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Preparation, characterization and performance of acetylated cellulignin membranes obtained by green methods from biomass

L.A. Soto-Salcido[a], G. González-Sánchez[b,*], B. Rocha-Gutierrez[a], R. Peralta-Perez[a], F.J. Zavala-Díaz[a], L. Ballinas-Casarrubias[a,*]

[a] Facultad de Ciencias Químicas; Universidad Autónoma de Chihuahua, Mexico
[b] Centro de Investigación en Materiales Avanzados, S.C. Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chih., C.P. 31136, Mexico

ABSTRACT

The main objective of this work was the preparation, characterization and evaluation of membranes made from agave bagasse biomass through environmental friendly techniques. An Ethanosolv pretreatment (with four factors: temperature, ethanol, catalyst and residence time) was performed to recuperate cellulose using a central composite design $2k + 2k$, $k = 4$ obtaining a response surface equation. The biomass obtained at maximal cellulose recovery was further acetylated by a Fisher process, in which the biomass reacted primarily with acetic acid. Afterwards, acetylated cellulignin membranes were produced by an evaporation-precipitation method. The resulting membranes (ABM) were characterized by SEM, AFM, FTIR, TGA and DMA, comparing with a CTA membrane obtained in the same conditions. Other membranes from cellulose obtained by acid-alkaline (AA), thermal (AT) and organosolv (AC) pretreatments were prepared. A comparison was made in terms of flux, fluoride rejection and acetylation yields. ABM achieved lower fluxes than AA, AT and AC. Only ABM rejected fluoride (98% removal for a 406 ppm solution). Afterwards, removal of the main cations and anions was assessed using ABM, from well water (Chihuahua, Mexico) which was as high as 99.99%. Biofouling was presented after 20 days of continuous operation.

Agave bagasse, evaporation-precipitation method, acetylated cellulignin membranes, ion removal.

1. Introduction

Water supply has always been of vast importance for human beings, from the origins of civilization to the present day, considering that societies were built near to natural water resources with the objective of meeting the quality and quantity requirements for its consumption. Water quality has impacted population health historically. Nowadays, according to the World Health Organization (WHO), approximately 28% of the global population lacks safe potable-water resources [1]. Heavy metal ions, and emergent contaminants are considered as the most serious pollutants which affect health and biodiversity. For instance, water scarcity and quality mitigation have promoted the development of technology aimed to increase water supply specifically for human consumption.

Filtration membrane processes are considered a very good alternative over other separating technologies due to their significant low energy consumption, simple scaling-up and versatility. Membrane technology is a separation technique considered in process integration with the aim to obtain higher separation selectivity and effectiveness. The most widely filtration membrane processes used to remove undesired compounds from water are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), forward osmosis (FO), among others. The filtration membrane feasibility is related to their inner properties which have an effect on transport, selectivity, fouling and bio-fouling propensity [2,3]. The last properties are produced by a pore blocking the membrane surface, forming an impermeable layer that reduces considerably fluxes in the membrane [4].

For a proper performance, it is essential to select a membrane suitable for the filtration process. The major factors from the material science point of view, are membrane material and configuration, searching for high rejection ratios and high fluxes [4,5].

Polymeric membranes have been used for desalination because of their selectivity, good permeability, mechanical stability, chemical resistance. as well as its low-cost production. Polyamide is used in different configurations for RO and NF processes, followed by cellulose acetate. Despite the great advantages, organic membranes usually

* Corresponding authors.
E-mail addresses: guillermo.gonzalez@cimav.edu.mx (G. González-Sánchez), brocha@uach.mx (B. Rocha-Gutierrez), mperalta@uach.mx (R. Peralta-Perez), fzavala@uach.mx (F.J. Zavala-Díaz), mballinas@uach.mx (L. Ballinas-Casarrubias).

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present an implicit hydrophobic character which increases the fouling propensity on their surfaces, increasing operational costs and shortening membrane lifetime [4–6].

Cellulose acetate (CTA) is employed in a wide range of membrane applications, being considered as one of the most important cellulose derivatives. The reason is that it exhibits a low toxicity and a relatively low production cost [7]. In addition, CTA shows a hydrophilic behavior, which provides an inherent fouling resistance. Their main disadvantages are their low pH and temperature resistance, in comparison with other materials [8]. Cellulose diacetate and cellulose triacetate have been extensively used in membrane filtration processes, especially in desalination processes since 1960. The challenges on cellulose derivatives membranes are directly linked to improving its selectivity and permeability. The phase inversion method is used to prepare UF and RO membranes from cellulosic derivatives with desired physicochemical properties [9].

In recent years, following the environmental trends, many materials from biomass wastes have been assessed for membrane development. Several biomasses have been used as raw material to produce cellulose acetate, such as wheat straw, corn fiber, rice hulls [10], sugar cane bagasse [11], rice husk [12], and *pinus* sp. sawdust [13]. For cellulose recovery from biomass, it is fundamental to fractionate the components by means of a suitable pretreatment. Ethanosolv pre-treatment target is to separate the different fractions from biomass using organic solvents. The most commonly solvents used are methanol, ethanol, ethylene glycol, acetone, and glycerol. Ethanosolv pretreatment is usually performed at high temperatures and by using acid catalysts. It is considered as a promising alternative over other pre-treatment methods as well-known Kraft method [14–16].

The resulting solid residue conformed almost of pure cellulose is then acetylated, with the objective of forming cellulose acetate. This takes place when the cellulose is treated with acetic anhydride and acetic acid as a solvent in the presence of a catalyst, usually sulfuric acid or perchloric acid. This process is known as Fisher acetylation, where hydroxyl groups in cellulose are replaced with acetyl groups [10,11,17]. Cellulose acetate resulting from the acetylation process is eligible to produce membranes. Acetylated cellulose membranes were created by Pusch [18] using the precipitation-evaporation method by dissolving the cellulose acetate in a mixture of solvents such as dioxane and acetamide. This method was subsequently used to produce cellulose acetate membrane from sugar cane bagasse [19].

Membranes can also be prepared by the same method using a solvents mixture mainly of dichlorometane, followed by a fraction of formic acid and finally a small quantity of ethanol; these membranes were a composite of PANi and cellulose acetate. The addition of PANi was made with the objective of enhancing mechanical properties of cellulose acetate membranes produced from sugar cane bagasse [20]. This method was also used to prepare acetylated cellulose membranes from *Pinus* sp. sawdust using only dichloromethane to dissolve the cellulose acetate at 35 °C and 20% of relative humidity (RH), producing membranes that can be used in filtration processes such as NF and UF [21].

The raw material to produce Tequila with "Denominación de Origen" (denomination of origin) is *Agave tequilana*. Bagasse is the final waste produced after the head of the plant is cooked and pressed to extract the sugar liquor which will consequently produce Tequila by fermentation with *Saccharomyces cerevisiae*. According to the National Consortium of Tequila, 350,000 tons on dry basis of bagasse waste are produced annually related to 14.1 million of tequila liters produced during 2012 [22]. For instance, using the bagasse from *Agave tequilana* is really attractive, from both an economic and environmental point of view. This residue is cellulose enriched and can be, as other biomasses, pre-treated to separate its lignocellulosic fractions. The main objective of this work is to obtain cellulose acetate membranes from agave bagasse through biomass pre-treating for a subsequent cellulose acetylation and finally, to produce cellulose membranes capable of removing ions from water.

2. Methodology

2.1. Agave bagasse characterization

Agave bagasse was obtained from a tequila production process (Casa Cuervo), carried out in Jalisco, Mexico. Before biomass pretreatment and acetylation, a characterization of raw material was performed.

Before the Ethanosolv pretreatment was performed, the agave bagasse was dried at 100 °C, milled with a grinder, and sieved using mesh 20 and 80, as presented by Caspeta et al. (2014) [22]. The resulting material maintained by mesh 80 was chosen to achieve the pre-treatments.

2.1.1. Water samples

Approximately, 20 L of water were taken from a local house sink in a community named La Cruz in Chihuahua, Mexico (27.8656° N, 105.2071° W). Ionic chromatography was used to detect and quantify anions and cations contained as explained in 2.6.1.

2.1.2. Ethanosolv pretreatment

Ethanosolv pretreatment was achieved using ethanol (J.T. Baker 99.97%) as solvent, and sulfuric acid (J.T. Baker 97.20%) as catalyst. 10 g of agave bagasse and 50 mL mixture of ethanol/water and a fixed quantity of sulfuric acid were placed into a stainless-steel reactor. Subsequently, the reactor was introduced into an oil bath at high temperatures for a prolonged period. Then, the reactor was cooled down to room temperature.

A central composite design 2^4 with 7 center points was carried to obtain optimal Ethanosolv pretreatment conditions using Minitab 17 Statistical software. Additionally, a response surface methodology was implemented, 4 variables and one response were used with the objective of obtaining optimal cellulose recoveries conditions. Ethanol concentration, temperature, catalyst concentration (sulfuric acid), and residence time were selected as factors and its respective levels. Cellulose recovery was the analyzed response.

Statistical non-significant factors were discarded and a posterior refined analysis of variance was performed. The statistical analysis was made to obtain optimal Ethanosolv conditions in cellulose recovery, thus, more cellulose is reachable to posterior acetylation.

2.1.3. Other bagasse pretreatments

2.1.3.1. Acid hydrolysis/alkaline delignification. An acid hydrolysis and alkaline delignification were performed to an agave bagasse sample. The acid hydrolysis conditions were 190 °C of temperature, 1% (*w*/w) of sulfuric acid (J.T. Baker) concentration, one hour of reaction time. In a 500 mL reactor, a sample of dried agave bagasse were placed and mixed with a solution of sulfuric acid in a 1:10 (*w*/*v*) relation. Once the reaction was completed, the resulting biomass was washed with distilled water until a pH 7 was obtained. Posteriorly, the sample was dried at 105 °C for 24 h. Subsequently, an alkaline delignification was done. In a 500 mL reactor, hydrolyzed biomass was put inside, and mixed with a NaOH (CTR Scientific) 1% (*w*/*v*) solution in a 1:10 relation at 100 °C, using an oil bath. Once the temperature was reached, the reactor was kept inside the oil bath for one hour. Afterwards, the reactor was cooled with ice cubes. Then, it was washed with distilled water until pH = 7. Finally, the biomass was dried at 115 °C for 24 h.

2.1.3.2. Acetosolv. A sample of agave bagasse was impregnated in a 1:3 (w/v) acetic acid (J.T. Baker, VETEC Química Fina) solution for 24 h. Subsequently a solution of 80% (*w*/w) acetic acid and 0.3% (w/w) hydrochloric acid (J.T. Baker, VETEC Química Fina) as catalyst was added. Temperature was set to 100 °C for 2 h. Then, the biomass was washed with distilled water until pH 7, and dried at 70 °C for 6 h.