



**INDIAN INSTITUTE OF TECHNOLOGY  
GUWAHATI**

---

Name of the Student: Aviti Katare

---

Roll Number: 196107001

---

Programme of Study: Ph.D.

---

Thesis Title: Thermally Stable Moisture Responsive Chitosan based  
Mixed Matrix Membranes for Selective CO<sub>2</sub> Separation

---

Name of the Thesis Supervisor: Prof. Bishnupada Mandal

---

Date of Completion of Viva-Voce Exam: 07/06/2024

---

Keywords for description of Thesis: Chitosan; Mixed Matrix Membranes; CO<sub>2</sub> separation; Flue Gas; GO; MIL-100(Fe); UIO-66(Zr); Biodegradable polymer

**Short Abstract of Ph.D. Thesis**

CO<sub>2</sub> is the major component of greenhouse gases and is responsible for the surge in global temperature. Therefore, carbon capture, utilization, and sequestration (CCS) are the need of the hour to control global warming. Chitosan (CS) polymeric membranes containing amine carriers have received much attention in CO<sub>2</sub> separation because of their easy fabrication, low cost, and excellent separation performance. The optimum performance of CO<sub>2</sub>/N<sub>2</sub> was observed at 85 °C temperature, 2.21 bar feed pressure, and 1.21 bar sweep pressure, with feed and sweep moisture flow of 0.03 mL/min and 0.05 mL/min, respectively. Neat CS membrane with ~0.6 μm active layer thickness showed CO<sub>2</sub> separation results with CO<sub>2</sub> permeance of 60 GPU and CO<sub>2</sub>/N<sub>2</sub>

selectivity of 21. The membrane performance could not surpass the Robeson upper-bound Trade-off. To improve the separation performance many techniques were utilized and presented in this thesis. To increase amine content in the matrix, covalent conjugation of L-tyrosine (Tyr) onto CS was accomplished by using carbodiimide as a coupling agent. The defect-free dense selective layers of tyrosine-conjugated-chitosan with a thickness within the range of  $\sim 0.6 \mu\text{m}$  were cast and employed for mixed gas ( $\text{CO}_2/\text{N}_2$ ) separation study. It showed reasonably good  $\text{CO}_2$  permeance of around 103 GPU,  $\text{CO}_2/\text{N}_2$  selectivity of 31 and the separation performance was stable up to 150 h. However, it did not show promising outcomes and could not surpass the Robeson curve. Further modifications in the CS matrix were done with phenylalanine (Phe) and we compared the effects of two approaches: amine blending and grafting with polymer matrix and their contribution to gas separation (GS) performance. The results suggest that the grafting and blending of Phe with the CS matrix boosted the  $\text{CO}_2$  permeance and  $\text{CO}_2/\text{N}_2$  selectivity of the fabricated membranes, respectively, when compared to the bare CS membrane and Tyr-c-CS membrane. The highest obtained  $\text{CO}_2$  permeance was 106 GPU in the Phe-grafted-CS (Phe-g-CS) membrane and optimal selectivity was 97 in the 20 wt% Phe-blended-CS (Phe-b-CS) membrane when both the membranes had  $4 \mu\text{m}$  thick selective layer onto polyethersulfone (PES) support. The stability tests were also conducted for both types of membranes. The results suggested that chemical grafting is more stable than physical blending due to its high durability upon long run of almost 400 h. Advanced membrane materials with higher gas separation capabilities have developed a lot of interest in  $\text{CO}_2$  separation. So, we created MMMs of the CS matrix using L-lysine conjugated graphene oxide (Lys-c-GO) nanosheets as nanofillers. The fabricated defect-free dense layer with a selective layer thickness of  $\sim 4 \mu\text{m}$  demonstrated  $\text{CO}_2$  permeance of 44 GPU and strong  $\text{CO}_2/\text{N}_2$  selectivity of 88. MOF materials have gained enormous attention as nanofillers in the field of MMMs. Taking this into consideration, MIL-100(Fe) nanoparticles were created using HF-free environment at ambient conditions and utilized as nanofillers in the CS matrix to fabricate MMMs with the desired thickness of  $\sim 1\text{-}1.5 \mu\text{m}$  onto the PES support. The fabricated MMM 15-weight % MIL-100(Fe) loaded membrane showed  $\text{CO}_2/\text{N}_2$  selectivity and permeance of 59 and 85 GPU, respectively. Further, a  $\text{CO}_2$ -philic zirconium-based MOF NPs (Zr BDC or UIO-66) was synthesized, decorated with L-lysine amino acids, and utilized as a nanofiller into a CS matrix to synthesize MMM. The high porosity and surface area of the MOF NPs aided in the  $\text{CO}_2$  separation permeance, while the selectivity was addressed by the amine functional groups present in L-lysine. After successful characterization studies, it was discovered that fabricated MMMs with a 7 wt % loading of lysine-conjugated Zr BDC (lys-c-ZrBDC) NPs with  $\sim 4 \mu\text{m}$  selective layer thickness demonstrated better results than the pristine CS and the Zr BDC-embedded CS MMM. The composite Lys-c-ZrBDC incorporated CS MMM showed a  $\text{CO}_2$  permeance of 135.2 GPU and a steady  $\text{CO}_2/\text{N}_2$  separation factor of 71.5 under humid conditions. Furthermore, extensive studies have demonstrated that, when subjected to optimal conditions, the engineered membranes, namely Phe-g-CS, Phe-b-CS, and Lys-c-ZrBDC/CS, have not only shown promising separation performances but also surpassed the Robeson upper bound curve. This remarkable achievement showcases the exceptional performance and potential of these membranes for practical and commercial applications.