



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Development of Novel CO₂-Selective Chitosan Membrane Blended with Synthetic Amines and Natural Amines of Silk Fibroin and Sericin.

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SHORT ABSTRACT

The major objective of the present work is to develop a thermally stable biopolymer-based membrane for CO₂ separation using facilitated transport mechanism. The biopolymer chitosan (CS) enables facilitated transport of CO₂ by dint of the amine group present in its structure, is thermally stable in absence of crosslinking and possess good film forming ability. The CO₂ permeance of the CS membrane with poly(ether sulfone) (PES) as a support, was 12.5 GPU and CO₂/N₂ selectivity was 54 at 90 °C with water flow rate of 0.03/0.05 ml/min (feed/sweep) and absolute pressure of 2/1.21 bar (feed/sweep) for binary gas mixture. The pristine CS membrane proved to be thermally stable under the operating conditions. Hence, the CS membrane was further explored by incorporation of synthetic and natural amines as carriers for improving and facilitating the transport of CO₂ gas molecules. There exists only one amine group per monomer of the CS polymer that can act as carrier. In order to increase the total amine content in the active layer, tetraethylenepentamine (TEPA) was blended and the CO₂ separation performance was evaluated. The CO₂ permeance increased two fold as compared to pure CS membrane to 24.7 GPU and CO₂/N₂ selectivity reached to 80 by blending 30 wt % of TEPA, at similar operating conditions. The poly(allylamine) (PAA) consists of mainly primary amine groups which is very brittle in the dry state with inability to form stable films alone. The blending of PAA with CS at optimized content of 70 wt % of CS and 30 wt % of PAA (PAA30) resulted in further improvement in the CO₂ separation performance. However, CO₂ separation with long-term stability, simultaneously with high permeance through eco-friendly and cost-effective materials is of utmost concern. Hence, a novel approach was undertaken to substitute the synthetic amines by the inherent amines of another versatile biopolymer silk fibroin (SF). In the rational blend of the two biopolymers (CS/SF): CS acted as a matrix and SF aided CS as a carrier for CO₂ facilitated transport. The optimum CO₂ permeance of 140 GPU and CO₂/N₂ selectivity of 103 for binary gas were observed at 90 °C. An unprecedented stability of 30 days was demonstrated by the SF induced CS membrane under the applied conditions. Sericin (SC) a polymeric protein has to be removed during extraction of SF from the silk cocoons by dissolving in sodium carbonate (Na₂CO₃). Further, this SC solution was exploited as fixed natural carrier along with the aid of Na₂CO₃ as a mobile carrier inside the CS matrix and the membrane (M3) was tested for CO₂ separation performance. The XPS depth profiling revealed evenly distributed elemental composition across the depth

of the M3 membrane which confirmed the formation of homogenously blend membrane. The M3 membrane displayed encouraging CO_2/N_2 selectivity of 73 at 0.05 ml/min of feed sweep water flow rate. The selectivity was least affected at 90 °C temperature. This selectivity was higher than the CS membranes prepared with only SC or Na_2CO_3 in the matrix. CO_2/N_2 and CO_2/H_2 selectivity were found to be 43 and 10, respectively at 2 bar. An initial drop perceived in the CO_2 permeance was due to increase in the effective thickness of the active layer by support pore filling phenomena that adversely affected the overall permeance. Hence, a novel strategy was designed by preparing a mixed matrix nanocomposite membrane by incorporating graphene nanoparticles (GNP) into the CS/SF matrix (CS/SF/GNP) to counteract the support pore blockage during gas separation test. The positive effect of GNP in the CS/SF/GNP was apparent in the CO_2 permeance inconsequential drop of ~ 7 % during the initial 12 h, in the presence of moisture and pressure. The CS/SF/GNP membrane exhibited CO_2 permeance of 159 GPU and CO_2/N_2 selectivity of 93 at 90 °C. The thermogravimetric analysis (TGA) isotherm specified the thermal stability of CS/SF/GNP membrane up to 150 °C even in absence of any crosslinking within the membrane. X-ray photoelectron spectroscopy (XPS) specified that the surface chemistry of the membrane remained consistent at temperature up to 120 °C. This encouraging work enabled us to distinctively envision the utilization of the whole of the raw silk for CO_2 separation.

