetrate into the pore due to the high Laplace pressure. Some aging or compaction can also explain this observation.

On the other hand, the fact that a decrease of the conversion was not observed suggested that there was not (or only a minor) poisoning of catalyst. If by-products were synthesized, they were not accumulated at the surface (where the catalyst is located) but inside the membrane, participating eventually to the membrane fouling. In fact, it was interesting to compare the conversion evolution in relation to the observed flux. Conversion increased while observed flux decreased (Fig. 9). We explain this result by considering the residence time of the solution in the catalysis layer at the surface of the membrane: when the catalyst accessibility is the limiting step, lower fluxes mean higher residence time what corresponds to a higher conversion. Bearing this in mind, one can suggest that our membrane reactor acts as a perfectly agitated reactor where diffusion is negligible compared to convection (here, due to the applied pressure). So, in our experimental conditions, we can

assume that the reaction rate is low in front of the value of the flux of reactants.

Finally, tangential filtration mode was expected to prevent fouling and to lead to a more stable process but obtained results did not show a clear tendency. As observed in Fig. 8, the efficiency of the process increased with the applied pressure and so did the permeate flux. Contrary to the dead-end filtration configuration, here better efficiencies were obtained for higher fluxes. Moreover, conversion seemed to be stable during the time but the production of hydrogen inside the tank during the experiment (due to the poor stability of NaBH₄ in solution [36,37]) jeopardizes the applicability of this configuration in a real water treatment application. Gas-liquid contactors configuration could be a better mode to work with this kind of modified fibers.

5. Conclusions

Hollow fibers modules have been tested in both dead-end and cross-flow filtration setups, and the experimental results show that complete 4-nitrophenol degradation is possible by optimizing operation parameters such as applied pressure and permeate flux. This reaction was selected just to demonstrate the potentiality of these new modified membranes.

Dead-end filtration appears to be more efficient than tangential filtration mode due to the easiest reaction and filtration control conditions. However, system configuration needs to be improved since it is necessary to purge H₂ bubbles formed inside the module which can displace water avoiding a good contact between the membrane and the solution. Almost total conversion is promising for future applications, but flux must be increased.

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