5.1 Summary & Conclusion

The study done so far is having "***Photo-irradiation***" as a pivotal for whole of the work. Various aims and objectives in terms of membranes performances have been achieved through photo-irradiation technique.

In this study, the role of photo-irradiations on membrane performances is exploited. It is achieved by making use of photo-irradiation during both preparation condition and operation condition (i.e. during permeation). Wet phase inversion technique is employed to prepare the base polymer membranes. These membranes are modified for tailor made specifications upon-irradiations. Membranes are also developed to study 'stimulus-response' phenomenon which regulates the separation performance. This is achieved by photo-modification and incorporation of some photo-responsive moiety on the membrane.

The ***second chapter*** explores the way to prepare the membranes with tailor made specification by incorporating acrylic acid upon photo-irradiations. This is observes to develop surface functionality on the membrane surface and to reduce sieving effect due to acrylic acid incorporation. These membranes are utilized for the removal of various pollutants from water and separation of rose pigments to study the stimuli responsive behavior e.g. pH. The first section of the chapter reveals surface functionalization of polysulfone membranes which are having propensity towards nanofiltration. The photo-modification of membranes by photo-irradiations without sensitizer supports the intrinsic photo-sensitive behavior of polysulfone as well as acrylic acid. The pore tightening and increase in hydrophilicity is observed proportional to the acrylic acid incorporation and the two depend upon the concentration and dipping time of the polysulfone membrane in acrylic acid solution. Porometric study also reflects incorporation of acrylic acid in the similar trend in terms of mean pore flow diameter which is maximum for virgin membrane (0.101 µm) than the membranes treated with 10% solution of acrylic acid (0.05 µm for 10 min dipping and 0.035 µm for 30 min dipping). The salt rejection analysis of the membrane correlates the content of functionality on the membrane and show somewhat preferential separation of bivalent to monovalent ones. The rejections of the ions follow the order SO_4^{2-} (50 %) > Cl^- (20.4 %). The retention of organic molecules (glucose and 2,4-dichlorophenol) also depends on the acrylic acid content on the membrane and it is achieved up to 78 % for glucose and 58 % for 2,4-

dichlorophenol . The retention of glucose by the modified membrane is higher with respect to 2,4-dichlorophenol is due to higher molecular weight and low polarity of glucose.

Similarly, the acrylic acid functionalized polysulfone membranes upon photo-irradiation have displayed better separation results for anthocyanin pigments from rose extract than virgin polysulfone. The photo-modified membranes have also reflected changes in the separation behavior with the content of acrylic acid (maximum for membrane treated with 3% acrylic acid solution than 1% acrylic acid solution and virgin polysulfone) incorporation along with pH of the solution. The NaCl salt separation in little extent also features the ionic character in it due to function –COOH group incorporation. The membrane shows better performance in pH 5 (94.5 % rejection) with respect to pH 2 (92.8 % rejection) as at low pH the acrylic acid chains remain contracted due to their higher pKa value (the pKa of acrylic acid is 4.26 and it is 4.7 for the poly (acrylic acid). Time dependence study features that the performance is quite steady at pH 5 (91.2%). But, at acidic pH (pH 2), the performance deteriorates (71.8 %) as a result to counter balance the charge due to more permeation of chloride ions. The performance deterioration is also low for the membrane with high content of acrylic acid which imparts more hydrophilic character to the membranes surface.

The last section of the second chapter highlights the preparation and acrylic acid modification of polypiperazinimide based thin film composite membrane. The sequence of the acrylic acid and polypiperazinimide layer is altered for the membranes. The acrylic acid incorporation on the membrane through photo-irradiation technique is reflected from FTIR-ATR, SEM studies. The weight difference also supports the incorporation of acrylic acid which in turn is maximum for the membrane treated with higher concentration of acrylic acid and is having the acrylic acid layer in direct contact to polysulfone surface comparatively. The acrylic acid treated membranes are exploited for the separation of various organic pollutants from water. The separation of organics follows the order Atrazine > Simazine > 2,4,6-TCP > 2,4-DCP based on preferably size exclusion. Apart from this, the lower log P value and higher polarity factor also favor the decrease in simazine rejection compared to atrazine, as well as 2,4,6-TCP and 2,4-DCP. The rejection performances of the acrylic acid photo-modified thin film composite membrane are higher in comparison to the unmodified membrane. The blocking effect of the membranes with acrylic acid layer sandwiched between Polyamide layer and polysulfone membrane surface is observed more than the membranes with acrylic acid layer at the top of polyamide layer and unmodified thin film composite membrane.

The ***third chapter*** outlines the implementation of technical approaches for the betterment of membrane performances. *m*-phenylene and trimesoyl chloride based thin film composite membranes are prepared by photo-treatment after interfacial polymerization to develop cross-linked polyamide layer instead of conventional thermal curing due to their better results towards salt rejection. These photo-treated membranes are exploited for the separation of pentachlorophenol and simazine pollutants by addition of surfactants to the solution. The presence of surfactant in solution affects steric (size) exclusion due to aggregation of the solute molecule with surfactant and electrostatic interaction (charge repulsion). Hence, enhanced separation behavior of the membranes is observed due to pore blocking and increase in the size of the pollutants. The rejection is observed to increase from 36% to 56% for more porous membrane and from ~ 81% to 88% for less porous membrane due to interaction of sodium dodecyl sulphate with pentachlorophenol. The betterment towards rejection is observed for more porous membrane in terms of glucose and sucrose separation. The improvement in PCP separation performances are inversely correlated with the PCP separation performances. The pore blocking is observed due to the presence of the surfactants in the feed is also another factor for better rejection. The value of log P is found to be another factor which acts as a descriptor.

Similarly the rejection behavior of simazine by photo-membranes is observed to show similar trend as glucose, salt and water permeability. Sodium dodecyl sulphate (cationic) and cetyl tertiary ammonium bromide (anionic) surfactants are used to study their interaction with simazine solution in terms of separation through photo-treated membranes. The addition of sodium dodecyl sulphate to the feed shows more enhancements in rejection (~12%) for more porous membrane in terms of organic marker. On the other hand, the addition of cetyl tertiary ammonium bromide to the feed shows no improvement in rejection (~4%). The pure water flux recovery ratio of both the membranes is also calculated and it shows that flux recovery ratio is better when the membranes are dealt with the sodium dodecyl sulphate compared to cetyl tertiary ammonium bromide.

The ***fourth chapter*** in nutshell highlights the photo-regulation behavior through photo-responsive membrane. The photo-active azo-moiety is incorporated in to the asymmetric polysulfone membrane by non-conventional method by well known diazotization reaction of m-phenylene diamine on the membrane surface. Photo-responsive behavior of the azo-moiety (bismarck brown) i.e. photo-isomerization, has been exploited towards the photo-regulated separation of monochlorophenol isomers from water through azo-composite membranes. It is observed that the separation of monochlorophenol isomer is governed by hydrophilic and polar nature of the membrane which is induced as a result of photo-isomerization of azo-moiety. The rejection observed for the 2-chlorophenol and 4-chlorophenol are 79.39% and 78.81% in dark condition respectively which reduces further to 69.33% and 64.31% respectively for the two. The decrease in rejection for 4-chlorophenol is observed to be more due to its higher dipole moment (1.477 D) than 2-chloro-phenol (0.9388 D). This rejection of the two deteriorates further during second run of the experiment due to polarization of the membrane surface at the similar conditions of experiment. But overall trend of rejection remains similar for both the isomers. The azo-moiety incorporation on the membrane surface is further exploited for their biocidal effect as an extension of this study for different applicability. The hindrance of the bio-film formation by *Vibrio* sp. for the modified azo-polysulfone membrane is observed which is due to the development of better hydrophilic character on the membrane surface as result of azo-moiety. For this azo-composite membrane the bacterial count is found to be less than 10^{4} in comparison to virgin polysulfone membrane on treatment with H_2O_2.

Overall this work is a contribution towards the separation of various pollutants along with some other small organic molecules of interest from water by making use of photo-irradiation technique during preparation and operational conditions of the membranes. This work also highlights the use of technical approach (e.g. addition of surfactants to the solution) along with photo-irradiation for removal of these pollutants through membranes.