Modification of Alumina Membranes by Dip-Coating with Dryguard® for Ammonia Separation by Membrane Distillation

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Growing environmental pollution has driven research and development into technologies for treating industrial and urban effluents. In this scenario, the treatment of swine waste is of essential importance and necessity due to the high load of substances present in its composition that can cause pollution of the air, soil, and, significantly, water resources due to improper disposal [6]. Among these highly harmful substances is ammonia, one of the main forms of nitrogen present in domestic, industrial, and agricultural wastewater. Ammonia is responsible for much of the environmental imbalance, so dealing with effluents with a high nitrogen concentration is an emerging environmental challenge [7]. According to José Giacomini et al. (2009) [9], around 40 to 70% of the total nitrogen found in swine waste is in the ammoniacal form (N-NH₃). Currently, there are some processes for removing and/or recovering nitrogenous compounds from swine waste, such as nitrification and denitrification. In these processes, ammonia (NH_3) is converted into nitrate (NO_3^-), and then anaerobic bacteria convert the nitrate (NO_3^-) into gaseous nitrogen (N_2), releasing it into the atmosphere [2]. Anammox is another method for removing ammonia, which has the advantage of lower energy consumption compared to the previous process [4]. However, both processes can generate a large accumulation of iodine, increasing the cost of treatment [2]. Another technique that has gained prominence in ammonia recovery in recent years is membrane distillation. This technology is based on the principle of phase equilibrium, using a microporous hydrophobic membrane [1]. Generally, polymeric membranes are used in this process, but they can present problems under extreme conditions. Inorganic membranes, which offer greater chemical and physical resistance, can solve this. However, their hydrophilicity makes them unsuitable for membrane distillation. For this reason, works have been conducted on modifying inorganic membranes to make them hydrophobic and suitable for membrane distillation. This technique is based on the process in which evaporation and condensation occur on the pore surfaces of the membrane on the feed and permeate side, respectively, so that the membrane behaves as a selective barrier [10]. There are four main membrane distillation configurations, and their driving force varies according to the conditions applied on the permeate side of the membrane. In direct contact membrane distillation (DCMD), the driving force is promoted by a temperature gradient between a feed solution (heated) and a drag solution (cooled) [1,3]. Thus, this work aimed to hydrophobize hydrophilic α-alumina ceramic porous membranes and evaluate their efficiency in recovering ammonia from synthetic wastewater (representing a swine manure with a high nitrogen concentration). The membranes were modified using a commercial hydrophobic compound at a concentration of 40 g/L. The ceramic membranes were subjected to the dip-coating technique, with two consecutive immersions in the hydrophobic solution for 30 minutes. The modified and original membranes were characterized regarding their crystallinity by X-ray diffraction (XRD), the presence of functional groups by Fourier transform infrared spectroscopy (FTIR), structural morphology by scanning electron microscopy, and the hydrophobicity by water contact angle. Membrane performance was evaluated in the ammonia recovery, using a feed solution with an N-NH₃ concentration of 5000 mg/L and a sulfuric acid stripping solution with 0.1 mol/L. The pH of the feed solution was adjusted to 8.5 and heated to 38 °C, while the carrier solution was cooled to 23 °C. Both solutions circulated continuously in countercurrent, with 0.5 and 0.3 L/min flow rates, respectively. The functionalized membranes used in the permeation tests had an effective area of approximately 26.4 cm^2. During the permeation process, 2 ml of stripping solution was collected every hour to determine the flow of N-NH₃ through the membrane. In the XRD, well-defined α-alumina peaks could be identified in the control membrane and the membranes functionalized with the hydrophobic agent, but only changes in the intensity of the peaks in the modified membranes could be observed. Morphological analysis of the membranes showed agglomerates of the agent on the outer surface and fibers on the inside. These agglomerates and fibers on the modified membrane indicate that the commercial product was able to form a hydrophobic film on the membrane surface. The FTIR analyses for the original and functionalized membranes revealed similar vibration bands. The peaks around 3500 cm^{-1} were attributed to the hydroxyl group (O-H), meanwhile the peaks near 500 cm^{-1} and 800 cm^{-1} were all attributed to the Al-O bond. According to Ferreira Niero et al. (2022) [5], the separation of this broadband into two characteristic peaks indicates that the peaks at 500 cm^{-1} and 750 cm^{-1} and those at 800 cm^{-1} describe the octahedral and tetrahedral geometry of α-alumina, respectively. The contact angle test showed an average angle of 119 ± 0.02°, characterizing the outer surface of the modified membrane as hydrophobic [8]. The permeation results indicate that the N-NH₃ flux ranged from 56222 mg·N-NH₃/m^2 in the first hour to 26784 mg·N-NH₃/m^2 after 6 hours of experimentation. In this sense, using the commercial hydrophobic agent to modify ceramic membranes for nitrogen recovery proved promising.

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