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Morphological, chemical surface and filtration characterization of a new silicon carbide membrane

M.C. Fraga[a], S. Sanches[b], V.J. Pereira[b,*], J.G. Crespo[a], L. Yuan[c], J. Marcher[c], MªV. Martínez de Yuso[d], E. Rodríguez-Castellón[e], J. Benavente[f]

[a] *REQUIMTE-LAQV, Department of Chemistry, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal*
[b] *Instituto de Biologia Experimental e Tecnológica, Apartado 12, 2781-901 Oeiras, Portugal*
[c] *LiqTech International A/S, DK-2750, Ballerup, Denmark*
[d] *Laboratorio de Fotoelectrones de Rayos X, SCAI, Universidad de Málaga, E-29071 Málaga, Spain*
[e] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain*
[f] *Departamento de Física Aplicada I, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain*

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ABSTRACT

A new silicon carbide ceramic membrane consisting of a unique top layer on a SiC support for application in oily wastewaters filtration was produced and characterized in terms of morphology and chemical surface composition by scanning electron microscopy and X-ray photoelectron spectroscopy measurements. The manufacturing process of this new membrane allows time and economic savings when compared with a two layers membrane previously obtained. The new membrane has a smooth top layer with controlled porosity and a higher permeability compared to already developed commercial membranes. Moreover, it is extremely efficient to remove total suspended solids as well as oil and grease and, consequently, it can be applied to effective treatment of industrial oily wastewaters.

1. Introduction

Oily wastewaters are generated by different industries. In particular, vegetable oil wastewater from the food industry shows high content in solids, chemical oxygen demand as well as oil and grease components [1–3]. Numerous techniques can be employed for the removal of emulsions: conventional physical and chemical treatment approaches include gravity separation and skimming, coagulation, flocculation, sedimentation, and flotation. However, these methods present disadvantages such as low efficiency in the treatment of stable emulsions, high sludge production, high operation costs and need of chemical addition [4].

Membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis are increasingly being applied for treating oily wastewaters, metal polluted waters and desalting processes [4]. Among other advantages, membrane filtration processes present high efficiency for oil removal, moderate energy cost and compact design compared with the conventional treatment methods [5]. However, membrane fouling caused by the deposition (or adsorption) of solution particles and solutes on the membrane surface and pore walls, is the main factor limiting the application of membranes filtration processes, since it reduces the permeate flux and impairs separation properties [6]. Consequently, frequent membrane cleaning protocols need to be applied sequentially which partially affects the selection of a particular membrane.

Commercial synthetic membranes are produced from two distinct classes of material: polymers consisting of organic material (e.g. polysulfone, regenerated cellulose, poliamide and polyvynilfluoride) or inorganic materials (mainly ceramics) [7,8]. Ceramic membranes have advantageous properties when compared to polymeric membranes such as higher mechanical, chemical and thermal stability, which are basic requirements for adequate cleaning protocols and, consequently, higher membrane lifetime [9,10]. Furthermore, depending on the used materials, they can present a higher hydrophilicity [11–13].

The improvement of membrane hydrophilicity and fouling reduction through the use of membrane coatings with nanoparticles are currently a challenge [14,15]. Silicon carbide (SiC) ultrafiltration (UF) membranes exhibit high hydrophilic membrane surface, high porosity, and rather uniform pore size distribution

* Corresponding author.
E-mail addresses: vanessarpjp@gmail.com, vanessap@itqb.unl.pt (V.J. Pereira).

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[16,17]. Higher membrane fluxes, lower fouling, and longer membrane lifetime are, therefore, expected using these membranes [12]. Further membrane structure modifications could still be tested to reduce production time and costs, while maintaining the membrane efficiency.

In this work, a new SiC ceramic membrane (with a single retentive layer above the substrate) was developed (referred in this work as 2nd generation membrane) and compared with a previously developed and commercialized SiC membrane with two layers above the substrate (1st generation membrane). These membranes were characterized in terms of morphology and chemical composition by scanning electron microscopy and X-ray photoelectron spectroscopy measurements. Both membranes were also tested with respect to their possible application in the treatment of vegetable (sunflower) oil wastewaters. Their efficiency was evaluated in terms of their effectiveness to remove solids, chemical oxygen demand and oil and grease.

2. Material and methods

2.1. Silicon carbide membranes

Two different 100% silicon carbide (SiC) membranes (1st generation and 2nd generation) were manufactured by LiqTech. The membranes were prepared in tubular configuration and were used for surface characterization and to perform filtration tests of sunflower oily wastewater.

The 1st generation membrane consists of a highly porous SiC substrate, prepared by extrusion, and two top layers applied by push-pull-coating. The first membrane layer was sintered on the substrate by high temperature thermal treatment ($T > 2000\,^{\circ}C$) in an argon atmosphere, followed by an oxidation step. Subsequently, the final selective layer is coated on the top of this layer and a second sintering takes place ($T > 1800\,^{\circ}C$) to achieve the appropriate pore size.

Considerable evidence suggested that the surface properties of the support (roughness, inhomogeneity and defect density) influence the uniformity and the integrity of the coated membrane. Therefore, a new procedure was developed to produce a new membrane (2nd generation membrane), in which a single top layer is applied directly on the substrate (without the intermediate membrane layer present in the 1st generation membrane). The advantage of this new procedure is the fact that one firing step can be eliminated in the production process, reducing significantly both the production time and the manufacturing costs (approximately 30%). Since sintering the membrane layer is the manufacturing bottleneck, this process change may increase a factory capacity by 100%. Moreover, the microstructure and the surface of the substrate is better controlled, since the whole process has one less high temperature firing, thus, making the final layer smoother and with less defects.

2.2. Scanning electron microscopy (SEM)

The surface and cross section of 1st and 2nd generation membranes were characterized by scanning electron microscopy (SEM) using a field emission gun scanning Electron Microscope (FEG-SEM from JEOL) model JSM7001F with an acceleration voltage of 15 kV. The samples were placed in a sample holder with carbon double sided adhesive tape and were then coated with a film of chromium using a Quorum Technologies Q150T ES.

The SEM images were processed using the ImageJ software developed by Wayne Rasband (http://rsb.info.nih.gov/ij/docs/intro.html), a public domain Java image processing program that superseded the Image Macintosh software developed by the National Institute of Health (USA).

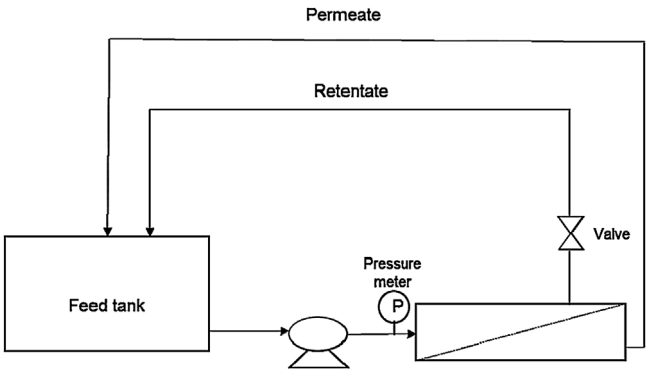

Fig. 1. Experimental set-up used for the ultrafiltration experiments.

2.3. X-ray photoelectron spectroscopy (XPS)

The chemical characterisation of the surface of the studied membranes was performed by XPS. A Physical Electronics spectrometer (PHI 5700) with X-ray Mg Kα radiation (300W, 15 kV, 1253.6 eV) as the excitation source was used for these measurements. High-resolution spectra were recorded at a given take-off angle of 45° by concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Under these conditions, the Au $4f_{7/2}$ line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. Each spectral region was scanned several sweeps until a good signal to noise ratio was observed. The pressure in the analysis chamber was maintained lower than 5×10^{-6} Pa. The software package PHI ACCESS ESCA-V6.0 F was used for data acquisition and analysis. A Shirley-type background was subtracted from the signals. The recorded spectra were fitted using Gauss–Lorentz curves according to the methodology described in detail elsewhere [18], in order to determine more accurately the binding energy (BE) of the different element core levels. Atomic concentration percentages of the characteristic elements on the sample surfaces were determined taking into account the corresponding area sensitivity factor [18] for the different measured spectral regions.

In order to eliminate possible surface contamination (sample manufacture or environmental contamination), measurements using a non-invasive technique such as angle resolved XPS (ARXPS) using five values of the take-off angle ($15^{\circ} \leq \alpha \leq 75^{\circ}$) were also performed, which provide chemical information for depth ranging, approximately, between 2.5 nm and 9.5 nm [19].

2.4. Membrane filtration: experimental set-upand ultrafiltration procedure

A comparison of the performance of 1st and 2nd generation membranes was carried out using a laboratory scale filtration unit operated with total recirculation of permeate and retentate due to volume constrains. Fig. 1 shows a scheme of the filtration system while the characteristics of the membranes used are indicated in Table 1.

The filtration unit is composed of a feed vessel, a high pressure pump, a valve to regulate pressure on the retentate side, three pressure sensors and the membrane housing (LiqTech, Denmark). Pressure readings of permeate, feed, and retentate were acquired in real-time and used for the determination of transmembrane pressure (TMP).

The hydraulic permeability of the 1st and 2nd generation membranes was determined by setting different permeate fluxes and

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