ULTRAFILTRATION HOLLOW FIBRE MEMBRANE BASED TAP FILTER - DRINKING WATER APPLICATION

THESIS

Submitted by

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DECLARATION BY THE SCHOLAR

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BONAFIDE CERTIFICATE

This is to certify that the project report entitled "**ULTRAFILTRATION HOLLOW FIBRE MEMBRANE BASED TAP FILTER- DRINKING WATER APPLICATION**" submitted by **LAKSHMI PRIYA N (R670215005),** to the University of Petroleum and Energy Studies, for the award of the degree of **MASTER OF TECHNOLOGY** in **Chemical Engineering with specialization in Process Design Engineering** is a bonafide record of project work carried out by her under our supervision. The results embodied in this project review report are based on the literature and the research in Technorbital Advanced Materials Pvt. Ltd. Technorbital reserves all rights to patent, publish and present the data. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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ABSTRACT

Ultrafiltration is becoming one of the more prominent and preferred technology for water treatment in recent times. Polyacrylonitrile (PAN) can undergo surface modifications easily. The hollow fiber membranes produced were of PAN. The process parameters which need to be optimized in Ultrafiltration are the Polymer concentration, Air gap distance variations, water and solvent concentration in bore side. The polymer concentration has an effect on the dope viscosity and in turn the stretching ability of the fibers. Fibers developed with a greater air gap distance, 100% water concentration in the bore fluid gave a better flux and rejection. Higher polymer concentration yielded in thinner fibers with a good cross section. Trials were carried out with spinneret plates of O.D 0.8 mm and 0.5 mm and needles of 0.2 mm and 0.3 mm. Optimum flow rates for the tap filters were around 60l/h.

The fibers and membranes will be having commercial applications as household tap filter. These filters developed will be having longer lifetime compared to existing tap filters and remove pathogens. These filters would also be cost effective hence making pure, clean drinking water easily available to all parts of under-developed and developing countries.

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INTRODUCTION

1. Introduction

Safe drinking water is essential for life and a primary human right. 70% of the Earth's surface is covered with water out of which 97.2% is saline water and 2.8% is fresh water. Two thirds of this fresh water is trapped frozen in glaciers and polar ice caps. The remaining one third is available for consumption to all humans in the form of rivers, lakes, ponds, etc. Despite being a renewable resource, the supply of fresh water especially groundwater is constantly decreasing.

Drinking water, also known as ***potable water*** or improved drinking water is that which is fit for consumption and without causing any health issues [19]. Every individual's drinking water requirement varies depending on factors like age, gender, physical activity, health and environmental conditions. This requirement varies from one to sixteen liters per day.

Due to pollution of various fresh water resources, access to clean drinking water is not easily available to all human beings. The water from the source is directly tapped or transported to the required destinations through the form of pipelines.

Water contamination leads to more than half a million deaths per year. Some of the common health hazards which are a result of water contamination or pollution are cholera, typhoid, diarrhea, fluoride and arsenic poisoning [20]. For safe consumption of water, it must undergo proper treatment and meet drinking water regulations. This gave rise to the concept of ***water purification***.

Water treatment is any process that makes the water acceptable for a specific end-use. The use may be industrial, drinking, irrigation, recreation and many other uses including safe discharge back to the environment. Treatment removes or reduces concentration of contaminants to make it fit for the end-use.

Drinking water treatment requires removing pollutants from the raw water to yield pure water fit for human consumption. Suspended solids, bacteria, algae, viruses, fungi and minerals such as iron and manganese are removed during treatment. The choice of water treatment depends on the quality of the water being treated, the cost of the treatment process and the quality standards expected of the processed water.

1.1 Water Quality

The physical, chemical, biological and radiological attributes of water describes its quality. It is used by reference to a set of standards by which compliance can be assessed, e.g. health of ecosystems, safety of human contact and drinking water.[19]

Drinking water quality describes the quality parameters set for drinking water. Most of the developed countries have their own water quality standards, e.g. Europe has the European Drinking Water Directive, United States has the United States Environmental Protection Agency (EPA), and in India it is the Indian Council of Medical Research (ICMR). For countries without a legislative and administrative framework for such standards, the World Health Organization (WHO) publishes guidelines on the standards that should be achieved.

Parameters for drinking water quality fall under these categories:

Physical- turbidity, Total Suspended Solids (TSS), color, and odor

Chemical- pH, heavy metals, COD, BOD, nitrates, and phosphates

Microbiological- E. coli, bacteria, viruses and other pathogens
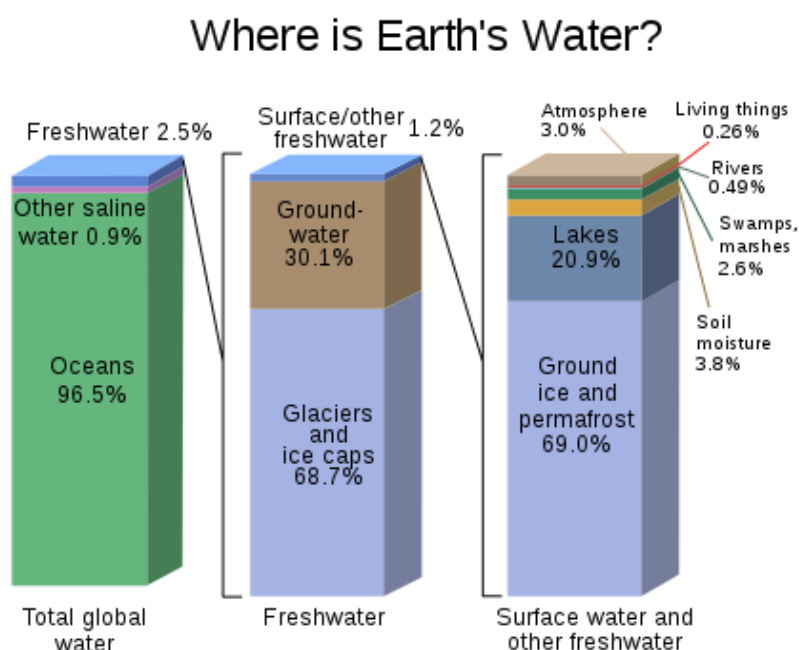
Figure 1: A graphical distribution of the locations of water on Earth

Table 1 Comparison of a selection of parameters for concentrations by WHO, the European Union, EPA and Ministry of Environmental Protection of China [22]

Parameter	World Health Organization	European Union	United States	China
Acrylamide	"	0.10 µg/l	"	"
Arsenic	10µg/l	10 µg/l	10µg/l	50µg/l
Antimony	ns	5.0 µg/l	6.0 µg/l	"
Barium	700µg/l	ns	2 mg/L	"
Benzene	10µg/l	1.0 µg/l	5 µg/l	"
Benzo(a)pyrene	"	0.010 µg/l	0.2 µg/l	0.0028 µg/l
Boron	2.4mg/l	1.0 mg/L	"	"
Bromate	"	10 µg/l	10 µg/l	"
Cadmium	3 µg/l	5 µg/l	5 µg/l	5 µg/l
Chromium	50µg/l	50 µg/l	0.1 mg/L	50 µg/l (Cr6)
Copper	"	2.0 mg/l	TT	1 mg/l
Cyanide	"	50 µg/l	0.2 mg/L	50 µg/l
1,2-dichloroethane	"	3.0 µg/l	5 µg/l	"
Epichlorohydrin	"	0.10 µg/l	"	"
Fluoride	1.5 mg/l	1.5 mg/l	4 mg/l	1 mg/l
Lead	"	10 µg/l	15 µg/l	10 µg/l
Mercury	6 µg/l	1 µg/l	2 µg/l	0.05 µg/l
Nickel	"	20 µg/l	"	"
Nitrate	50 mg/l	50 mg/l	10 mg/L (as N)	10 mg/L (as N)
Nitrite	"	0.50 mg/l	1 mg/L (as N)	"
Pesticides (individual)	"	0.10 µg/ l	"	"
Pesticides — Total	"	0.50 µg/l	"	"
Polycyclic aromatic hydrocarbons I	"	0.10 µg/	"	"
Selenium	40 µg/l	10 µg/l	50 µg/l	10 µg/l
Tetrachloroethene and Trichloroethene	40µg/l	10 µg/l	"	"

1.1.1 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) are a measure of the joined substance of all inorganic and natural substances contained in a fluid in sub-atomic, ionized or small scale granular (colloidal sol) suspended shape. For the most part the operational definition is that the solids must be sufficiently little to survive filtration through a channel with two-micrometer (ostensible size or littler) pores. Add up to broke down solids are ordinarily talked about just for freshwater frameworks, as saltiness incorporates a portion of the particles constituting the meaning of TDS. The vital utilization of TDS is in the

investigation of water quality for streams, waterways and lakes, in spite of the fact that TDS is not by and large considered an essential contamination (e.g. it is not esteemed to be related with wellbeing impacts) it is utilized as a sign of tasteful qualities of drinking water and as a total pointer of the nearness of a wide cluster of concoction contaminants.

Total dissolved solids are differentiated from total suspended solids (**TSS**), in that the last can't go through a strainer of two micrometers but are inconclusively suspended in arrangement. The expression "settle-able solids" alludes to material of any size that won't stay suspended or broken down in a holding tank not subject to movement, and prohibits both TDS and TSS. Settle-able solids may incorporate bigger particulate matter or insoluble particles. Water can be classified by the level of TDS in the water:

Fresh water: less than 500 mg/L TDS=500 ppm

Brackish water: 500 to 30,000 mg/L TDS=500-30 000 ppm

Saline water: 30,000 to 40,000 mg/L TDS=30 000-40 000 ppm

Hyper saline: greater than 40,000 mg/L TDS>=40 000 ppm

TDS Measurement

The two foremost strategies for measuring complete broke up solids are gravimetric examination and conductivity. Gravimetric techniques are the most exact and include dissipating the fluid dissolvable and measuring the mass of buildups left. This technique is by and large the best, despite the fact that the time has come devouring. On the off chance that inorganic salts contain the colossal larger part of TDS, gravimetric strategies are suitable.

Electrical conductivity [21] of water is specifically identified with the grouping of broke up ionized solids in the water. Particles from the broke up solids in water make the capacity for that water to lead an electric ebb and flow, which can be measured utilizing an ordinary conductivity meter or TDS meter. At the point when corresponded with lab TDS estimations, conductivity gives an inexact incentive to the TDS fixation, for the most part to inside 10% precision.

The relationship of TDS and specific conductance of groundwater can be approximated by the following equation:

TDS = k_eEC

where TDS is expressed in mg/L and EC is the electrical conductivity in microsiemens per centimeter at 25 °C. The correlation factor k_e varies between 0.55 and 0.8.

1.2 Water Purification and Treatment

Water treatment is any procedure that makes water more worthy for a particular end-utilize. The end utilize might drink, modern water supply, water system, waterway stream upkeep, water entertainment or numerous different uses, including being securely come back to nature. Water treatment expels contaminants and undesirable segments, or lessens their focus so that the water ends up plainly fit for its coveted end-utilize.

Treatment for *drinking water* creation includes the expulsion of contaminants from crude water to deliver water that is sufficiently immaculate for human utilization with no here and now or long haul danger of any unfavorable wellbeing impact. Substances that are expelled amid the way toward drinking water treatment incorporate suspended solids, microscopic organisms, green growth, infections, parasites, and minerals, for example, iron and manganese.

The procedures required in evacuating the contaminants incorporate physical procedures, for example, settling and filtration, substance procedures, for example, sanitization and coagulation and organic procedures, for example, moderate sand filtration.

Measures taken to guarantee water quality not just identify with the treatment of the water, however to its movement and dissemination after treatment. It is accordingly regular practice to keep leftover disinfectants in the treated water to murder bacteriological pollution amid conveyance.

The techniques utilized incorporate physical procedures, for example, filtration, sedimentation, and refining; natural procedures, for example, moderate sand channels or organically dynamic carbon; substance procedures, for example, flocculation and chlorination and the utilization of electromagnetic radiation, for example, ultraviolet light.

1.2.1 Aim of Purification

The points of the treatment are to evacuate undesirable constituents [23] in the water and to make it safe to drink or fit for a particular reason in industry or restorative applications. Broadly differed strategies are accessible to evacuate contaminants like fine solids, miniaturized scale living beings and some broke up inorganic and natural materials, or ecological tenacious pharmaceutical toxins. The decision of strategy will rely on upon the nature of the water being dealt with, the cost of the treatment procedure and the quality guidelines expected of the handled water.

The processes below are the ones commonly used in water purification plants. Some or most may not be used depending on the scale of the plant and quality of the raw (source) water.

1. *Pre-treatment*

   i.   Pumping and containment
   ii.   Screening
   iii. Storage
   iv.   Pre-chlorination
   v.   pH Adjustment
   vi.   Coagulation and Flocculation
   vii. Sedimentation
   viii. Sludge Storage and Removal
   ix.   Floc blanket clarifiers
   x.   Dissolved air flotation
   xi.   Filtration
   xii. Rapid sand filters
   xiii. Slow sand filters

2. *Membrane filtration*

Membrane filters are generally utilized for sifting both drinking water and sewage. For drinking water, film channels can evacuate essentially all particles bigger than 0.2 μm—including giardia and cryptosporidium. Layer channels are a successful type of tertiary treatment when it is coveted to reuse the water for industry, for constrained residential purposes, or before releasing the water into a waterway that is utilized by towns encourage downstream. They are broadly utilized as a part of industry, especially for refreshment

planning (counting filtered water). However no filtration can evacuate substances that are really disintegrated in the water, for example, phosphorus, nitrates and overwhelming metal particles.

3. *Removal of ions and other dissolved substances*

Ultrafiltration membranes utilize polymer layers with synthetically framed infinitesimal pores that can be utilized to sift through broken down substances staying away from the utilization of coagulants. The sort of layer media decides how much weight is expected to drive the water through and what sizes of smaller scale life forms can be sifted through.

Ion exchange: Ion exchange systems use ion exchange resin- or zeolite-packed columns to replace unwanted ions. The most common case is softening consisting of removal of Ca^{2+} and Mg^{2+} ions replacing them with benign (soap friendly) Na^+ or K^+ ions. Ion exchange resins are also used to remove toxic ions such as nitrite, lead, mercury, arsenic and many others.

Precipitative softening: Water rich in hardness (calcium and magnesium ions) is treated with lime (calcium oxide) and/or soda-ash (sodium carbonate) to precipitate calcium carbonate out of solution utilizing the common-ion effect.

Electrodeionization: Water is passed between a positive electrode and a negative electrode. Ion exchange membranes allow only positive ions to migrate from the treated water toward the negative electrode and only negative ions toward the positive electrode. High purity de-ionized water is produced continuously, similar to ion exchange treatment. Complete removal of ions from water is possible if the right conditions are met. The water is normally pre-treated with a reverse osmosis unit to remove non-ionic organic contaminants, and with gas transfer membranes to remove carbon dioxide. A water recovery of 99% is possible if the concentrate stream is fed to the RO inlet.

1.3 Ultrafiltration

Ultrafiltration (UF) is a type of membrane filtration in which hydrostatic pressure forces a liquid against a semipermeable membrane. A semipermeable membrane is a thin layer of material capable of separating substances when a driving force is applied across the membrane. Once considered a viable technology only for desalination, membrane processes are increasingly employed for removal of bacteria and other microorganisms, particulate material, and natural organic material, which can impart colour, tastes, and odours to the water and react with disinfectants to form disinfection by-products (DBP).

Applications of Ultrafiltration

Ventures, for example, synthetic and pharmaceutical assembling, sustenance and drink handling, and waste water treatment, utilize ultrafiltration with a specific end goal to reuse stream or increase the value of later items. Blood dialysis additionally uses ultrafiltration.

Drinking water

UF can be used for the removal of particulates and macromolecules from raw water to produce potable water. It has been used to either replace existing secondary (coagulation, flocculation, sedimentation) and tertiary filtration (sand filtration and chlorination) systems employed in water treatment plants or as standalone systems in isolated regions with growing populations. When treating water with high suspended solids, UF is often integrated into the process, utilising primary (screening, flotation, filtration) and some secondary treatments as pre-treatment stages. UF processes are currently preferred over traditional treatment methods for the following reasons:

No chemicals required (aside from cleaning)

Constant product quality regardless of feed quality

Compact plant size

Capable of exceeding regulatory standards of water quality, achieving 90-100% pathogen removal

UF processes are currently limited by the high cost incurred due to membrane fouling and replacement. Additional pre-treatment of feed water is required to prevent excessive damage to the membrane units.

In many cases UF is used for pre filtration in reverse osmosis (RO) plants to protect the RO membranes.

Other applications of Ultrafiltration:

- Filtration of effluent from paper pulp mill
- Protein concentration
- Cheese manufacture, see ultrafiltered milk
- Removal of pathogens from milk
- Process and waste water treatment
- Enzyme recovery
- Fruit juice concentration and clarification
- Dialysis and other blood treatments
- Desalting and solvent-exchange of proteins (via diafiltration)
- Laboratory grade manufacturing
- Membrane Fouling

Membrane fouling- is a process whereby, a solution or a particle is deposited [13] on a membrane surface or in membrane pores so that the membrane's performance is degraded.

Membrane fouling can cause severe flux decline and affect the quality of the water produced. Severe fouling may require intense chemical cleaning or membrane replacement. This increases the operating costs of a treatment plant. There are various types of foulants: colloidal (clays, flocs), biological (bacteria, fungi), organic (oils, polyelectrolytes, humics) and scaling (mineral precipitates).

Fouling can be separated into reversible and irreversible fouling in view of the connection quality of particles to the film surface. Reversible fouling can be evacuated by a solid shear compel or discharging. Development of a solid network of fouling layer with the solute amid a ceaseless filtration process will bring about reversible fouling being changed into an irreversible fouling layer. Irreversible fouling is the solid connection of particles which can't be evacuated by physical cleaning.

Measurement

Flux, transmembrane pressure (TMP), Permeability and Resistance are the best indicators of membrane fouling. Under constant flux operation, TMP increases to compensate for the fouling. On the other hand, under constant pressure operation, flux declines due to membrane fouling.

Types of Fouling

The following models describe the mechanisms [13] of particulate deposition on the membrane surface and in the pores:

Standard blocking: macromolecules are uniformly deposited on pore walls

Complete blocking: membrane pore is completely sealed by a macromolecule

Cake filtration: accumulated particles or macromolecules form a fouling layer on the membrane surface, in UF this is also known as a gel layer

Intermediate blocking: when macromolecules deposit into pores or onto already blocked pores, contributing to cake formation

Scaling

As a result of concentration polarization at the membrane surface, increased ion concentrations may exceed solubility thresholds and precipitate on the membrane surface. These inorganic salt deposits can block pores causing flux decline, membrane degradation and loss of production. The formation of scale is highly dependent on factors affecting both solubility and concentration polarization including pH, temperature, flow velocity and permeation rate.

Biofouling

Microorganisms will adhere to the membrane surface forming a gel layer – known as biofilm. The film increases the resistance to flow, acting as an additional barrier to permeation. In spiral-wound modules, blockages formed by biofilm can lead to uneven flow distribution and thus increase the effects of concentration polarization.

Membrane Arrangements

Depending on the shape and material of the membrane, different modules can be used for ultrafiltration process. Commercially available designs in ultrafiltration modules vary according to the required hydrodynamic and economic constraints as well as the mechanical stability of the system under particular operating pressures. The main modules used in industry include:

1. *Tubular modules*

The tubular module design uses polymeric membranes cast on the inside of plastic or porous paper components with diameters typically in the range of 5 – 25 mm with lengths from 0.6 - 6.4 m. multiple tubes are housed in a PVC or steel shell. The feed of the module is passed through the tubes, accommodating radial transfer of permeate to the shell side. This design allows for easy cleaning however the main drawback is its low permeability, high volume hold-up within the membrane and low packing density

2. *Hollow fibre*

This design is conceptually similar to the tubular module with a shell and tube arrangement. A single module can consist of 50 to thousands of hollow fibres and therefore are self-supporting unlike the tubular design. The diameter of each fibre ranges from 0.2 – 3 mm with the feed flowing in the tube and the product permeate collected radially on the outside. The advantage of having self-supporting membranes as is the ease at which it can be cleaned due to its ability to be backflushed. Replacement costs however are high, as one faulty fibre will require the whole bundle to be replaced. Considering the tubes are of small diameter, using this design also makes the system prone to blockage.

Figure 2 Sample Hollow Fiber Membrane module. [source: Patu Nl,2009]

3. *Spiral-wound modules*

These are composed of a combination of flat membrane sheets separated by a thin meshed spacer material which serves as a porous plastic screen support. These sheets are rolled around a central perforated tube and fitted into a tubular steel pressure vessel casing. The feed solution passes over the membrane surface and the permeate spirals into the central collection tube. Spiral-wound modules are a compact and cheap alternative in ultrafiltration design, offer a high volumetric throughput and can also be easily cleaned. However it is limited by the thin channels where feed solutions with suspended solids can result in partial blockage of the membrane pores.
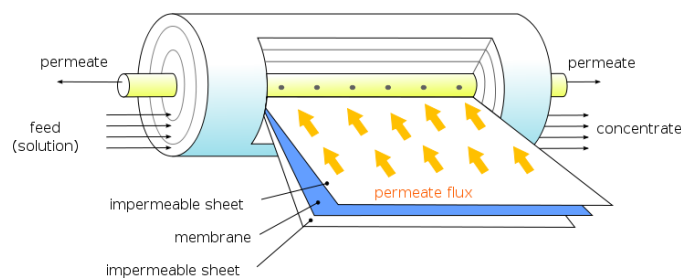
Figure 3 Typical Spiral-wound Module
[source:Daniele Pugilesi,2008]

Plate and frame

This uses a membrane placed on a flat plate separated by a mesh like material. The feed is passed through the system from which permeate is separated and collected from the edge of the plate. Channel length can range from $10 - 60$ cm and channel heights from $0.5 - 1$ mm. This module provides low volume hold-up, relatively easy replacement of the membrane and the ability to feed viscous solutions because of the low channel height, unique to this particular design.

Process Characteristics

The process characteristics [6] of a UF system are highly dependent on the type of membrane used and its application. Manufacturers' specifications of the membrane tend to limit the process to the following typical specifications:

Table 2 Comparison of Process Characteristics for different systems

[source: J. G. Jacangelo et al. (1997)]

	Hollow Fibre	Spiral-wound	Ceramic Tubular
pH	2-13	2-11	3-7
Feed Pressure (psi)	9-15	<30-120	60-100
Backwash Pressure (psi)	9-15	20-40	10-30
Temperature (°C)	5-30	5-45	5-400
Total Dissolved Solids (mg/L)	<1000	<600	<500
Total Suspended Solids (mg/L)	<500	<450	<300
Turbidity (NTU)	<15	<1	<10
Iron (mg/L)	<5	<5	<5
Oils and Greases (mg/L)	<0.1	<0.1	<0.1
Solvents, phenols (mg/L)	<0.1	<0.1	<0.1

Existing tap filters are based on activated carbon, iodine resins and microfiltration. The limitation with the existing technology is that while it removes certain range of bacteria, germs, dirt and smell it doesn't remove viruses, color and odor completely. Another limitation is the short lifetime of the filters which are about 3-6 months.

CHAPTER 2

LITERATURE REVIEW

H.R.Lokhare et al.[1] studied the surface modification of Polyacrylonitrile (PAN) based Ultrafiltration membrane. This membrane was prepared by phase inversion method and with zinc chloride as an additive. The surface modification was studied using ethanolamine, triethylamine, sodium hydroxide and potassium hydroxide solutions.

They also investigated the effect of base treatment time and temperature on water flux and rejection. It was found that the membranes exhibited swelling by NaOH treatment followed by deswelling by HCl post-treatment, similar to pH responsive membranes. The treatment by organic as well as inorganic bases improved water flux with a slight lowering in BSA rejection by dead-end mode type treatment. A 230% increase in water flux was achieved by sodium hydroxide treatment in cross-flow mode without a noticeable pore swelling by SEM. The contact angle of the modified membranes was decreased as compared to the unmodified one indicating appreciable surface modification. As the treatment time or temperature increased, the ESCA analysis showed increased population of Na-carboxylate groups.
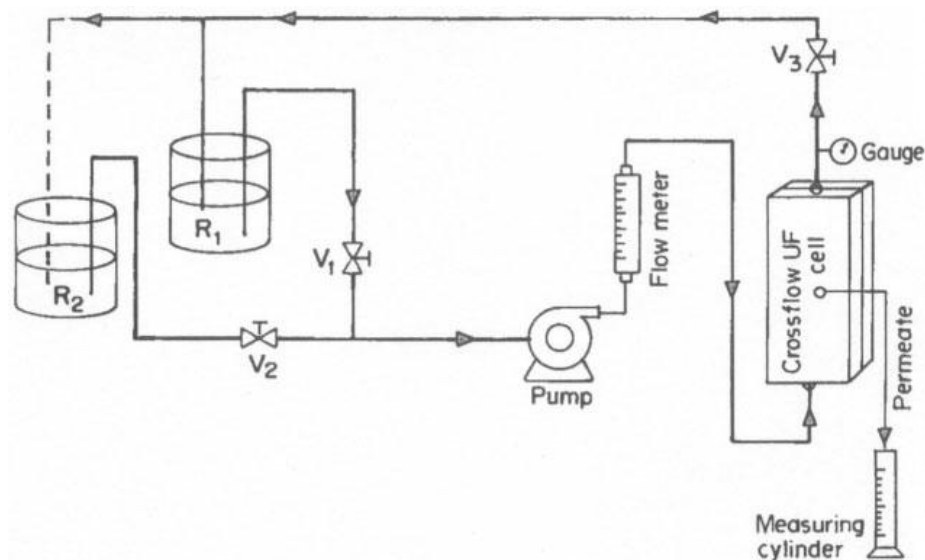

Figure 4 Schematics of the Cross-flow setup [1]

They concluded that an increase in the water flux was achieved by surface treatment of PAN membranes either by organic bases (TEA, EA) or by inorganic bases (NaOH, KOH). The inorganic bases were found to be more effective. The morphological changes leading to large pore size variations were not evident from the different flux behaviour offered by NaOH and post-HCl treatment. This also shows that the PAN surface modification has a potential to offer membranes that are pH responsive. The SEM also depicted absence of noticeable changes in membrane pore size. The treatment by crossflow mode was more effective than by dead-end mode. A maximum increase of 152% in water flux was achieved by dead end mode within 20 h, while crossflow offered maximum increase of 230% in just 2.5 h duration at 45°C. The extent of percent change in water flux was highly dependant on treatment mode (dead-end or crossflow) and treatment temperature. The variations in BSA rejection and water flux are attributed mainly to the surface hydrophilicity. This investigation shows that the optimum surface modification of PAN membrane by bases can lead to a large improvement in the water flux, without causing pore swelling.

Ulhas Kharul et al. worked [2] on the optimization of preparation parameters of an Ultrafiltration membrane. They prepared supported ultrafiltration (UF) membranes based on poly(acrylonitrile) while varying crucial parameters responsible for controlling membrane porosity like polymer concentration, solvent and additives in the dope solution. AFM, SEM, water flux, solute rejection, bubble point and pore size distribution analyses were carried out to obtain data on the membrane porosity and morphology . It was found that merely increasing polymer concentration does not necessarily reduce pore size of membranes. Among four solvents used for the dope solution preparation, N-methyl pyrrolidone was found to offer membranes with optimal combination of flux and rejection of various solutes. Some of the PAN17 (17% w/w PAN concentration in the dope solution) membranes prepared using organic acid as the additive (citric acid, tartaric acid or maleic acid) offered 1.2–1.7 times higher flux than the membrane prepared using inorganic salt, ZnCl2 as an additive. The porosity of PAN17 membrane prepared using CA as an additive was larger as compared to membrane prepared using ZnCl2 as an additive. Atomic force microscopy (AFM) analysis of this membrane exhibited higher surface roughness as compared to the ZnCl2 based membrane. Both these membranes exhibited bacteria (E. Coli) log reduction value (LRV) of at least 6; depicting applicability of these membrane for

water disinfection. With increase in the polymer concentration, though the viscosity of the dope solution was increased and water flux decreased as could be anticipated, these variations were not monotonous. Bubble point measurement of these membranes revealed that till the dope solution concentration of 20.5%, the size of largest pore decreased with increase in the dope solution concentration. Beyond this concentration of the dope, the pore size again increased, which could be due to the delayed gelation as a result of very high viscosity. Membranes prepared using 17% PAN concentration in the dope solution (PAN17) exhibited a good combination of flux and rejection of different solutes. Though at higher dope concentration, effect of solvent used for making dope solution was negligible, at lower concentrations (15, 18.5 and 20.5%), NMP as the dope solvent offered membranes with better control on flux and rejection of different solutes. PAN17 membrane prepared with citric acid as an additive offered 1.7 times higher water flux than ZnCl2 as an additive, exhibiting similar BSA rejection. The pore size distribution analysis revealed that the surface porosity of the earlier type of membrane was 1.48%, while that of later, it was just 0.9%, resulting in a large variation in water flux. With a bacteria (E. Coli) load of 106 CFU/ml, log reduction value was found to be 6 with both these types of membranes. Thus, systematic variations in membrane preparation parameters resulted into a membrane prepared with NMP as a solvent, citric acid as an additive and 17% PAN in the dope solution; which offered excellent combination of water flux, BSA and bacteria rejection. Some of these membranes could be used for water disinfection, owing to their high fluxes and adequate rejection performances.

H. R. Lokhare et al. studied [4] the applicability of PAN-based negatively charged ultrafiltration (UF) membrane for effective arsenic removal. The hydrolysis of

PAN-based UF membrane surface by NaOH leading to the formation of carboxylate(COO−) groups and reduction in initial pore size rendered As-V rejection capability by Donnan exclusion principle. A lowering in pore size was indicated by the reduction in water flux and elevation in rejection of protein and polyethylene glycol (PEG). NaOH treatment leading to formation of carboxylate group on the membrane surface was indicated by FTIR-ATR, while contact angle measurement indicated increased hydrophilicity. This treatment rendered membrane surface smoothening as confirmed by SEM and AFM analyses. The molecular weight cut off after the NaOH treatment was found to be 6 kDa. The rejection of pentavalent arsenic (As-V) by these surface modified

membranes was studied with different feed concentration, crossflow velocity, pressure, temperature and pH. Experiments with 50 ppb As-V in feed showed that arsenic rejection was close to 100% and remained constant up to 6 h. Feed sample concentration of 1000 ppb and

50ppm of As-V showed >95% rejection at pH 7 and room temperature, but for 1000ppm feed concentration; the rejection was 40–65%. For concentrations ≤50ppm of arsenic in the feed, the rejection coefficient was not dependent on cross-flow velocity or transmembrane pressure. The rejection for 1000ppm concentration of As-V varied from 40 to 65% with variation in the cross-flow velocity and transmembrane pressure as the concentration polarization was important.

T.S. Chung et al. worked on developing the governing equations to describe the velocity profile of nascent hollow [3] fiber during formation in the air gap region and to predict the fiber dimension as a function of air- gap distance. They have related the velocity profile of the nascent hollow fiber membrane as a function of gravity, mass transfer, surface tension, drag forces, spinning stress and rheological parameters of spinning solutions. The effects of air-gap distance or spin-line stress on nascent fibre morphology, gas performance, and mechanical and thermal properties can be qualitatively explained by our mathematical equations. In short, the spin-line stresses have positive or negative effects on membrane formation and separation performance. A high elongational stress may pull molecular chains or phase separated domains apart in the early stage of phase separation and creates porosity, whereas a medium stress may induce molecular orientation and reduce membrane porosity or free volume. As a result, glass transition temperature (*Tg*) of dry-jet wet-spun fibres may be lower than that of wet spun fibres, and *Tg* decreases with an increase in air-gap distance. This conclusion is valid no matter whether the selective layer is located in either the inner or outer skin.

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals

Proprietary grade Polyacrylonitrile (PAN) was manufactured at Technorbital, Kanpur; N, N-dimethylformamide (DMF) was obtained from Mumbai;RO Water was processed and obtained at Technorbital, Kanpur;Disodium Hydrogen Phosphate (Na_2HPO_4) was purchased from Avantor Performance Materials Ltd. Thane; Citric Acid was purchased from Thomas Baker Mumbai.

3.2 Equipments and Instruments

The various equipments used for the experiments were

    i.   Conical Flask
    ii.   Weigh Balance
    iii.   Glass Rod
    iv.   Microscope (Magnus-MSZ)
    v.   Vacuum Oven
    vi.   Petri Dish
    vii.   Needle (0.3 mm, 0.2 mm)
    viii.   Spinneret
    ix.   Measuring Cylinder
    x.   UV Spectrophotometer (Shimazdu UV-1800)

3.3 Procedure

Spinning

The required tubing for spinning is properly cleaned and installed. Pressurized air is passed through the tubes to check for leaks and ensure air tight fittings. The spinneret parts were cleaned, dried and assembled. Centering of the spinneret needle was done with the help of a microscope. The spinnerets are then installed firmly in their slots on the spinning machine. The dope kettle is then pressurized to start the dope flow. This line is primed for

a few minutes and the connected to the spinneret. Once the dope starts to flow from the spinneret orifice, the bore fluid line is connected to the spinneret too to start the bore fluid flow immediately. The bore fluid back pressure is set high initially to prevent the needle from getting blocked. The fiber is drawn at free fall; after which the dope pressure is increased simultaneously with draw speed; while the back pressure is decreased. The fiber is then examined for any roughness along the length and its cross-section studied under a microscope. If found being smooth along its length and possessing symmetric cross-section, the fibers are collected over the winder.

Module Making

The collected fiber bundles are cured in water for 24 hours at room temperature. The fibers then undergo post-treatment. They are centrifuged for 30 seconds after post-treatment to remove any excess water. The potting end of the fiber bundle is dried with a blower for another 30 seconds. Damaged fibers (if any) are removed from the bundle. The modules are potted using epoxy. Potting refers to forming a tube sheet around a fibre bundle end, in which the walls of the said mould, used to form a tube sheet, become a mechanical element in the pressure module assembly.The potting room, is maintained at a temperature of 30°C. Once the epoxy cures the block is cut to open the fiber ends. The modules are set for curing for 3-4 days at 30°C.

Leak Test and Repotting

The fully cured modules are completely soaked in water to wet the fibers. Excess water is removed and air is passed through one end at a particular pressure. The potting end is immersed in water and inspected for bubbles. The leaks (if any) are marked and repotting is done using epoxy glue. This glue is inserted into the leaks with the help if a syringe. After 24 hours, the leak test is again performed on these modules to endure proper potting.

Process Parameters

The various parameters that were varied during the hollow fiber spinning trial were

1. Polymer Concentration:
   - 15.5 %
   - 14 %
2. Air Gap Distance Variations:
   i. 3.5 cm

    ii.   5 cm

   iii.   7 cm

3. Water concentration in bore fluid:

   - 100 %

   - 87 %

   - 70 %

4. DMF concentration in bore fluid:

   - 0%

   - 13%

   - 30%

5. Viscosity of dope varying from 10.6 s- 25 s

6. Take up velocity : 8.5m/min -27 m/min

7. Spinneret Temperature: 25°-30°C

8. Dope Pressure varying from 40-60 psi

9. Bore fluid back pressure varying from 5.75-29.87 psi

10. Spinneret OD/ID

    - 0.8mm/0.3mm

    - 0.5mm/0.3mm

    - 0.8mm/0.2mm

11. External coagulant : RO water

12. Temperature : 25°-30° C

BSA Rejection analysis of Membrane modules

- **Preparation of Buffer solution**

The McIlavaine buffer is used for the preparation of BSA solution that is to be used for the rejection analysis of membranes. The buffer solution is prepared as follows

i.   In a 2 L conical flask, insert a magnetic needle; add 56.78 g of Na_2HPO_4 and 2 L of distilled water, stir on a magnetic stirrer till the entire solid is dissolved.

ii.   In another 2 L conical flask, insert a magnetic needle; add 4.8031 g of citric acid and 250 ml of distilled water. Stir it on a magnetic stirrer till the entire solid is dissolved.

iii. In a separate conical flask of 2 L capacity , insert a magnetic needle, add 1845ml of Na_2HPO_4 solution and 155ml of citric acid solution as prepared above; stir well for 20 minutes.

iv. Check pH of the solution by pH meter. The pH must be 7.5, if not, adjust by addition of few drops of citric acid or Na_2HPO_4 solution, as necessary.

v. Store 5ml of buffer solution in a conical flask, stopper it. Use this solution as a reference during UV analysis.

- **Preparation of 0.1% BSA solution**

In a 2 l conical flask, insert a magnetic needle, 2g of BSA and 2 l of buffer solution as prepared in section 1.1 above, stir for 20 minutes or till the BSA dissolves completely.

- **BSA Rejection**

i. For a particular module, BSA rejection can be done either by 'out-to-in' or 'in-to-out' mode. Use the same assembly and operation protocol as used for the water flux measurement; except instead of water, use the BSA solution as prepared in the above section 1.2.

ii. BSA has a tendency to get adsorbed on the membrane surface. Thus it is very crucial to attain 1 bar pressure very quickly as compared to water flux analysis. Collect approximately 5ml of the permeate sample in a weighed, clean and dry test tube. Similarly collect approximately 5ml of the feed sample from the reservoir in another clean and dry test tube. From the known weight of the permeate tube, exact weight of the permeate sample can be determined to calculate BSA flux in $l.m^{-2}.h^{-1}$.

iii. Record absorbance of the feed BSA solution using UV spectrophotometer at wavelengths of 260 and 280 nm. Use the buffer solution as the reference. Calculate the concentration(C_F) of the BSA present in the feed solution using the following equation

$C_F= (A_{280}*1.55)-(A_{260}*0.76)$

iv. Similarly find out the UV absorbance of the permeate solution. Calculate the BSA concentration in the permeate sample Cp using the above equation.

v. From the concentration of BSA in the feed and permeate sample , calculate the BSA rejection 'R' (%) using the following equation

$R (\%) = (1-(Cp/C_F))*100$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Flux Testing

Water Flux analysis was carried out on the various membrane modules and the results are tabulated.

Flux (J) = Q_p/A_m; $Lm^{-2}h^{-1}$

Where,

Q_p – filtrate flow rate through the membrane (l/h)

A_m- surface area of the membrane (m^2)

Actual weight [i] (g) = Weight of beaker[i] – Empty weight of beaker[i]

Empty weight of beaker 1: 51.85 g

Empty weight of beaker 2: 51.9 g

Table 3 Flux data for trial 1

S.No.	Module Date	Air Gap (cm)	Active Length (m)	% Water Concentration in bore	No. of Fibres	wt. of beaker 1 (g)	Time taken for beaker 1 (s)	Actual wt. 1 (g)	Wt. of beaker 2 (s)	Time taken for beaker 2 (s)	Actual wt. 2 (g)	LMH
1.	28/12/2016	5.0	0.085	100	140	153.24	27.22	101.39	184.74	33.13	132.84	620.98
2.	28/12/2016	5.0	0.075	100	120	132.18	32.56	80.33	141.73	37.79	89.83	514.25
3.	09/12/2016	3.5	0.08	87	130	102.38	54.72	50.53	114.72	69.12	63.02	168.59
4.	09/12/2016	3.5	0.075	87	100	82.33	78.72	30.48	87.59	93.47	35.69	97.97
5.	08/12/2016	5.0	0.07	87	60	88.72	84.69	36.87	83.8	74.9	31.9	195.92

Empty weight of beaker 1: 38.62 g

Empty weight of beaker 2: 34.74 g

Table 4 Flux data for trial 2

S.No.	Module Date	Air Gap (cm)	Active Length (m)	% Water Concentration in bore	No. of Fibres	wt. of beaker 1 (g)	Time taken for beaker 1 (s)	Actual wt. 1 (g)	Wt. of beaker 2 (s)	Time taken for beaker 2 (s)	Actual wt. 2 (g)	LMH
1.	28/12/2016	3.5	0.095	100	780	219.49	10.46	180.87	288.91	15.58	254.17	433.29

Empty weight of beaker 1: 39.47 g

Empty weight of beaker 2: 34.44 g

Table 5 Flux data for trial 3

S.No.	Module Date	Air Gap (cm)	Active Length (m)	% Water Concentration in bore	No. of Fibres	wt. of beaker 1 (g)	Time taken for beaker 1 (s)	Actual wt. 1 (g)	Wt. of beaker 2 (s)	Time taken for beaker 2 (s)	Actual wt. 2 (g)	LMH
1.	07/12/2016	3.5	0.08	100	160	165.35	75.41	125.88	164.14	75.9	129.7	252.15
2.	07/01/2017	3.5	0.075	100	110	176.7	73.25	137.23	172.18	71.72	137.74	421.29
3.	07/01/2017	3.5	0.08	100	120	175.75	84.65	136.28	163.03	80.31	128.59	340.88
4.	07/01/2017	5.0	0.10	100	420	275.06	21.94	235.59	238.22	20.76	203.78	467.56
5.	06/01/2017	5.0	0.10	100	360	246.5	28.53	207.03	231.05	29.44	196.61	369.82

Empty weight of beaker 1: 33.6 g

Empty weight of beaker 2: 33.91 g

Table 6 Flux data for trial 4

S.No.	Module Date	Air Gap (cm)	Active Length (m)	% Water Concentration in bore	No. of Fibres	wt. of beaker 1 (g)	Time taken for beaker 1 (s)	Actual wt. 1 (g)	Wt. of beaker 2 (s)	Time taken for beaker 2 (s)	Actual wt. 2 (g)	LMH
1.	10/01/2017	3.5	0.08	87	160	164.08	66.66	130.48	173.46	68.58	139.55	297.98
2.	09/01/2017	5.0	0.07	87	180	181.26	58.66	147.66	176.43	62.22	142.52	364.56
3.	10/01/2017	3.5	0.10	87	380	218.96	45.63	185.36	214.11	47.47	180.2	237.09
4.	10/01/2017	3.5	0.10	87	400	198	40.34	164.4	187.83	36.59	153.92	197.82

Empty weight of beaker 1: 38.23 g

Empty weight of beaker 2: 33.92 g

Table 7 Flux data for trial 5

S.No.	Module Date	Air Gap (cm)	Active Length (m)	% Water Concentration in bore	No. of Fibers	wt. of beaker 1 (g)	Time taken for beaker 1 (s)	Actual wt. 1 (g)	Wt. of beaker 2 (s)	Time taken for beaker 2 (s)	Actual wt. 2 (g)	LMH
1.	11/01/2017	5.0	0.08	70	153	127.4	92.22	89.17	125.50	98.72	91.58	177.46
2.	06/01/2017	5.0	0.07	100	130	125.17	43.16	86.94	125.05	50.27	91.13	482.18
3.	NCL Fibers		0.11		115	81.82	119.28	43.59	76.58	110	42.66	113.78
4.	NCL Fibers		0.09		124	72.71	80.22	34.48	74.93	76.91	41.01	164.89

Table 8 BSA Rejection Data

S.No.	Module Date	Air gap (cm)	Feed Wavelength (nm)		Permeate Wavelength (nm)		C_f	C_p	Rejection (%)
			A_{280}	A_{260}	A_{280}	A_{260}			
1.	09/12/2016	3.5	0.636	0.508	0.044	0.057	0.59972	0.02488	95.85139732
2.	07/12/2016	3.5	0.626	0.495	0.053	0.05	0.5941	0.04415	92.56859115
3.	07/01/2017	3.5	0.61	0.473	0.011	0.011	0.58602	0.0001425	99.97567694
4.	07/01/2017	3.5	0.612	0.477	0.019	0.023	0.58608	0.01197	97.95761671
5.	06/01/2017 0.5 mm OD spinneret	3.5	0.614	0.482	0.124	0.105	0.58538	0.1124	80.79879736
6.	11/01/2017	5.0	0.537	0.386	0.034	0.036	0.53899	0.02534	95.29861407
7.	06/01/2017	5.0	0.561	0.412	0.031	0.03	0.55643	0.02525	95.46214259
8.	05/04/2017	5.0	0.473	0.349	0.033	0.03	0.46791	0.02835	93.94114
9.	31/03/2017	5.0	0.443	0.33	0.072	0.065	0.43585	0.0622	85.72904
10.	0.9mm Fibers		0.573	0.417	0.063	0.048	0.57123	0.06117	89.29153
11.	1.25mm Fibers		0.482	0.362	0.079	0.066	0.47198	0.07229	84.68367
12.	NCL Fibres Module 'A'		0.526	0.36	0	-0.001	0.5417	0.00076	99.85970094

The fibers prepared with no addition of solvent in the bore fluid and just water showed higher flux values than those fibers which were prepared with 13% and 30% addition of DMF in the bore fluid. Addition of a solvent in the bore enabled stretching of the fibers to a better extent.

4.2 BSA Rejection Analysis

BSA Concentration = $(A_{280}*1.55) - (A_{260}*0.76)$

Rejection (%) = $(1-(C_p/C_f))*100$

Rejection Analysis was carried out with the help of Bovine Serum Albumin. It was found that the fibers developed with 100% water concentration in the bore gave higher values of rejection compared to those fibers manufactured with the addition of a solvent in the Bore.
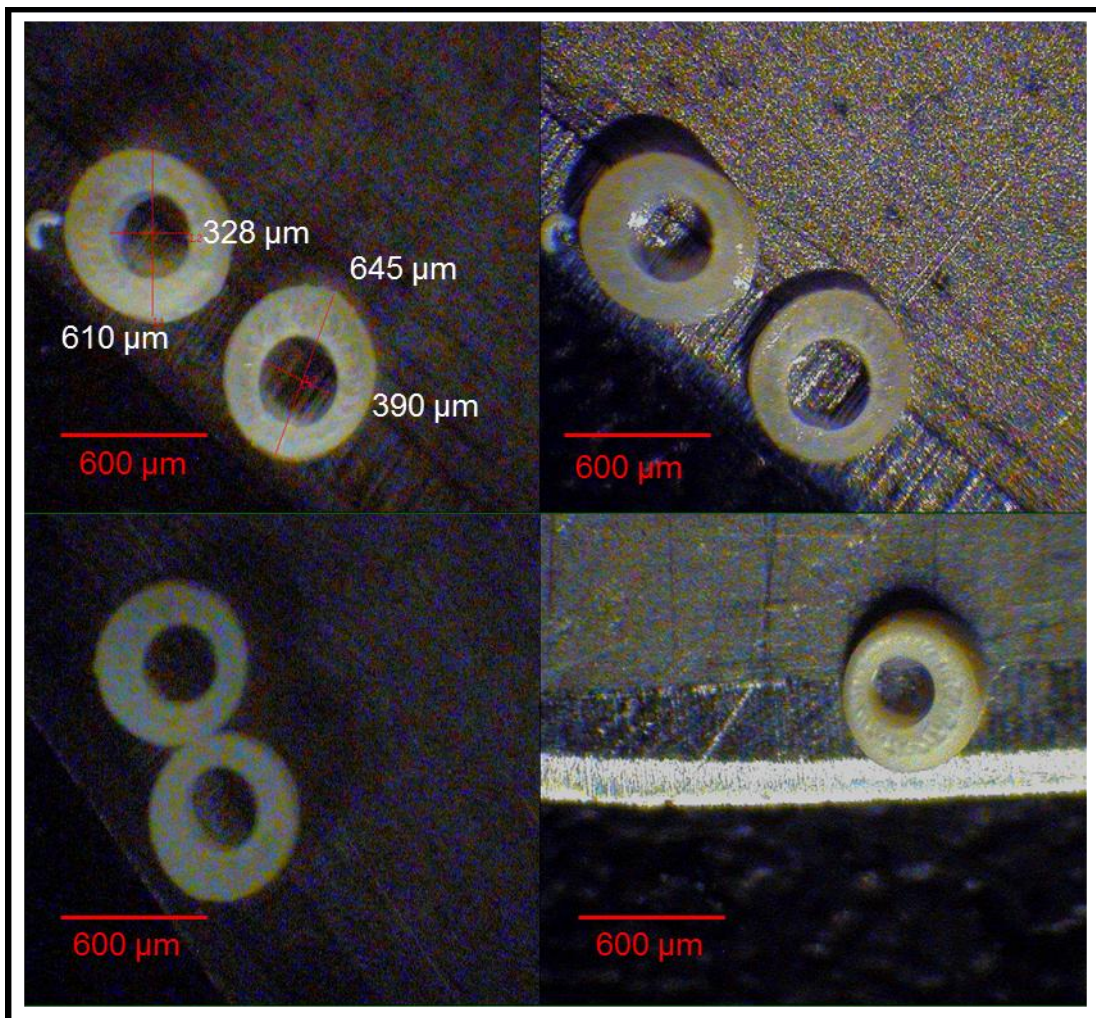
A few sample thin fibers were obtained from CSIR-NCL, Pune and the flux and rejection analysis were carried out for those too. While they had high rejection values in the range of 96.88-99.86 %, these fibers had very low flux values, in the order of 113-169 lmh.

4.3 Fiber Cross-Section Study

The cross-section of the various fibers developed was studied under a microscope and the fiber dimensions were measured. The porosity and symmetric cross-section are the ideal conditions expected out of the fibers for good performance of the membranes. The different cross-section images are given below with the respective details.
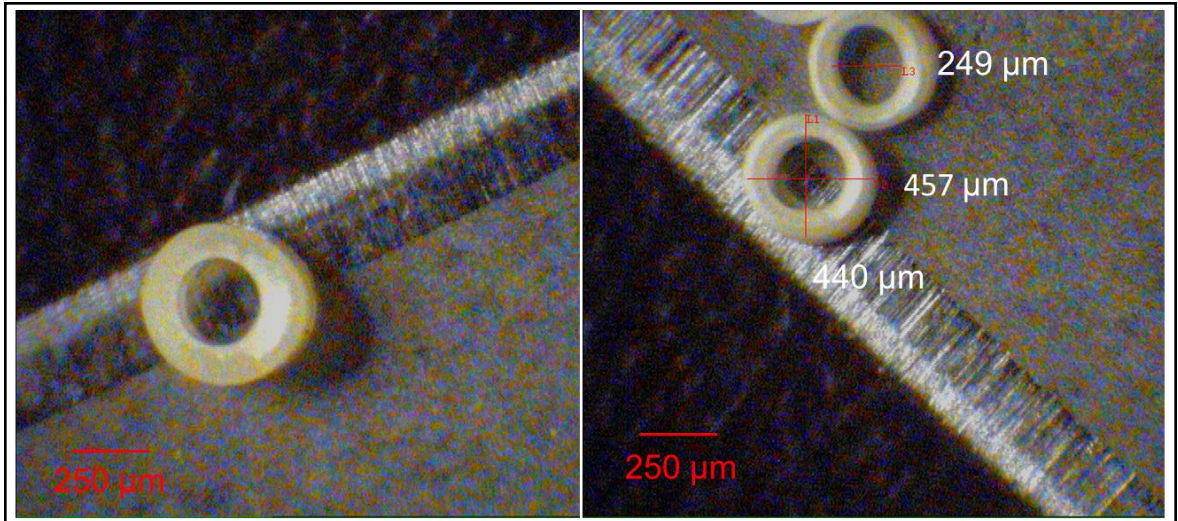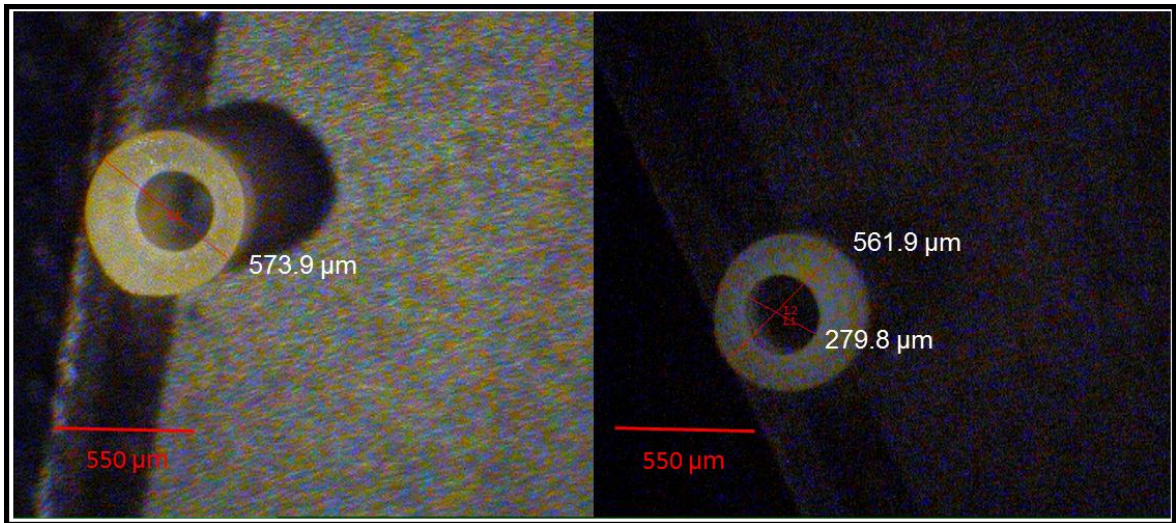
Figure 5 Cross Section of the thin fiber developed. O.D ~ 450 micron, I.D ~ 250 micron. 15.5% polymer concentration. 7cm air gap
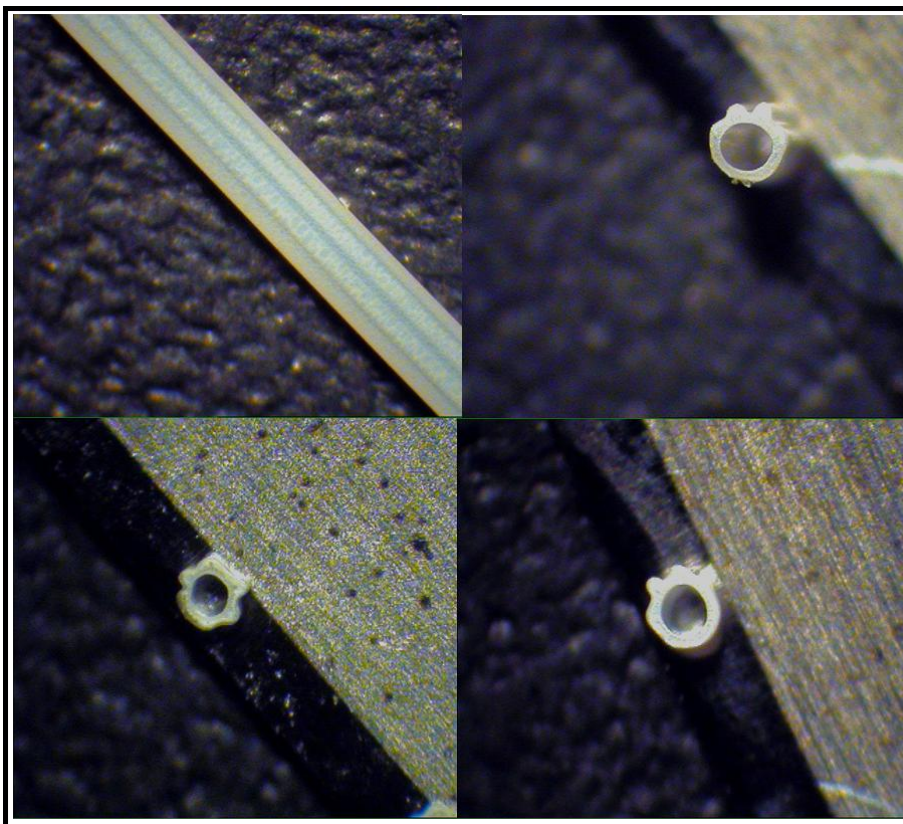

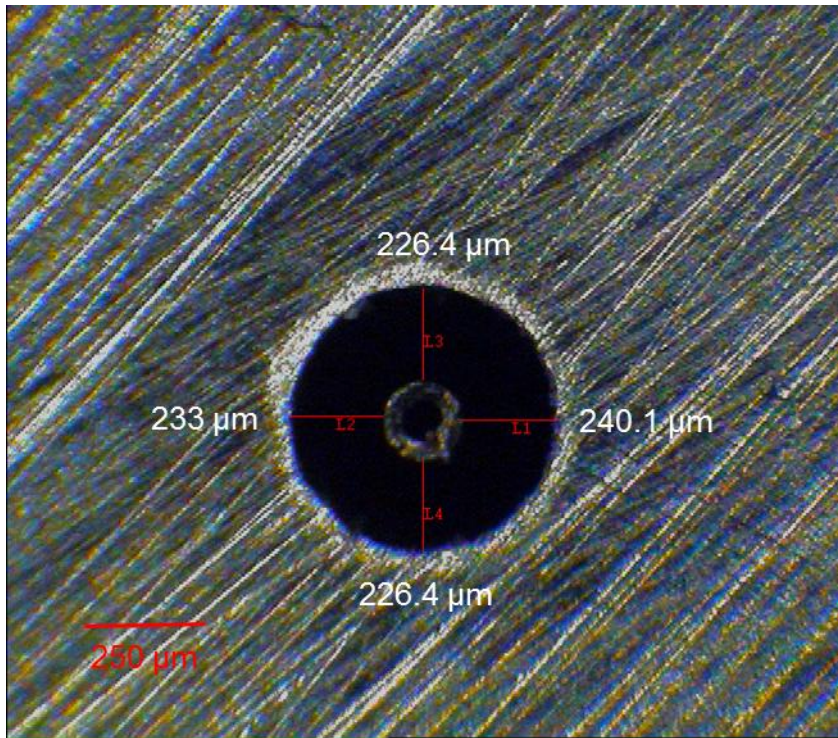**Figure 6 Cross section of thin fibers. 14% polymer concentration. 5cm air gap.**

Figure 7 Cross section of fibers. Polymer concentration 14%. Air gap 7cm. O.D. ~560 micron . I.D. ~ 280 micron.

Figure 8 Cross section of sample thin fibers obtained from CSIR-NCL, Pune.

Figure 9 Spinneret and needle set-up used for hollow-fibre spinning

CONCLUSIONS

The thin hollow fibers were developed after various trials. It was observed that the flow rate for these fibers lies in the range of 50-70lph. At a greater air gap distance the fibers were found to have a better flux and rejection values. Also when compared to the addition of 13% and 30% DMF in the bore fluid and 100% water , fibers spun with 100% concentration of water in the bore fluid gave higher values of flux and % Rejection. Solvent was added to the bore fluid to try and increase the stretching capability of the fibers. Spinning was done initially with the help of a 0.3mm O.D. needle and a spinneret plate of O.D 0.8mm. Later trials were conducted using a needle of 0.2mm O.D. needle and spinneret plate of O.D. 0.8mm.The thin fibers obtained in the final stage had good porosity with O.D. ~ 457 µm and I.D. ~ 250 µm.

Future Scope: This project work can be further developed or studies using other kinds of membranes like ceramic membranes and also using other base materials instead of PAN. Also nanomaterials can be implemented and filter can be developed for heavy metal removal.

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