FUNCTIONALIZATION OF CERAMIC MEMBRANES WITH POLYDOPAMINE AND POLYDIMETHYLSILOXANE FOR THE NH_3 REMOVAL FROM ANAEROBIC DIGESTION

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ABSTRACT

This work aimed to modify ceramic membranes with polydopamine nanoparticles (nPDA) and polydimethylsiloxane (PDMS) for applying in the ammonia (NH_3) recovery from a synthetic solution similar to swine waste using a direct contact membrane distillation (DCMD) system. Field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) analyses showed a homogeneous distribution of the nanoparticles and PDMS on the membrane surfaces. The coatings provided a significant gain in hydrophobicity for the membranes, with contact angles of over 120°. The membrane modified with 0.5% of PDMS showed the highest NH_3 recovery efficiency, with a 14.89 gN-NH_3 m^{-2} h^{-1} removal rate in the first hour of test. These results indicate that using a DCMD system with these membranes can prevent the accumulation of ammonia in biodigesters and improve biogas production by minimizing NH_3 interference with methanogenic microorganisms. Therefore, modifying ceramic membranes with nPDA and PDMS is a promising approach for the combined management of NH_3 recovery and renewable energy generation.

Keywords: Ceramic membranes. Polydopamine. Polydimethylsiloxane. Ammonia recovery. DCMD.

1 INTRODUCTION

Population growth in recent decades has significantly boosted the expansion of the livestock industry. In 2022, Brazil produced almost 5 million tons of pork, ranking 4th in the world in this segment. This expansion has also led to a substantial increase in the generated swine waste, increasing environmental pollution[1,2]. On the other hand, the use of this waste as fertilizer is a widespread practice due to its high concentration of nitrogen (N), phosphorus (P), and potassium (K), essential nutrients for maintaining agricultural soil[3]. However, the nitrogen present in this waste, mostly in ammoniacal form (N-NH_3: NH_4^+ + NH_3), makes it susceptible to losses due to free ammonia (NH_3) volatilization during storage and after application to the soil[4]. In addition, excessive use of biofertilizers can lead to runoff into nearby surface waters, causing an imbalance in the concentration of N in these environments. Excess N can trigger eutrophication, compromising aquatic life and causing human health problems such as methemoglobinemia and cancer[3,4]. To mitigate these adversities, various treatment techniques have been employed. Anaerobic digestion is a promising solution that treats waste efficiently and generates biogas, a renewable energy source. However, a high N-NH_3 load can interfere with the anaerobic digestion process, as NH_3 can penetrate the cell membranes of microorganisms, reducing biogas production and possibly collapsing process[1]. Therefore, techniques to reduce the concentration of N-NH^3 in the effluent used in biodigesters have been explored, such as direct contact membrane distillation (DCMD). This thermal process uses microporous hydrophobic membranes to transport volatile ammonia molecules through their pores selectively. However, the polymeric membranes used in this process can become disadvantageous under extreme chemical and physical conditions. To overcome this problem, ceramic membranes, with high chemical, thermal, and mechanical resistance, have been the subject of studies[5]. One challenge in using ceramic membranes is their hydrophilic nature, which makes their use in membrane distillation unfeasible. Therefore, modifications to the surfaces of these membranes have been constantly evaluated to make them hydrophobic and suitable for DCMD. The aim of this study was to modify the surface of ceramic membranes with polydopamine nanoparticles (nPDA) and polydimethylsiloxane (PDMS) and evaluate their efficiency in recovering NH_3 from a synthetic solution simulating swine waste using a DCMD system.

2 MATERIAL & METHODS

Tubular porous ceramic membranes were modified after surface activation in an ultrasonic bath with an aqueous solution of absolute ethyl alcohol and dried at 70 °C for 24 hours. The modification began with the deposition of nPDA on the inner and outer surfaces of the membrane using a vacuum filtration system. After drying (60 °C, 48 h), a layer of PDMS was applied by dip-coating the membrane in the polymer solution (the silane and its curing agent -10:1- were solubilized in hexane to obtain solutions with concentrations of 0.1, 0.3, and 0.5%wt. PDMS). The membranes were immersed in these solutions for 12 hours at 30 °C and then cured at 120 °C for 2 hours to obtain MCnPDAPDMS0.1%, MCnPDAPDMS0.3% and MCnPDAPDMS0.5% membranes.

Modified membranes were characterized and evaluated in terms of their ammonia recovery efficiency. Contact angle analysis was used to determine the hydrophobicity of the membranes, while field emission scanning electron microscopy (FESEM) allowed the evaluation of the microstructure. Energy dispersive spectroscopy (EDS) measurements made it possible to determine the surface elemental composition of the membranes. In addition, the size and shape of the nPDA were analyzed by transmission electron microscopy (TEM). Ammonia recovery efficiency was evaluated using a direct contact membrane distillation system. Thus, an ammonium chloride feed solution with a concentration of 5000 mgN-NH_3 L^{-1} (38 °C, pH 8.5) was circulated at 0.5 L min-

[1] in countercurrent with a sulfuric acid solution (0.1 mol L^{-1}, 25 °C) at a flow rate of 0.3 L min^{-1}. The ammonia recovery rate was then determined using Nessler's colorimetric method.

3 RESULTS & DISCUSSION

Figure 1 shows the morphology of the outer and inner surfaces and the cross-section of the MCnPDAPDMS0.5% membrane before and after coating with nPDA and PDMS, and the characteristics of the nPDA particles. The original ceramic membrane has a consistent porous surface (Fig. 1a,b,c), which has become rougher with the formation of angular concave structures due to the random distribution of spherical polydopamine particles (Fig. 1d,e,f). This roughness creates spaces that help to trap air, intensifying the capillary effect and minimizing the contact of the liquid feed with the membrane. This phenomenon helps the spherical movement of the droplets over the surface, preventing pollutants from penetrating the pores or adhering to the surface, improving the anti-fouling performance of the membrane[6]. TEM analysis (Figure 1g) reveals that the nPDA particles have an average size of 272 ± 14 nm.

As confirmed by EDS analysis, more nPDA particles were observed on the membrane's outer surface. Initially, the analysis revealed a high concentration of Al in the original membrane, indicating that AlO_2 was the predominant component. However, after coating the membrane with nPDA and PDMS, N and Si were detected, which are elements in the composition of nPDA and PDMS, respectively. The detection of the new elements resulted in a marked decrease in the concentration of Al. The introduction of nPDA and PDMS not only changed the surface's elemental composition but also contributed to altering the hydrophobic properties of the membrane, as indicated by contact angle analyses.

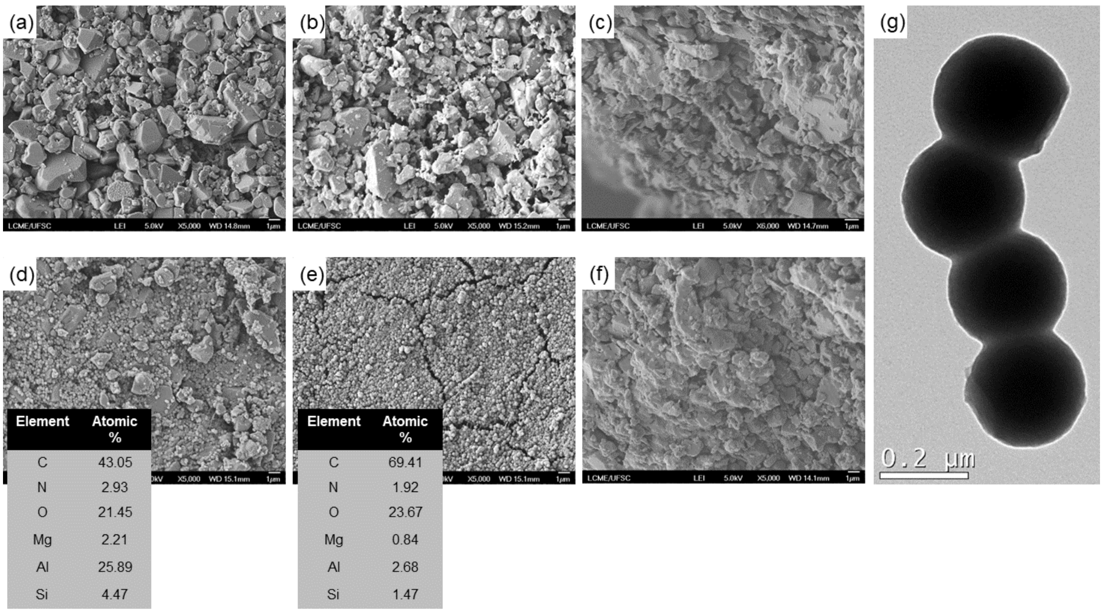

Figure 1 – FESEM images of the outer (a), inner (b), and cross-sectional (c) surfaces of the original membrane and the inner (c), outer (d), and cross-sectional surfaces of the MCnPDAPDMS0.5% membrane. TEM photograph of the nPDA nano-particles (g).

Figure 2a shows the contact angles of the MCnPDAPDMS0.1%, MCnPDAPDMS0.3%, and MCnPDAPDMS0.5% membranes. The measured values of 121.5°, 138.3°, and 137.2°, respectively, show that the coated membranes are very hydrophobic. Figure 2b shows the variation in ammonia flux of the three membranes in the experiment with synthetic effluent. The ammonia recovery flux using the CMnPDAPDMS0.5% membrane was 14.89 gN-NH_3 m^{-2} h^{-1}, while the CMnPDAPDMS0.1% and CMnPDAPDMS0.3% membranes showed recoveries of 2.19 and 3.19 gN-NH_3 m^{-2} h^{-1} in the first hour of the experiment. At the end of the 3-hour experiment, the recovery rates were 6.5, 3.75, and 1.79 gN-NH_3 m^{-2} h^{-1}, respectively. This removal flow would prevent the accumulation of ammonia in the reactor through filtration with the modified membranes so that methane gas production would not be altered by the ammonia attack on the bacteria responsible for producing the gas.

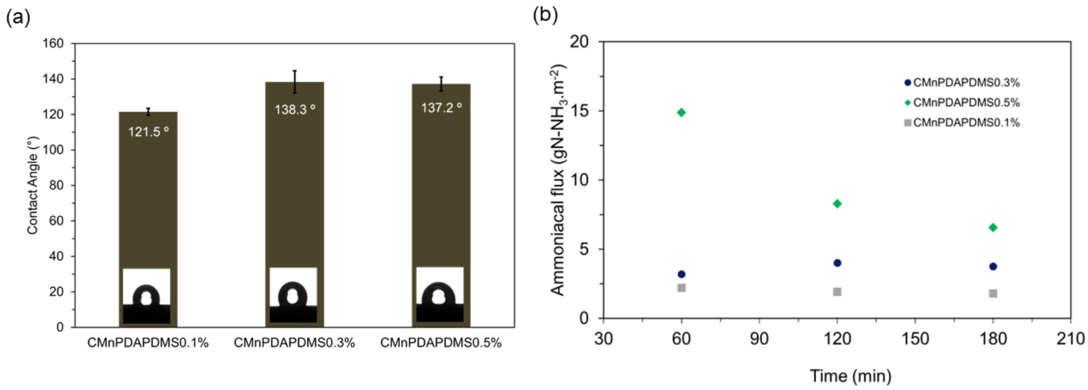

Figure 2 – Results and photographs of the contact angle analysis (a) and variation in ammonia recovery through the modified membranes (b).

4 CONCLUSION

Surface modification of ceramic membranes with polydopamine nanoparticles and polydimethylsiloxane proved to be an effective approach for recovering ammonia from synthetic solutions simulating pig waste. Analysis of the modified membranes revealed a significant increase in hydrophobicity, with contact angles greater than 120°, which is crucial for the efficiency of the direct contact membrane distillation process. In addition, the evaluation of the ammonia recovery flux showed that the membrane with 0.5% PDMS had the highest efficiency, with an ammonia removal rate that would, therefore, prevent the accumulation of ammonia in the reactor and potentially improve biogas production by minimizing NH_3 interference with the microorganisms responsible for methanogenesis. These results indicate that modifying ceramic membranes with nPDA and PDMS is a promising technique for managing swine waste, offering a sustainable solution that combines nutrient recovery efficiency with renewable energy through anaerobic digestion. However, further studies are needed to optimize the modification and operating parameters and assess this technology's economic viability and large-scale application.

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