The major objective of this research is the development of novel polymeric membranes for the separation of organic solvent/water mixtures by pervaporation, which is a rapidly advancing green unit operation for effective, economical and safe processing of liquid mixture systems in chemical process industries. A secondary objective was to assess the performance of commercial tubular and hollow fiber membranes for pervaporation of organic/water liquid mixtures of considerable industrial significance.

Hydrophilic PEBAX-2533 membrane was synthesized for dehydration of hydrazine by pervaporation technique whereas separation of glycerol-water mixtures was performed using commercial microporous hydrophobic poly(tetrafluoroethylene) (PTFE) membrane by membrane distillation technique and compared with the performance of dense PEBAX-2533 membrane aided pervaporation under similar operating conditions. Dense membrane made of the natural biopolymer chitosan was prepared from aqueous acetic acid and modified by ionic crosslinking with phosphoric acid to investigate its pervaporation performance in terms of flux and selectivity for separation of ethanol-water azeotropic mixture. PEBAX membrane incorporated with 30% 4A zeolite was crosslinked with toluene diisocyanate for the successful dehydration of \( n \)-methyl-2-pyrrolidone (NMP) which is a widely used solvent in the bulk drug industry. Dehydration of acetonitrile solvent was
studied at varying feed composition, flow rate and feed temperature using a commercial silica tubular membrane (HybSi) coated with polydimethyl siloxane for a locally based pharmaceutical industry.

Extraction of important industrial VOCs such as methyl-tert-butyl ether (MTBE), ethylene dichloride (EDC), iso-propanol (IPA) and n-butanol from aqueous solutions was successfully carried out using commercial hydrophobic poly(etheretherketone) (PEEK) hollow fiber membrane. Its performance was compared with that of indigenously synthesized hydrophobic poly(dimethysiloxane) (PDMS) or silicone rubber membrane. Characterization of these new polymer membranes was carried out using Fourier transform infrared spectroscopy (FTIR) to determine intermolecular interactions and new functional groups, X-ray diffraction studies (XRD) to evaluate degree of crystallinity and d-spacing, scanning electron microscopy (SEM) to study surface and cross-sectional morphologies, differential scanning calorimetry (DSC) to assess glass transition temperature ($T_g$) and thermal gravimetric analysis (TGA) to evaluate thermal stability.

Mathematical models for complete mixing and plug flow modes of feed transport were developed to simulate effect of these two flow patterns on membrane area requirement and exit streams’ composition for given inputs of feed/retentate composition and stage cut on the basis of experimental data. To understand the hydrodynamic scenario within the pervaporation module along with pressure and velocity profiles,
simulation was carried out using computational fluid dynamics (CFD). Design of a pilot plant for NMP dehydration by a hybrid process of pervaporation and distillation is presented.

The study revealed the promising potential of indigenous membranes as economic alternatives to highly expensive imported membranes for application in pervaporation based separations for solvent recovery and effluent treatment through removal of hazardous VOCs in chemical and pharmaceutical industries. The feasibility of assembling indigenous pervaporation systems could get a boost in our country wherein pervaporation is still not considered a commercially viable choice for separations pertaining to homogeneous liquid mixtures.