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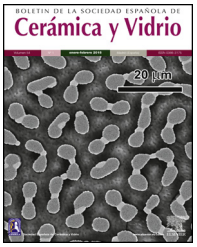

Comparison of porosity assessment techniques for low-cost ceramic membranes

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ABSTRACT

Several characterization methods were applied to low cost ceramic membranes developed for wastewater treatment in membrane bioreactors (MBRs) and/or tertiary treatments. The membranes were prepared by four different procedures (uniaxial pressing and extrusion, both with and without starch addition to generate pores). The pore size of these symmetric ceramic membranes was measured by two different methods: bubble point and intrusion mercury porosimetry. A good agreement between both methods was achieved, confirming the validity of the bubble point method for the measurement of the mean pore size of membranes. Air and water permeations of these ceramic membranes were also studied. The relationship between the permeation of both fluids is consistent with the ratio of viscosities, according to the Hagen–Poiseuille equation.

Comparación de técnicas de medida de la porosidad en membranas cerámicas de bajo coste

Palabras clave:
Membranas
Porosidad
Conformado
Método de punto de burbuja
Porosimetría de intrusión de mercurio

RESUMEN

En el presente trabajo se han caracterizado mediante diferentes métodos membranas cerámicas de bajo coste desarrolladas para tratar aguas residuales en reactores biológicos de membrana (MBR) o mediante tratamientos terciarios. Las membranas se prepararon mediante diferentes procedimientos (prensado uniaxial y extrusión, con o sin adición de almidón como material generador de poros). El tamaño del poro de estas membranas cerámicas simétricas se determinó mediante 2 métodos diferentes: punto de burbuja y porosimetría de intrusión de mercurio. Los resultados obtenidos mediante ambos métodos mostraban concordancia, lo que confirma la validez del método de punto de burbuja para la medida del

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tamaño del poro medio de las membranas. Además, se ha estudiado la permeabilidad al aire y agua de estas membranas cerámicas: la relación entre la permeabilidad de ambos fluidos es consistente con el ratio de viscosidades, de acuerdo con la ecuación de Hagen-Poiseuille.

Introduction

Membrane bioreactors (MBR) combine a biological degradation process with the direct separation of activated sludge and liquid-solid by filtration membranes [1]. In addition, MBRs have important advantages such as space reduction relative to conventional activated sludge process, which leads to a decrease in their environmental impact, the capability of operating with higher concentrations of suspended solids, and the production of better quality effluent. However, one of the main drawbacks of MBR is membrane fouling. Despite the high cost of commonly used ceramic membranes (made of alumina, zirconia or titania), it is known that they are more hydrophilic than polymeric membranes, which means that ceramic membranes have a lower membrane fouling rate. Ceramic membranes are also more chemically, mechanically and thermally resistant. Other characteristics that influence membrane fouling are pore size and configuration (tubular, flat or hollow fiber) [2,3]. Currently, polymeric hollow fiber membranes are the most widely used in the industry because the manufacturing cost of ceramic membranes based on high purity oxides is higher than that of their polymeric counterparts. However, hollow fiber membranes are more likely to develop higher fouling rates and consequently give rise to higher maintenance costs [1]. As an alternative, low cost ceramic membranes whose composition is mainly based on clays and organic pore formers are cheaper, similar to the cost of polymeric membranes. The preparation of low cost ceramic membranes was described in a previous paper [4].

This work attempts to characterize two key parameters of low cost ceramic membranes: mean pore diameter and permeability. Several techniques can be used to measure the pore size distribution and average pore size (d_{50}) of a membrane: nitrogen adsorption, intrusion mercury porosimetry, permporometry, the bubble point method, solute resistance tests and electronic microscopy (SEM, TEM). In this work, we will compare the results obtained by intrusion mercury porosimetry and the bubble point method. Both are simple and rapid techniques which have been widely used to evaluate the pore size of ceramic materials. They are standardized, repeatable and reproducible test methods.

The goal of this study is to draw a comparison between the average pore size results obtained using bubble point and intrusion mercury porosimetry characterization techniques applied to a set of low cost symmetrical ceramic membranes. As mercury manipulation has been restricted, this comparison could open up an alternative to intrusion mercury porosimetry. This work also addresses the relationship between the water and air permeabilities of the membranes.

Table 1 – Compositional range used to obtain ceramic membranes with very different porosity characteristics (total pore volume and size distribution).

Raw material	Compositional range (wt%)
Clay	40–85
Chamotte	0–20
Feldspar	0–15
Calcium carbonate	7–20
Starch (different sources)	0–20

Experimental method

Membrane preparation

Low cost ceramic membranes were prepared from raw materials normally used in the ceramic tile sector (clays, chamotte, feldspar and calcium carbonate) and organic pore formers (different starches provided by Roquette Laisa España, S.A.). The components were mixed in suitable proportions so that they could be easily processed by uniaxial dry pressing or extrusion. To obtain membranes with a broad range of porosity and pore sizes, the forming methods were combined with the addition of different proportions of starch to some compositions. Table 1 shows the compositional range used to obtain the ceramic membranes, where the proportion of clay, chamotte, feldspar, calcite and starch have been modified. Four different groups of membranes were prepared in this way, referred to as P, PS, E and ES (Table 2).

The process for producing the pressed membranes started with dry homogenization (manually and by means of an automatic mixer) of the different raw materials. The resulting compositions were moistened to 5.5 kg H_2O/100 kg dry solid. Cylindrical test specimens, 0.7 cm thick and 5 cm in diameter, were formed from this powder by uniaxial dry pressing using an automatic laboratory press (Nannetti SpA, Italy). The test samples were oven-dried at 110 °C to a constant weight.

Each batch of raw materials for the extruded membranes was kneaded to a consistency of 5 kg, determined by penetrometry (using a cylinder with 1.5 cm diameter) (Analogic penetrometer Geotester 0-6 kg, Novatest S.r.l., Italy) [5], and allowed to stand for 24 h to achieve uniform moisture in the mass. The water content of the compositions varies between 20 and 32 wt%. Test pieces 1 cm thick and 5 cm in diameter were shaped from an extruded sheet, using a laboratory auger with a de-airing chamber (Model 050 C, Talleres Felipe Verdés, S.A., Spain). The test samples were weighed and afterwards dried at room temperature for 24 h, and oven-dried at 110 °C to a constant weight.

After drying, all the samples were weighed and the bulk density was measured by the mercury immersion method [6].

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