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Stabilisation of the water permeability of mineral ultrafiltration membranes: An empirical modelling of surface and pore hydration

Stabilisation de la perméabilité hydraulique de membranes minérales d'ultrafiltration : modélisation empirique de l'hydratation des pores et de la surface

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A B S T R A C T

This work focuses on the study of the hydration phenomenon operating in Na–mordenite membranes during the conditioning step (stabilisation of filtration properties). First, experimental (filtration of pure water) tests are carried out immediately after putting the membrane in its casing and until the stabilization of the membrane permeation flux. The evolution of the hydraulic permeability shows that there are two separate steps during the conditioning of the membrane. A numerical approximation of the hydraulic permeability during the conditioning step was carried out. The first part of the equation expresses a fast decrease in the membrane's permeability during the beginning of the conditioning step (several hours). This behaviour is attributed to a surface hydration of the membrane and also to a modification of the crystalline framework. The second one is a slower phenomenon that takes place until the end of the conditioning step. It is attributed to the (intra-crystalline) hydration of micropores.

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R É S U M É

Ce travail porte sur l'étude de la phase de conditionnement de membranes céramiques (mordénite sodique ou TiO$_2$) et plus particulièrement sur le phénomène d'hydratation de la couche filtrante lors de sa mise en eau (stabilisation des propriétés de filtration). Le conditionnement des membranes est caractérisé par le suivi de leur perméabilité hydraulique lors de flux à l'eau, réalisés dès leur introduction dans le pilote d'UF/NF. L'évolution de la perméabilité hydraulique des membranes étudiées comporte deux phases bien distinctes : la première consiste en une baisse rapide de la perméabilité

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hydraulique et est attribuée à l'hydratation de la surface intercristalline de la couche active de la membrane, la seconde, bien plus lente, est attribuée à la phase d'hydratation de la surface intra-cristalline de la couche filtrante. Une approche numérique a permis de mettre en évidence qu'il existe une corrélation entre la phase d'hydratation intra-cristalline et le volume microporeux de la couche active des membranes étudiées.

1. Introduction

Mordenite zeolites are often presented as catalytic materials [1] and they are also used as membrane layers for pervaporation or fuel cell applications [2]. The reason why mordenite is also used as a membrane is because zeolites present some interesting characteristics and properties, as for example uniform and molecular-sized pores, surface acidity, inter-crystalline porosity, hydrophobicity. Mordenite is a zeolite that has a low Si/Al ratio, with an ideal composition of the unit cell corresponding to $Na_8[Al_8Si_{40}O_{96}]\cdot nH_2O$. Synthetic mordenite is characterized by a Si/Al ratio ranging from 5 to 10, which directly depends on the chemical composition of the reagents mixture. Mordenite was synthesised for the first time by Barrer et al. [3] in 1948, and it was used as a membrane active layer by Suzuki et al. [4] in 1990. Due to its composition, mordenite presents a hydrophilic behaviour and its catalytic properties directly depend on the Si/Al ratio related to Brønsted and Lewis acidities [5–7]. The Na–mordenite system presents uniform and molecular-sized pores and a surface negatively charged, which both induce a high retention of organic molecules and a particular selectivity for the filtration of salts [8]. In a previous work [9], we showed that Na–mordenite membranes could also be used for the separation of halide salt mixtures. These results were obtained with a Na–mordenite membrane synthesized by sol–gel methodology and impregnated onto a tubular ceramic alumina support. The active layer of the membrane presented a double porosity: mesopores (corresponding to the inter-crystallinity of the mordenite crystals) and nanopores (corresponding to the intra-crystalline porosity of the mordenite framework). We observed that the use of these membranes required a previous step, corresponding to the stabilization of the membrane permeability, obtained by the filtration of pure water at a constant transmembrane pressure and a constant temperature. As shown by Weber et al. with different ceramic membranes [10], the stabilization of membrane permeabilities, corresponding to the conditioning phase, depends on the filtration active layer and/or the support of the membrane.

The hydration phenomenon of mineral porous surfaces and more particularly those of mordenite is not trivial, and it has been little described in the literature. Especially, Demuth et al. [11] presented that the water molecule could be adsorbed in two different ways on an acid mordenite surface: the water molecule may be physisorbed at the Brønsted acid sites of the zeolite, and it can be also adsorbed after the formation of a hydroxonium cation (H_3O^+). Ab initio investigations showed that the physisorbed form is stabilized by the existence of two hydrogen bonds, while the adsorption of the hydroxonium cation does not lead to a stable structure [11–13]. It may correspond more to a transition state than to a steady state of the water molecule on the mordenite surface. Maurin et al. [12] studied the hydration phenomenon in a Na^+–mordenite zeolite by using the dielectric relaxation spectroscopy (DRS) methodology coupled with molecular dynamics simulations (MDS). They showed that Na^+ cations were situated half in the 8 T channels (small ones) and half in the 12 T channels (big ones). They simulated different hydration levels of the unit cell, from 1 to 24 water molecules. The results showed that, if the Na^+ cation located in the small channels was not affected by the presence of water, the mobility of the Na^+ cation situated in the main channel increased and that this cation was shifted to another position in the channel. Then, the mobility of this Na^+ cation increased a lot after the introduction of more than two molecules of water, leading to a weak interaction between this cation and the zeolite framework. These results [11,12] indicate that the water molecules may interact both with the zeolite surface and adsorb on different sites, but also with the Na^+ cations present in the channels (cation hydration).

Even if the diffusion rate of a nanoconfined water molecule remains low, it increases in nanopores by the complete destruction of the hydrogen-bonded networks, as presented by Zhu et al. [13]. The presence of Na^+ cations inside the mordenite pores is also important because water molecules may hydrate the Na^+ cations and also be physisorbed on the mordenite surface, as shown previously. In another work, Li et al. [14] showed that the hydraulic permeability of ceramic membranes could be predicted by the Carman–Kozeny equation at the steady state. Their results indicated that the hydraulic permeability is controlled by the pore size, the thickness and the porosity of the membrane. This result indicates that there is a relation between the membrane microstructure and the membrane permeability.

It is essential to note that before performing the filtration tests with the different Na–mordenite membranes, the permeation flux must be stabilized, which means that the membranes must be conditioned with water (surface hydration). This point is very important in order to reach the membrane permeation equilibrium. The phenomena that take part in Na–mordenite membrane surface stabilization are complex because many parameters must be taken into account. Only few works have studied and reported the evolution of the hydraulic permeability of mineral membranes during the stabilization phase (conditioning step) [10,15].

The purpose of this work is to study the hydration phenomena that operate during the conditioning step of