

# Protein adsorption in pores of ultrafiltration membranes

P. Dutournié, S.M. Miron, A. Ponche

Institut de Sciences des Matériaux de Mulhouse IS2M - UMR CNRS 7361, 3 bis rue A. Werner, Université de Haute Alsace, Mulhouse, 68098, France

Keywords: adsorption, pore size, filtration performances, efficiency  
Presenting author email: [patrick.dutournie@uha.fr](mailto:patrick.dutournie@uha.fr)

Food and pharmaceutical industries use filtration processes to concentrate or separate molecules from adhesive and viscous solutions. Solutions containing proteins and other bio-molecules are especially known to decrease the membrane performances and to assist a biofilm development. In this case, the process should be stopped and the filtration-plant cleaned by chemical treatments to recover its initial performances. The process efficiency will significantly decrease and can jeopardize the economic and environmental viability of the operation.

In this work, successive filtration tests of protein (Lysozyme) or amino-acids (L-Tyrosine, L-Phenylalanine) water solutions were performed to investigate the modification of the membrane performances. For this, between each filtration test of protein solution, pure water and neutral solute filtrations tests are performed to follow the molecule selectivity and the membrane hydraulic performances.

From the rejection rate of the neutral solute (vitamin B12) filtration performed between the tests of Lysozyme, an average pore radius is estimated by using equation 1, which is the analytical solution of the Nernst-Planck equation for neutral solutes (Bowen, 2002).

$$R = 1 - \frac{\phi K_c}{1 - (1 - \phi K_c) \exp\left(-\frac{K_c r_p^2 \Delta P}{8 \mu K_d D_\infty}\right)} \quad \text{with} \quad \phi = \left(1 - \frac{r_s}{r_p}\right)^2 \quad \text{eq.1}$$

Figure 1 shows a decrease of the mean pore radius and of the membrane hydraulic permeability, suggesting a probable protein adsorption in the larger pores of the membrane.

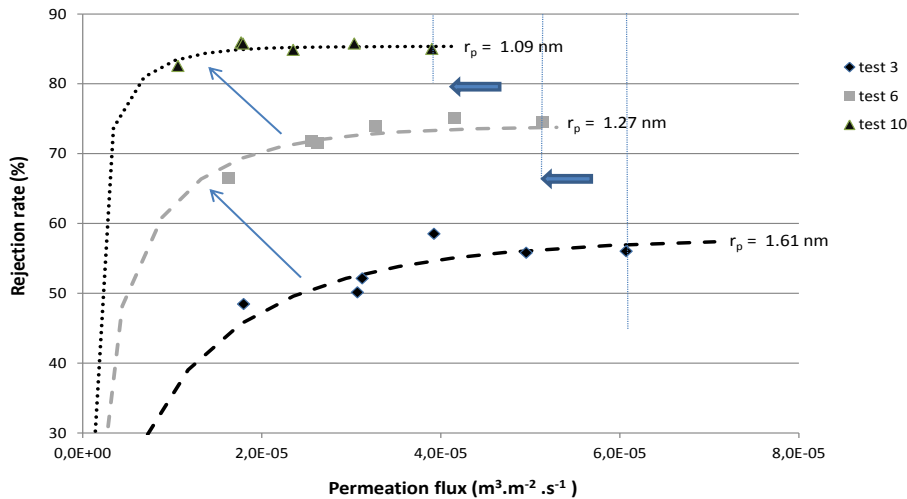


Figure 1: Rejection rate of Vitamin B12-water solution and corresponding permeation flux.

Indeed, the decrease of the hydraulic performances and the increase of neutral solute selectivity suggest that the smaller pores are not changed while the larger ones are progressively decreasing in size. The same trend is observed for the successive filtration of protein or amino-acids (Miron, 2018) and notwithstanding the difference in size of the molecules ( Lysozyme; 14.3 kDa, Stokes radius = 1.9 nm, L-Phenylalanine 165.2 Da, Stokes radius = 0.37 nm and L-Tyrosine; 181,2 Da, Stokes radius = 0.38 nm).

To illustrate this behaviour, filtration tests were performed with a new membrane or after integral regeneration (hydraulic and selectivity performances are the same as after the conditioning step). The maximal rejection rates of Lysozyme obtained during the first filtration test is significantly different if an amino-acid was previously filtrated, i.e. 65% just after the conditioning step, 93% after L-phenylalanine and 96 % after L-Tyrosine filtration. In all cases, a second filtration test of Lysozyme leads to a quasi-total rejection of the filtrated protein. These results show that the molecule (amino-acid or protein) is rapidly adsorbed in the pore, limiting the flow rate and changing the apparent size of pores.

To investigate adsorption phenomena occurring in the pore, successive filtration tests of Lysozyme were performed with different membranes. The Lysozyme is completely rejected after two or three successive tests, but the hydraulic membrane permeability has been gradually decreasing as filtration tests were performed.

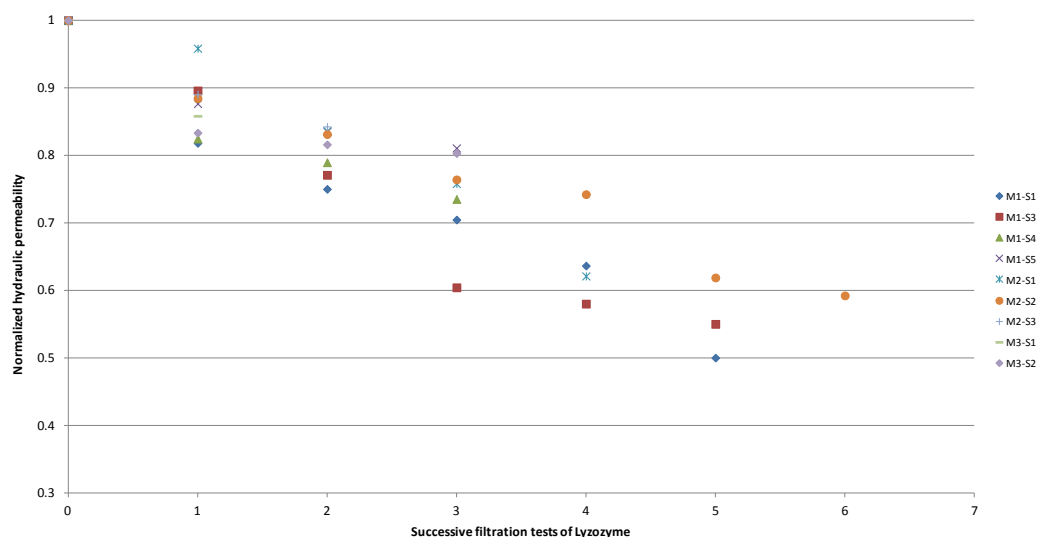


Figure 2: Evolution of hydraulic permeability (normalized to initial permeability) as Lysozyme filtration tests performed for different TiO<sub>2</sub> membranes (M1 to M3) and series (S)

The results show a linear decrease of the hydraulic permeability for all the membranes with the same slope as filtration tests are performed. This indicates that the adsorption kinetic is the same whatever the membrane studied and his history. These results suggest that the interactions between Lysozyme and the surface are significant (leading to a three-fold decrease of permeation flow rate after ) but not very quick. Indeed, each filtration test lasts some hours and is followed by a pure water rinsing and filtration. This behaviour could be explained by an adsorption of Lysozyme at the pore surface (fast phenomenon) followed by a molecule rearrangement in the pore (limiting phenomenon).

W.R. Bowen *et al.* Linearized transport model for nanofiltration development and assessment, *AIChE J* 48 (2002) 760.

S.M. Miron *et al.* Filtration of protein-based solutions with ceramic UF membrane. Study of selectivity, adsorption and protein denaturation, *C. R. Chimie*, 2018.