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Studying and Analyzing Operating Conditions of Hollow Fiber Membrane Preparation Process: A Review Paper

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Abstract

Polymeric hollow fiber membrane is produced by a physical process called wet or dry/wet phase inversion; a technique includes many steps and depends on different factors (starting from selecting materials, end with post-treatment of hollow fiber membrane locally manufactured). This review highlights the most significant factors that affect and control the characterization and structure of ultrafiltration hollow fiber membranes used in different applications.

Three different types of polymers (polysulfone PSF, polyethersulfone PES or polyvinyl chloride PVC) were considered to study morphology change and structure of hollow fiber membranes in this review. These hollow fiber membranes were manufactured with different process conditions and a reasonable starting point for factors remained constant to study the changing effect of specific factors.

Keywords: Hollow fiber membranes, phase inversion, ultrafiltration, polymers

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1- Introduction

Membrane separation is the most flexible reliable and promising technology over the past decades. Membrane technology offers high performance among other processes Adsorption, Extraction, Distillation, and leaching in terms of environment friendly and cost effect [1], [2].

A membrane is described as a barrier separating two phases [3] made of high chemical stability materials. Membranes are often linked to their application to choose the right process and membrane module [4].

From the food industry to desalination (providing drinking water for millions around the world), dialysis (saving the life of kidney disease patients), automotive industry (electroplating bath recovery), and gas separation, membrane processes can be applied to a wide range of applications [4].

Fig. **1** describes membranes classification according to their morphology into dense, porous, and composite.

Asymmetric porous membranes invented by Loeb and Sourirjan, [5] are the most commercially available membranes in the present day. The structure of asymmetric membranes is a defect-free skin layer based on a porous layer [4]. This structure can be achieved by simple principles but is quite tricky with a process called phase inversion.

The process starts with polymer solution thermodynamically unstable by one of FOUR methods; immersion precipitation, vapor induced phase separation, thermally induced phase separation, and dry casting, which leads to polymer separation to polymer lean create pores and voids and polymer-rich phases the porous structure of membrane [4-6].

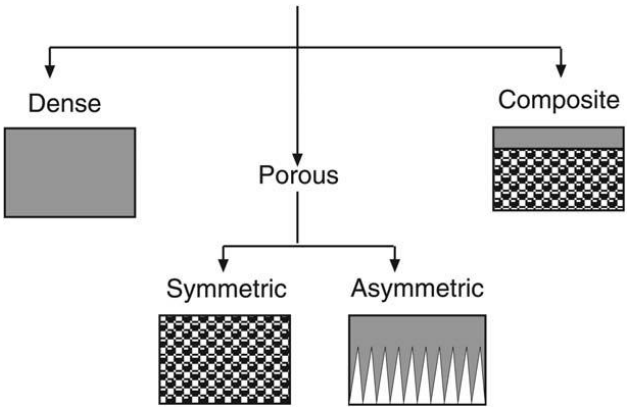

Fig. 1. Membrane classification according to structure morphology [4]

Hollow fiber ultrafiltration membrane was first stated in1966, this type of membrane is not suitable for RO or NF process which applied high pressure because of poor mechanical properties [7], however, it is one of the most interesting membranes modules as it has many advantages among other modules such as high productivity per unit volume [8], self-supporting and easy operation [4].

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The importance of hollow fiber membranes as low-pressure membranes (LPHF) is their ultrafiltration performance, ultrafiltration together with microfiltration gives good separation performance for drinking water. Recent studies suggest that MF and UF can remove all particles and colloids as well as viruses completely when used with suitable pre-treatment or post-treatment which gives this technology advantage to be the new technology generation for drinking water of the 21st century [9]. Fabrication of hollow fiber membranes is not an easy operation especially when specific structure morphology is required [10].

This review demonstrates literature from some researchers to simplify the process steps and give start point for researchers to study the change in hollow fiber membranes structure by changing one or two factors of the preparation process.

However, many researchers reported different and conflicting results for the same operating conditions but different polymers, in terms of permeation and rejection (membranes performance).

2- Preparation Main Steps and Factors

The purpose of studying membranes technology is to improve its performance (flux and rejection) via structure control as mentioned before [1]. The structure is usually sponge-like or finger-like with a selective skin layer on the surface as shown in Fig. **2**, sponge-like is the favored as finger-like leads to a lack in the mechanical stability of hollow fiber membranes [4].

Preparation steps are the dope solution, spinning process, and post-treatment of hollow fiber membranes, these steps are discussed in the next section, and all operating conditions remain constant except for the factor to be changed and studied.

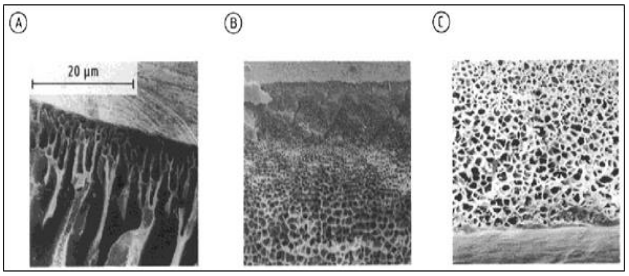

Fig. 2. (A) Finger-like structure, (B) Sponge-like structure, (C) Uniform sponge-like structure [11]

2.1. Dope Solution Preparation

The first step to prepare dope or polymer solution is to select a suitable polymer powder and good polymer solvent. After materials selection, a magnetic stirrer is required to homogenize the polymer solution as shown in Fig. **3**.

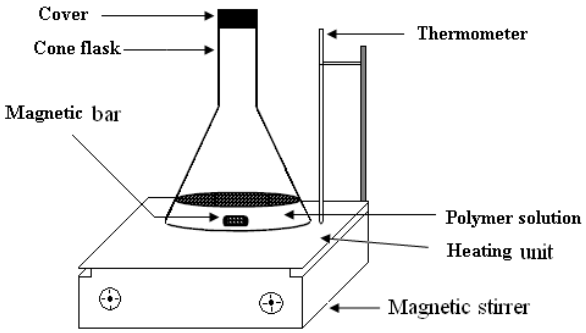

Fig. 3. Polymer Solution Preparation [12]

Firstly, polymer powder should be dried to remove moisture. For PSF polymer drying, 60 °C for at least 12 h is required then polymer powder added to NMP solvent of 22/88 PSF/NMP weight percent and mixed until homogenized at room temperature (25-27 °C) [13].

PVC polymer is a good inexpensive choice for hollow fiber manufacturing[N]. PVC powder was dissolved in di-methyl acetamide DMAC chemically and thermally stable solvent [14] after dried for 24 hr. at 70 °C under continuous mixing period (5 days) at room temperature (25 °C). PVC/DMAC ratio was 14/88 w/w, [10].

Mustaffar et al. [1] chose PES polymer with three different concentrations and polyethylene glycol PEG as polymer additive, 18/72/10, 20/70/10, and 28/62/10, PES/NMP/PEG weight percent of 100-gram polymer samples were stirred at 30 °C. Wang et al. [15] followed the system PSF/NMP/H_2O (water as a non-solvent additive) and also use three concentrations of PSF polymer 26/70/4, 28/68/4, and 30/66/4, PSF polymer powder was dried at 100 °C for 10 hr.

Adding PEG to polymer solution in the system of Mustaffar et al. [1] is to enhance porosity on the membrane skin layer. Polymer concentration together with the solvent ratio is the most significant parameter that directly affects membrane properties. Increasing concentration leads to an increase in dope solution viscosity, dense skin layer becomes thicker, and reduction in macro voids, [1] as well as transferring membrane structure from finger-like to sponge-like [7]. On the other hand, adding a specific amount of non-solvent (water, ethanol, acetone) to the polymer solution well provides a good membrane porous structure [13-16].

2.2. Spinning Process

The spinning process includes several stages as shown in Fig. **4**, starting with dope solution located in a spinning container Fig. 4 No.4 and leaving for 24 hr. to de-bubble or de-gas polymer solution [10], [16] [17].

The dope solution was pressed to a spinneret with a specific inner and outer diameter by nitrogen pressure, 0.5, 0.6, 0.75, or 0.8 bar are recommended pressure as the morphology of the hollow fiber membrane was not affected by changing dope solution pressure in this range [12].

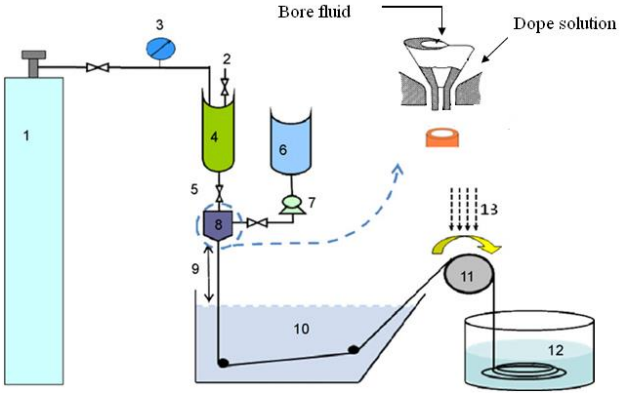

Fig. 4. Spinning process stages, (1) Nitrogen cylinder, (2) Pressure valve regulator, (3) Nitrogen pressure gauge, (4) Dope solution container, (5) Dope solution control valve, (6) Bore fluid container, (7) Dosing pump, (8) Spinneret, (9) Air gap, (10) Coagulants bath, (11) Take-up unit, (12) Hollow fiber collecting vessel, (13) Distilled water for extra wash [12]

a. Air gap

Airgap is defined as the distance between the spinneret and the external coagulants surface, this distance switches the phase inversion process from wet phase inversion to dry/wet phase inversion [10]. Many researchers study the effect of air gap length on the hollow fiber membrane's structure and came back with confusing results about how the air gap increase or decrease membrane performance in terms of permeation and rejection, Table 1 illustrates some of the researcher's conclusion about air gap length outcome for polysulfone PSF, Polyvinyl chloride PVC, and polyether sulfone PES.

Table 1. Effect of air gap on membrane performance reported by different researchers

Polymer	Air gap length	Permeation	Separation factor	Reference
PSF	Increased	Decreased	Increased	Aptel et al. [18]
PSF	Increased	No-effect	No-effect	East et al. [19]
PSF	Increased	Increased then decreased with further increase of airgap length	-	Kim et al. [20]
PSF	Increased	Not significantly affected	Increased	Tsai et al. [21]
PES	15-120 cm	Decreased	Increased	et al. [22]
PES	0-14.4 cm	Significant decrease	-	Chung and Hu [23]
PVC	5-25 cm	Increased	Decreased	Khayet et al. [10]

For PSF polymer Tsai et al. [21] explained the increase in the separation factor is due to the increase in the skin layer of the hollow fiber membranes structure. Chung and Hu [23] describe the change in permeation as related to the high elongation stress of hollow fiber membrane in the presence of an air gap. Khayet et al. [10] indicated an increase in the mean pores of outer hollow fiber membranes surface while the inner pore size almost remained the same with increasing air gap and also linked this change to elongation force.

b. Bore Fluid and Coagulants

Bore fluid or internal coagulant is maintained in a container Fig. 4 No. 6 and pumped with a dosing pump to the inner tube of spinneret together with a dope solution which inter the external spinneret tube, bore fluid fed with a very low flow rate (2, 3 or 4 ml/min), distilled water at room temperature is a good choice [10], [12]. Polymer falls from spinneret with a speed rate the same as gravity speed [10]. Bore fluid or internal coagulant also a key role to control membrane structure, distilled water is a good non-solvent for PSF while alcohol (ethanol) is weak, choosing the optimized ratio of water/alcohol mixture may reduce the big macro-voids in membrane structure [15].

Once the nascent hollow fiber membranes touch the external coagulation fluid (usually tap water), solvent non-solvent exchange occurred and form the asymmetric structure, generally the fast the coagulation rate the more finger-like macro voids formed while the slow coagulation rate gives the favored sponge-like structure [13].

To slow down the coagulation rate, a small amount of solvent additive to bore fluid or coagulant bath well reduces the coagulation and induces the formation of a sponge-like structure [15]. Appropriate additives should be environmentally friendly, low toxicity, and commercially available. The best coagulant to be used is water, the NMP and DMAC are the best as solvent additives [15].

The temperature of coagulants is considered an important factor to control membrane structure, Wang et al. reported that reducing coagulation bath temperature from 27 C to 20 °C increases the membrane permeation and decreases the selectivity, while further temperature reduction to 10-15 °C leads to a significant reduction in membrane selectivity performance due to the formation of macro voids on the membrane surface [15].

2.3. Post Treatment

The final step of fabrication of hollow fiber membrane is post-treatment, the importance of post-treatment is to avoid membrane collapse and get rid of residual solvent [10], [15], [16]. Many researchers reported a different kind of post-treatment to protect the membrane from damage.

Wang et al. [15] suggest keeping hollow fiber PSF membranes in water for 72 hr. followed by a drying step at conditions of 25 °C and (60-65%) relative humidity. Khayet et al. [10] made it three steps, first, wash hollow fiber PVC membranes with water for 48 hr. to remove the solvent, and second immerse hollow fiber membranes in glycerol aqueous solution of 40% volume ratio to avoid collapse, and third dry at room temperature.

Another method is to treat hollow fiber membranes with non-solvent with low surface tension such as ethanol [13], Mansourizadeh & Ismail [13] submerged PSF hollow fiber membranes in ethanol for half an hour and then let the non-solvent evaporate by air exposure at room temperature to prevent pores breakdown. For PES hollow fiber membranes, Mustaffar et al. recommended two days of water washing, two days of methanol immersion, and a drying period by hanging hollow fiber membranes for 7 days before use.

3- Hollow Fiber Membranes Characterization and Performance

The characterization of hollow fiber membranes was evaluated by Scanning Electron Microscope SEM as this device gives a clear image of membrane structure in terms of skin layer thickness; porosity distribution and pores shape also give a good indicator of inner and outer diameter measurements [16].

The inner and outer diameter also can be measured by a linear Vernier microscope with ±1μm. accuracy [10].

Permeation and selectivity performance required a specially designed lab-made unit as shown in Fig. **6** which was suggested by some researchers.

Before explaining the performance system the hollow fiber must be cut to more than 20 cm (depending on tube design) and secured in a special tube usually made of stainless steel with an inlet and outlet open on the side as shown in Fig. **5** and get a free end of membranes by sealing the two end of the tube with epoxy resins and let it cure for 24 hr. [12], [24].

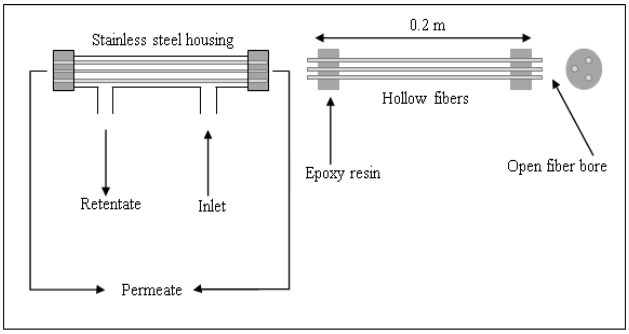

Fig. 5. Hollow fiber membrane special tube [24]

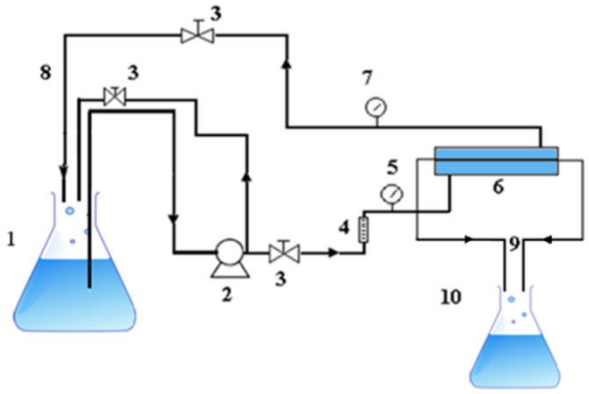

Fig. 6. Schematic diagram of hollow fiber membrane performance system, (1) feed tank, (2) pump, (3) control valve, (4) flow meter, (5) gauge pressure, (6) hollow fiber tube, (7) gauge pressure, (8) retentate, (9) permeate, (10) collecting tank [12]

Performance system for pure water permeation PWP includes forcing distilled water to the inlet tube with specific pressure and flow rate and passes through hollow fiber membranes from outer to the inner surface and by collecting permeates for a specific time, PWP can be calculated by the following equation:

$$PWPF = \frac{Q}{A\,\Delta P} \quad (1)$$

Where:
Q: volumetric flow rate, l/h
A: membrane surface area, m^2
ΔP: Pressure drop, bar [25]

For rejection calculation, a solution with a specific amount of PEG (800, 1000 ppm) [12], [16] is pumped instead of distilled water and the equation used was as follows:

$$R(\%) = (1 - \frac{Cp}{Cf}) \times 100 \quad (2)$$

Where:
Cp: concentration of PEG of permeation, ppm
Cf: concentration of PEG of the feed solution, ppm [25]

Note: UV spectrometer is used to find concentration by knowing PEG wavelength and create a calibration curve

4- Conclusion

There are many factors to be controlled in the fabrication of hollow fiber membranes. Some of these factors direly affect the structure of the membrane and eventually, the overall performance and even slight change give a different morphology.

It is important to keep operating conditions constant when studying the change of specific factor.

1- Polymer concentration is remarked as the most effective on the morphology of hollow fiber membranes, the high the concentration the thick the skin layer, and a more sponge-like structure is produced. From researcher reports, 14% of polymer concentration and above is a good start, not to forget the effect of suitable additives to the dope solution on the performance of the membranes. DMAC is a suitable solvent for a different type of polymers as it is miscible with water and have good thermal and chemical stability
2- The air gap was the most conflicting factor, however, 5-10 cm of air gap was expected to enhance membranes selectivity, especially for PSF and PES while decreasing it for PVC
3- Water is fantastic for bore fluid and coagulants with appropriate additives, alcohol in a coagulant bath gives a reduction in macro-voids formation. A small amount of solvent like DMAC to bore fluid or coagulation bath raises the sponge-like structure of membranes
4- Post-treatment of hollow fiber membranes has two main reasons, wash residual solvent, and prevent membrane collapse.
5- Finally, the favorite performance (increasing permeation or selectivity) of hollow fiber membranes depends on its application, gas separation, or drinking water production

Abbreviation

PSF:	Poly Sulfone
PES	Poly Ether Sulfone
PVC	Poly Vinyl Chloride
RO	Reverse Osmosis
NF	Nano Filtration
LPHF	Low Pressure Hollow Fiber
UF	Ultra-Filtration
NMP	N-methyl-2-pyrrolidone
DMAC	N,Ndimethyl acetamide
SEM	Scanning Electron Microscope
PWPF	Pure Water Permeation
UV	Ultraviolet

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ورقة مراجعة في دراسة وتحليل ظروف التشغيل لعملية تحضير الاغشية النفاذية المجوفة

زيد وعدالله رشاد

جامعة بغداد/كلية الهندسة

الخلاصة

تنتج الاغشية النفاذية المجوفة عن طريق عملية فيزيائية تسمى انقلاب الطور الرطب أو الجاف / الرطب. تتضمن التقنية العديد من الخطوات وتعتمد على عوامل مختلفة (بدءًا من اختيار مواد التصنيع، وانتهاءً بالمعالجة اللاحقة للاغشية النفاذية المجوفة المصنوعة محليًا). تسلط دراسة المراجعة هذه الضوء على أهم العوامل التي تؤثر وتتحكم في توصيف التركيب الداخلي لأغشية الألياف المجوفة ذات الترشيح الفائق المستخدمة في التطبيقات المختلفة.

تمت الدراسة بالاعتماد على ثلاثة أنواع مختلفة من البوليمرات (بولي سلفون PSF ، بولي إيثر سلفون PES و بولي فينيل كلوريد PVC) لدراسة تغير مورفولوجيا الاغشية الليفية المجوفة مع عوامل تصنيع مختلفة وإعطاء نقطة بداية معقولة للعوامل المؤثرة والتي يجب تثبيتها عند التشغيل وتغيير العامل المراد دراسة تاثير تغييره على الاغشية.

الكلمات الدالة: الاغشية النفاذية المجوفة, انقلاب الطور, عملية الترشيح, البوليمر