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Hydrophobization of Ceramic Membranes with Poly(dimethylsiloxane) and Polydopamine Nanoparticles for Ammonia Recovery by Membrane Distillation

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The high productivity of swine, cattle, and poultry has intensified the generation of waste and increased environmental pollution [1]. Using this waste directly as a soil fertilizer has been an alternative to reduce its environmental impact. However, this practice can cause environmental problems due to the significant loss of nitrogen in the form of gaseous ammonia (NH_3) in an uncontrolled manner [2]. Therefore, using them as raw material for anaerobic digesters has been evaluated. In this technology, anaerobic bacteria convert the organic matter present in this effluent into biogas [3]. However, high ammoniacal nitrogen (N-NH_3: $NH_{3(gaseous)}$ + NH_4^+) load can inhibit the anaerobic digestion process since NH_3 can penetrate the cell membranes of microorganisms, reducing biogas production and triggering the collapse of the anaerobic digestion process [4]. One alternative to solve this problem is removing ammoniacal nitrogen from biodigesters. For this reason, techniques to remove and/or recover NH3 from this type of waste have been developed and explored, such as direct contact membrane distillation (DCMD) [5,6]. In this thermally driven process, microporous hydrophobic membranes are used to selectively transport volatile molecules in vapor form through their pores [7,8]. The membranes often used for ammonia removal are made from hydrophobic polymers [9]. However, when faced with extreme conditions of temperature, pressure, and pH, traditional membranes can prove to be a hindrance. In such scenarios, the potential of inorganic membranes shines through, with their high thermal resistance and mechanical stability. Admittedly, their hydrophilic nature poses a challenge for membrane distillation. Yet, the ongoing surface modifications of ceramic membranes, which are aimed at making them hydrophobic and thus suitable for DCMD, are showing great promise as a potential solution [10]. In this study, we propose to surface-modify α-alumina membranes with polydopamine nanoparticles (nanoPDA) and polydimethylsiloxane (PDMS) and then characterize and evaluate them using DCMD technology in terms of NH_3 recovery from synthetic solutions similar to swine and poultry waste. Before modification, tubular ceramic porous membranes were washed with distilled water and absolute ethanol in an ultrasonic bath to increase the concentration of hydroxyl groups on the membrane surface and then dried at 70 °C for 24 hours. Next, a solution of nanoPDA was passed through the membrane in a vacuum filtration system, where the vacuum was carried out from in- to outside and then from out- to inside to deposit PDA nanoparticles on both surfaces of the membrane. After filtration, the membranes with nanoPDA were dried at 60 °C for 48 hours, washed to remove any particles not adhered to the membrane surface, and then dried again at 60 °C for 48 hours. Subsequently, the hydrophobization process was carried out by immersing the membranes in a solution of PDMS (0.5 wt.%) in hexane for 12 hours, stirring at 50 rpm at 30 °C. Finally, the membranes were cured at 140 °C for 2 hours and named nanoPDAPDMS. c The FESEM analyses showed significant changes in the surface morphology of the membranes functionalized with nanoPDA and PDMS. A large amount of PDA nanospheres could be observed on the inner and outer surfaces of the membrane, suggesting that a vacuum system is an excellent option for depositing nanoPDA on the surfaces of tubular ceramic membranes. The EDS analyses corroborate these results, as they show a high concentration of carbon and oxygen, followed by aluminum, nitrogen, silicon (from the siloxane), and magnesium. In addition, the EDS analyses showed a homogeneous distribution of the elements C, N, and Si along the membrane surfaces. The ammonia recovery flux in the DCMD system using the nanoPDAPDMS membrane guaranteed performance of 14.89 gN-NH_3 m^{-2} h^{-1} in the first hour. After two hours, the membrane remained at a constant NH_3 recovery rate with an average flux of 6.5 gN-NH_3 m^{-2} h^{-1} In this sense, using polydopamine nanoparticles together with polydimethylsiloxane to modify tubular ceramic membranes is an efficient strategy for producing hydrophobic membranes that can be used to recover ammonia from effluents with a high concentration of ammoniacal nitrogen.

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