Synopsis of the thesis entitled:

"Investigations in ultrafiltration membranes based on polyacrylonitrile and AB-polybenzimidazole"

By

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Preamble

Ultrafiltration (UF) is a pressure driven membrane separation process primarily based on the size exclusion principle. The pore size of UF membranes vary in the range of 100 – 1000 Å. Applicability of UF membrane technology is wide-spreading owing to its usefulness in various industries such as textile, chemical, food, dairy, pharmaceutical, metallurgy, paper, leather, water and waste water treatment, etc.

The majority of UF membranes are prepared by phase inversion method. Various parameters like dope solution composition, additives used, casting temperature, evaporation time, chemical treatment, etc. are known to play a crucial role in determining membrane porosity (size and density) [1-5]. In present study, some of these parameters are investigated using polyacrylonitrile (PAN) as the membrane material. PAN hydrolysis using bases is documented in the literature [6-9]. When this phenomenon is applied to UF membranes, most of the studies indicated flux decline due to pore size reduction [9-11]. It is known that PAN hydrolysis proceeds through intermediates [12]. If the hydrolysis of the UF membrane surface could be carried out in a controlled manner leading to only increased hydrophilicity and not to pore size reduction, water flux can be increased to advantage overall membrane productivity. This issue is addressed with PAN

membranes, which led to significant increase in water flux (up to 230 %) without large variation in the rejection performance. During the course of this work, pore size reduction was also observed, which was conveniently extended to synthesize negatively charged membranes that have arsenic (As-V) rejection capability following Donnan exclusion principle [13].

Use of UF membranes remained mostly confined to aqueous solutions. In view of wide-spreading applicability, investigations in UF membranes those would withstand stringent environments of acids, bases and solvent need to be broadened. With this aim, UF membranes based on polybenzimidazole were prepared and evaluated for their characteristics. Their stability towards organic solvents, concentrated acid (H_2SO_4) and base (NaOH) was investigated.

The work done is presented in following chapters.

Chapter 1: Introduction

This chapter begins with applications of UF membranes. Need for the investigations in UF membrane are described. The scope of the work is defined, followed by the objectives of the work. At the end of this chapter, organization of the thesis is presented.

Chapter 2: Literature survey

This chapter briefly reviews various methods for ultrafiltration membrane preparation and their performance evaluation. Factors affecting membrane performance and stability viz., fouling, concentration polarization, compaction, interactions of solutes with membrane material, etc. are briefed.

Chapter 3: PAN based UF membranes: Optimization of preparation parameters

This chapter begins with introduction and reviews various parameters affecting membrane performance. Experimental section describes the preparation of PAN based membranes by optimizing some of the crucial parameters. The rejection and bubble point analysis of membranes prepared while increasing dope solution concentration suggested that the decrease in water flux is not monotonous. The membranes prepared using NMP as a solvent and dope solution concentration of $\leq$ 20.5 % offered better combination of flux and rejection as compared to membranes prepared using other solvents (DMF, DMAc and DMSO). Organic acids as additive in dope solution showed significant improvement in the performance of resulting membranes. Improved flux (up to 2.5 times) without sacrificing BSA rejection in comparison to the membranes prepared with $ZnCl_2$ as an additive demonstrated importance of organic acids additives. The properties of porous fabric (woven and non-woven) used for the preparation of supported UF membranes was shown to have significant effect on the membrane performance in terms of flux, rejection, bubble point and membrane compaction. Potential of some of above membranes was examined for water disinfection through bacteria (E. coli) rejection analysis.

Chapter 4: Surface modification of PAN based UF membranes

Introduction of this chapter reviews literature on hydrolysis aspects of PAN and its membranes, preparation of PAN based membranes with low porosity, presence of arsenic in drinking water and its removal methods. PAN membrane surface modification was done with an aim of improving water flux of resulting membranes. Some of the

results on pore size reduction were thought to be beneficial for rendering As rejection capability, while tuning initial (unmodified) membrane properties.

The hydrolysis of PAN_{15} (subscript denotes polymer concentration in the dope) membrane surface was performed by using organic and inorganic bases with an objective of enhancement in the flux. Effects of treatment mode (dead end vs cross flow), nature of base, temperature and duration of hydrolysis was assessed. Results showed that inorganic bases are better than organic bases towards improving water flux. A maximum increase in flux of 152 % was achieved by dead end mode within 20 hours, while 230 % increase could be obtained by cross flow mode within 2.5 hours at 45 °C.

The manipulation of membrane porosity for arsenic (As-V) removal by UF membranes was explored with PAN_{23} membranes. The surface hydrolysis of this membrane by NaOH offered pore size of ~ 6 kDa molecular weight cut off (MWCO). The surface modification leading to the formation of $-COO^{-}Na^{+}$ on the membrane surface caused repulsive interactions and thus pore size reduction. This membrane showed almost quantitative rejection of As-V by following Donnan exclusion principle [13]. Variation in pH was found to have a strong effect on As-rejection. To address this drawback, grafting of styrene sulfonic acid on PAN_{23} membrane surface was done. Though reduction in water flux was observed indicating reduction in porosity as that of untreated PAN_{23} membrane, inferior rejection performance indicated that more work is required to pursue this approach.

Chapter 5: ABPBI based UF membranes

This chapter begins with literature survey on solvent resistant membranes. Few available explorations on PBI as a membrane material for nanofiltration (NF) and UF applications are presented. Experimental section describes synthesis and characterization

of ABPBI, its membrane preparations and characterization methods. Effects of various parameters viz., polymer concentration, solvents and non solvents used, porous support and casting parameters (air dry time, gelation temperature) on membrane performance was studied. The stability of ABPBI membrane towards organic solvents, concentrated acid and base was evaluated. The membrane was found to be stable towards common organic solvents (DMF, DMAc, IPA, THF, chloroform, toluene and hexane), 25N H_2SO_4 and 2.5N NaOH. This excellent membrane stability could be attributed to the rigid nature and inherent material stability of ABPBI. The effect of glycerol impregnation into pores was studied in order to prevent pore collapse.

Chapter 6: Conclusions

This chapter summarizes the results obtained and conclusions of this work.

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