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Research paper

Thermal treatment of clay-based ceramic membranes for microfiltration of *Acutodesmus obliquus*

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ABSTRACT

Tubular ceramic microfiltration membranes were prepared by extruding thermally treated clay (TC) and raw clay to form a porous tubular membrane with the addition of cationic manioc starch and toasted manioc flour. The influence of an applied thermal treatment on the proprieties of the clay and the microfiltration membranes was characterized by measuring the particle size distribution, pore size distribution, and mechanical strength and by conducting X-ray fluorescence analysis, X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, and differential scanning calorimetry. The membranes were used for microfiltration of *Acutodesmus obliquus* microalgae with various applied pressures in the range of 2×10^4–1×10^5 Pa with a volumetric flow rate of 6.94×10^{-5} $m^3 \cdot s^{-1}$ at a temperature of 10 ± 5 °C. The efficiency of each of the ceramic membranes was evaluated in terms of the permeate flux for water and microalgae and the microalga retention. The addition of TC to the membrane resulted in an optimal microalga permeate flux of 3.24×10^{-2} $kg \cdot m^{-2} \cdot s^{-1}$ and a microalga retention of 98.3% at 4×10^4 Pa and had positive impacts on the other proprieties measured. Overall, these results demonstrate a potential application of TC in ceramic membranes for crossflow microfiltration processes.

1. Introduction

The implementation of clean energy alternatives to reduce the impacts of global warming presents various challenges. The replacement of fossil fuels with renewable energy sources has been proposed as a potential solution to address this issue. Biofuels are the most promising alternatives to fossil fuels because they can be produced from food crops (termed first-generation biofuel), lignocellulosic biomass (second-generation biofuel), and algae (third-generation biofuels) (Nigam and Singh, 2011; Wei et al., 2014).

Microalgae present several unique characteristics that make them useful for biofuel production. These traits include high growth rate, high productivity, high oil concentration, and excellent adaptability to different environmental conditions. In particular, microalgae do not require large areas of arable land for cultivation (Chisti, 2008; Mata et al., 2010).

To ensure microalgae viability, recovery and concentration studies are required. The separation of algal biomass is particularly challenging because of the small size ($3–30 \times 10^{-6}$ m) and low density ($0.3–5 \cdot Kg \cdot m^{-3}$) of the algae and due to the large volume of water needed to perform the recovery (Molina Grima et al., 2003; Packer, 2009; Brennan and Owende, 2010; Zhang et al., 2010; Milledge and Heaven, 2013). Low-pressure filtration through membranes has been demonstrated as a promising separation process because the process is easy to conduct, requires low energy input, can provide high filtering efficiency, and does not require the addition of chemical contaminants to the system (Zhang et al., 2010; Zou et al., 2011).

The filtration processes are classified according to the pore size of the membranes used, including macro or conventional filtration ($> 1 \times 10^{-5}$ m), microfiltration (1×10^{-7}–1×10^{-5} m), ultrafiltration (1×10^{-8}–1×10^{-7} m), nanofiltration (1×10^{-9}–1×10^{-8} m), and reverse osmosis ($< 1 \times 10^{-9}$ m) (Crittendem et al., 2002).

Microfiltration is a membrane-based separation process that is most similar to classical filtration. Moreover, microfiltration the most

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appropriate process for retaining materials and suspensions because of the pore size of the membrane used and because it does not require a high pressure as the driving force (the required pressure rarely exceeds 3×10^5 Pa) (Crittendem et al., 2002; Milledge and Heaven, 2013; Gerardo et al., 2014). Microfiltration membranes are recommended for the separation and recovery of microalgae because they are capable of providing greater permeability and better fouling prevention than other membranes (Bilad et al., 2014).

Ceramic membranes have several advantages that enable their use in separation processes: good thermal stability, chemical inertia, high permeability, mechanical strength, long lifetime, and low thermal conductivity. The ceramic membranes used in the recovery processes described above are usually made from valuable synthetic materials such as zirconia, alumina, titania, and silica (Kumar et al., 2015).

Among the approaches to produce porous ceramic membranes, such as the use of various pore-forming agents, replicas, and gel casting, the incorporation of organic and/or inorganic compounds as pore-forming agents is one of the most widely used methods. In this method, the additives decompose during the sintering stage, leaving pores of different shapes and sizes based on the agent used (Chevalier et al., 2008; Yang and Tsai, 2008; Li et al., 2013).

Various studies have used wheat, peas, potato, and maize starch as pore-generating agents to attain satisfactory porosity (Yang and Tsai, 2008; Li et al., 2013; Lorente-Ayza et al., 2015). Studies of organic and/or inorganic materials as pore-generating agents in ceramic bodies have revealed that up to a certain limit, the final porosity of the material varies directly with the amount of the pore-generating agent added.

The development of porous ceramic membranes using low-cost raw materials combined with more efficient production processes such as extrusion can lead to the use of these membranes globally. The extrusion method allows porous ceramic membranes to be manufactured with controlled microstructures characterized by uniform pore sizes and unidirectional orientations, thereby making them applicable to crossflow processes such as microfiltration (Kumar et al., 2015; Lorente-Ayza et al., 2015).

Considering the potential benefits of membrane production from inexpensive raw materials for microalgae separation, this study aimed to develop tubular ceramic membranes by using thermally treated clay (TC) with organic additives such as pore-generating agents. As a result of the bibliographic review, and due to the lack of studies in the literature, the fabricated membranes were applied to crossflow microfiltration for the recovery of *Acutodesmus obliquus*. The efficiency of the membranes was evaluated in terms of the permeate flux and microalgae retention.

2. Materials and methods

2.1. Materials

A commercial faience clay obtained from Cermassas–Pastacer Ltda. (Campo Largo/PR-Brazil) was used to produce the ceramic membranes in this study. This clay was used in two forms: raw clay (NC) and thermally treated clay (TC), which was obtained by exposing the NC to a fixed temperature for a certain time interval with subsequent slow cooling.

To form the pores in the ceramic membrane, commercial cationic manioc starch (CMS) (Superion 300 with a degree of substitution in the range of 0.033–0.036 mol/mol obtained from Grupo Horizonte–Agrícola Horizonte Ltda. PR/Brazil) and toasted manioc flour (MF) were added to the clay mixtures.

2.2. Preparation of the membranes

The commercial clay was dried in an oven for 43,200 s and ground. Afterwards, a portion of the clay was thermally treated to evaluate the behavior of the sample under different conditions. The clay NC and TC samples were each crushed in a bench ball mill (TECNAL) with alumina balls for 14,400 s.

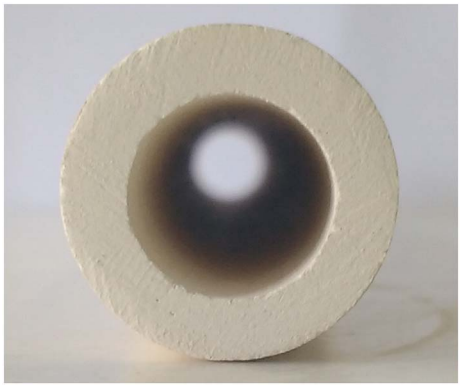

Fig. 1. Membrane dimensions.

Each of the clay samples and MF was passed through a sieve with #60 Tyler mesh (2.5×10^{-4} m). Then, 13.1% CMS and 0.9% MF were mixed with the clay (NC to form NC-1 membranes or TC to form TC-1 membranes) and homogenized with water to form a paste with an initial moisture content of 25%. The membranes were then formed via extrusion. The NC-1 and TC-1 membranes were then sintered at a temperature of 1050 °C for 1800 s.

The obtained membranes had a tubular shape with an outside diameter of 1.88×10^{-2} m, inside diameter of 1.07×10^{-2} m, thickness of 4.05×10^{-3} m, and length of 2.00×10^{-1} m, as shown in Fig. 1.

2.3. Characterization of clays and membranes

The clays (NC and TC) and ceramic membranes (NC-1 and TC-1) were characterized using a variety of techniques as follows:

Granulometric analysis was used to determine the distribution of the particles in the clay samples. The Microtrac S3500 particle size analyzer, which can measure particle sizes from 2.00×10^{-8} m to 2.80×10^{-3} m, was used.

X-ray fluorescence (XRF) tests were performed to quantitatively determine the chemical composition of samples. The tests were conducted using PANalytical equipment (Axios Max) with a rhodium X-ray tube. The loss of ignition of the samples was determined by calcination at 1000 °C for 7200 s.

X-ray diffraction (XRD) experiments were performed to identify the glass and mineral phases present in the samples. The analysis was conducted using an X-ray diffractometer (Empyrean, PANalytical) with a X'Celerator detector and a copper tube operating with Cu Kα radiation ($\lambda = 1.54060$ Å). X'Pert High Score Plus was used to interpret the results. The angle 2θ ranged from 3.5° to 70°. The SD, XRF, and XRD analyses were performed at the Laboratory of Analysis of Minerals and Rocks, Federal University of Paraná (UFPR).

Scanning electron microscopy (SEM) with a 10-kV beam voltage was used to estimate the particle sizes and morphologies of samples (Tescan, LMU; model, Vega 3). The imaging was performed at the Center for Electronic Microscopy, UFPR.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted using a thermogravimetry/differential thermal analyzer (Metler Toledo). The analyses were conducted on an aluminum panel under a nitrogen atmosphere with a flow rate of 8.33×10^{-7} $m^3 \cdot s^{-1}$ and over a temperature range of 30–1000 °C with a heating rate of 8.33×10^{-2} °C·s^{-1}.

A standard three-point bending test was performed to measure the maximum load supported by the membranes. A universal testing machine, EMIC-DL 30000, with a maximum load capacity of 3.00×10^5 N and a constant speed of 8.33×10^{-5} m·s^{-1} was used. The distance between the support points was 9.00×10^{-2} m. The mechanical