Carbon Membranes

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Abstract:

Carbon membranes are considered as a new relative addition to the mainstream of membrane material research. It shows tremendous growth and development efforts in this research field through significant numbers of publication in recent years. Carbon membranes can be fabricated by heat treatment from various types of polymeric precursor membranes such as Polyimide and derivatives, polyacrylonitrile, phenolic resin, polyacrylonitrile (PAN), polyfurfuryl alcohol (PFA), polyetherimide (PEI), polyphenylene oxide (PPO), polyvinylidene chloride (PVDC), and polyphthalazinone ether sulfone ketone (PPESK). Carbon membranes can be divided into two categories namely supported and unsupported. The typical characterization methods that used for carbon membranes can be classified into membrane performance evaluation and physical characterization. Physical characterization included thermogravimetry analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), adsorption and sorption experiments, and elemental analysis. Further explanation on each process parameter will be discussed in order to obtain carbon membranes in highest quality. In addition, the performances of various types of carbon membranes that developed by previous researchers for different gas separation applications were also summarized. Furthermore, the potential applications and future directions of carbon membrane in gas separation processes were identified in this review. Other potential processes for carbon membrane include pervaporation, water treatment, and membrane reactor was also emphasized. Although there are significant researches conducted since the carbon membranes inception, the need to extensively improve the gas permeation properties of these membranes still remains important if it become a viable membrane material for industrial applications.

Keywords: precursor; carbon membrane; stabilization; carbonization

1.0 THEORY OF CARBON MEMBRANE PROCESSES, GENERAL PROPERTIES OF CARBON MEMBRANES

1.1. Principles and properties of carbon membrane

The concept of carbon membrane for gas separation was found in the early 1970s. Barrer et al. compressed nonporous graphite carbon into a plug, called carbon membrane (1). Bird and Trimm used poly (furfuryl alcohol) (PFA) to prepare supported and unsupported carbon membrane. During the carbonization, they encountered shrinkage problems that lead to cracking and deformation of the membrane. Hence, they failed to obtain a continuous membrane (2). Carbon molecular sieves produced from the high temperature treatment (carbonization) of polymeric materials have proved to be very effective for gas separation applications by Koresh
and Soffer (3-5). Molecular sieve carbon can be easily obtained by carbonization of various types of polymers such as Polyimide and derivatives, polyacrylonitrile (PAN), phenolic resin, polyfurfuryl alcohol (PFA), and various coals such as coconut shell (3-5). They described that the pore dimensions of carbon were dependent on the morphology of the organic precursor and the chemistry of the heat treatment process (6).

In membrane process, the permeability and selectivity are the most basic properties of a membrane that need to be considered. It is well known that the membrane performance appears to be a trade-off between selectivity and permeability, i.e. a highly selective membrane tends to have a low permeability (7, 8). Lu et al. (9) stated that, the higher the selectivity and the more efficient the process, the lower the driving force (pressure ratio) required in achieving given separation; thus resulting in lower operating costs for the separation system. The higher the permeability, the smaller the membrane area required; hence the capital cost of the system is lower. Therefore, some attempts have been made to prepare membranes that can surpass Robeson’s upper bound. They have pointed out that the carbon membranes are potential to exceed such an upper bound (10-13). The previous studies proved that, the limitations and drawbacks of polymeric membranes can be resolved by using carbon membrane in the separation system. The comparison between polymeric and carbon membranes are summarized in Table 1.1 (14). This chapter gives an overview about the basic principles of carbon membrane and the challenges that faced by researcher in the development of carbon membranes.

**Table 1.1:** Carbon membrane versus polymeric membrane

<table>
<thead>
<tr>
<th></th>
<th>Polymeric membrane</th>
<th>Carbon membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structural property</strong></td>
<td><img src="image1.png" alt="Polymeric membrane" /></td>
<td><img src="image2.png" alt="Carbon membrane" /></td>
</tr>
<tr>
<td><strong>Separation mechanism</strong></td>
<td>• Solution diffusion</td>
<td>• Knudsen diffusion: &lt; 0.1 μm</td>
</tr>
<tr>
<td></td>
<td>• Surface diffusion: &lt; 0 - 20 Å</td>
<td>• Surface diffusion: &lt; 0.1 μm</td>
</tr>
<tr>
<td></td>
<td>• Capillary condensation: &gt; 30Å</td>
<td>• Capillary condensation: &gt; 30Å</td>
</tr>
<tr>
<td></td>
<td>• Molecular sieving: &lt; 6Å</td>
<td>• Molecular sieving: &lt; 6Å</td>
</tr>
<tr>
<td><strong>Advantages</strong></td>
<td>• Low production cost</td>
<td>• Excellent chemical stability</td>
</tr>
<tr>
<td></td>
<td>• Surpass the trade-off between permeability and selectivity</td>
<td>• Excellent thermal stability</td>
</tr>
<tr>
<td></td>
<td>• Excellent thermal stability</td>
<td>• Can be used at extreme operation</td>
</tr>
<tr>
<td></td>
<td>• Pore dimension and distribution can be fine tuning by simple thermochemical treatment</td>
<td>• Pore dimension and distribution can be fine tuning by simple thermochemical treatment</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td>• Poor thermal resistance</td>
<td>• Brittle</td>
</tr>
<tr>
<td></td>
<td>• Poor chemical resistance</td>
<td>• High production cost</td>
</tr>
<tr>
<td></td>
<td>• Arduous to beach the trade-off</td>
<td>• Vulnerable to adverse effect from</td>
</tr>
</tbody>
</table>
1.2. Separation mechanism

Various gas transport mechanisms across carbon membranes have been proposed depending on the properties of both the membranes and permeant (gas molecules). This includes Knudsen diffusion, surface diffusion, capillary condensation/partial condensation, and molecular sieving (15, 16). Details explanations of the separation mechanism occur across carbon membrane are illustrated in Table 1.2. The transport mechanism exhibited by most of carbon membranes is the molecular sieving mechanism.

1.3. Carbon membrane configurations/classifications

Carbon membranes can be divided into two categories: unsupported and supported carbon membranes. Unsupported membranes are generally produced as flat films, capillary tubes, or hollow fibers. Meanwhile, the supported membranes are generally in the form of flat sheets or tubes (17, 18). Supported membranes, sintered metals, alumina, or graphite materials normally used either in flat disk or tubular configurations. There are several methods to deposit the polymer solution on the support material such as dip-coating (19-22), spin coating (11, 17, 23-25), spray coating (26), and ultrasonic deposition. Numerous types of supported and unsupported carbon membranes have been reported in the literature (refer Volume II). Based on the previous researches, the supported carbon membrane is the most popular configuration because it is simple to prepare and lower cost. However, this type of configuration exhibits a problem of uniformity in deposition of polymer solution on the support. The cycle of polymer deposition/heat treatment need to be repeated several times in order to obtain an almost defect-free membrane (17, 25, 27).

Nevertheless, the numbers of report on hollow fiber carbon membrane have increased in 2000s. The beneficial features that contributed by hollow fiber which posses high separation efficiency, and offer flexibility where the separation can occur in two ways, either ‘inside-out’ or ‘outside-in’. Besides, it also posses high active surface area to volume ratios (>1000 m²/m³), able to operate at high pressure drops, low resistant to gas flow, and low production cost as compared to other types of configuration (31, 32).

1.4. The Challenges in carbon membrane development

1.4.1. Mechanical stability

The mechanical properties of the membrane are essential in the operation and the membrane module design. In the case of carbon membranes derived from polymeric material,
the major disadvantage in the commercialization is brittleness, which means that they require careful handling.

Table 1.2: Separation mechanism of carbon membranes (15, 16, 28-30)

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Description</th>
</tr>
</thead>
</table>
| Knudsen diffusion          | - Pore sizes: < 0.1 μm  
- Can occur either by concentration or by pressure gradients  
- The relative permeation rate of each component is inversely proportional to the square root of its molecular weight.  
- The selectivity is equal to the square root of the molecular-weight ratio of the largest to smallest gas.  
- Low selectivity and not practical to be applied in the industry separation process. |
| Surface diffusion          | - Pore size: < 10 - 20 Å  
- Separate non-adsorbable or weakly adsorbable gases (O₂, N₂, and CH₄) from adsorbable gases (NH₃, SO₂, H₂S, and CFCs)  
- In this mechanism, the diffusing species adsorb on the walls of the pore, and then readily transport across the surface in the direction of decreasing surface concentration.  
- The molecules with larger molecular weight and with larger polarity are selectively adsorbed on the membrane surface.  
- The concentration of adsorbed species is depends on the temperature, pressure, and the nature of the surface. |
| Capillary condensation /  | - Pore size: > 30Å  
- Capillary condensation mechanism occurs when one or more of the components in the feed stream condense in the pores and diffuse across the membrane.  
- A very high selectivity of separation of the condensable component can be achieved by this mechanism but the extent of removal of that component from the gas mixture is limited by the condensation partial pressure of the component at the system temperature, the pore size and the geometry of the membrane. |
| Partial condensation       |                                                                                                                                           |

Molecular sieving
In 1999, Tanihara and coworkers (33) studied the mechanical property of carbon membranes derived from asymmetric Polyimide hollow fiber membrane produced by UBE Industries. The elastic modulus significantly increased and the breaking elongation decreased as the heat treatment temperature is increased from 600 to 1000 ºC. The elastic modulus of the resultant carbon membrane carbonized at 800 ºC showed 9 times larger than membrane treated at 270 ºC. It was demonstrated that the aromatic fragments growth and crosslinking between the fragments was progressing during the heat treatment process. In addition, it also contributed by the asymmetric structure of the membranes that turn into dense with increasing treatment temperature. Similarly, the development towards the increased elastic modulus of the carbon membranes also found in PAN-based carbon fiber studies (34, 35).

An early work on the preparation of flexible carbon membrane from sulfonated polymer was claimed in 2002 (36). The precursor membranes were carbonized at low temperature of 450 ºC for 1.5 h. The results indicated that carbon membranes prepared at low carbonization temperatures have the ability to separate C₃H₆/C₃H₈ and CO₂/N₂ gas pairs with high selectivity. At carbonization temperature of 500 ºC, the derived carbon membranes were brittle and the gas permeation measurement could not be performed (36, 37). Recently, a flexible carbon membrane derived from sulfonated PPO was successfully prepared by Yoshimune and Haraya (38). The mechanical property of this membrane measured by means of a bending test technique on the glass tube. It was found that carbonization of carbon membrane in the range of 450 to 600 ºC produced more flexible carbon hollow fiber membrane with a smaller bending radius. However, for carbon membrane carbonized at 700 ºC, a less flexible and brittle carbon membrane was obtained due to the shrinkage effect during heat treatment. It was found that the outer diameter of the hollow fiber affected the mechanical property of the carbon membranes. Due to that, the bending radius has increased with the outer diameter of the carbon hollow fiber membrane increased.

In addition to these issues, Ismail’s group (30, 39) stated that brittleness problem can be minimized by using PAN as a precursor membrane for carbon membrane, since this polymer have been widely used in the production of high strength carbon fiber. Further study on the preparation of carbon membrane with high mechanical properties would be a major breakthrough in this field and would be given an opportunity for potential commercialization of the membranes. There are some available and modified polymers that possess the potential to produce carbon membrane with mechanical stability that fulfills the industrial qualifications.

Based on the authors’ knowledge, a study on the mechanical properties of the carbon membranes are still lacking in the open literature. One of the problems is related to the
experimental operation due to carbon membrane fragility. For brittle carbon membranes, the breaking elongation is relatively short, even at a long gauge length, the membrane elastic modulus is also high. Therefore, the incorrect measurement of the elongation of the membrane sample normally occurred once there is a motion deformation in the initial stretching. There are various types of damage of the membrane in the sample preparation and testing process, such as picking a carbon hollow fiber membrane from a bundle, mounting the membrane sample to the tensile machine, and adhering the membrane to a paper holder. Although these membranes have poor mechanical properties, it is still capable of being constructed into the module for gas permeation testing in the laboratory scale; and manifold studies on the gas permeation performance of the carbon membrane have been reported in the literature (40).

1.4.2. Membrane aging

Carbon membranes present significant problems regarding the performance stability even though it exhibit excellent chemical and thermal resistance. One of the problems faced by carbon membranes is the vulnerability to oxidation. The permeation properties of the membranes would drastically affected even with a small change in the size of pore constrictions, and the associated changes can be quite significant on time scales of weeks to years (41, 42). Upon air exposure (even at room temperature), oxygen atoms from air combine with some active sites can lead to creation of oxygen surface groups. Thus, oxygen chemisorptions can eventually reduce the open porosity towards gas transport and increase the number of the constrictions of the pore structure, offering additional restriction to diffusion, which is known as carbon aging. During aging, the rate of change in permeation properties is dependent on the size of the gas molecules and it is significantly affected by the permeation of larger molecules due to the loss of free volume (42).

An extensive study was conducted by a research group from Japan (19, 43) to investigate the stability of the carbon membranes by maintaining the membrane in the air at 100 °C for a month. During this treatment, oxygen in air reacted with the membrane and formed oxygen-containing functional groups, which continuously decomposed to CO₂. Later, the effects of aging on carbon membrane permeation properties associated with air oxidation were studied by Fuertes and Menendez (44, 45). The derived carbon membranes were stored under various types of environments such as dry air, humid air, propylene and nitrogen. The results showed that a rapid loss in permeance with time was observed for carbon membrane stored in dry and humid air. However, carbon membranes stored under propylene and nitrogen was protected from aging. It is considered that oxygen chemisorptions into carbon membranes instead of water physisorption is the main reason for the loss of permeance when a prepared carbon membrane is exposed to air. These findings were in agreement with the results reported by Lagorsse and coworkers (46).

In order to protect and minimize the carbon membrane from aging, the regeneration technique by exposure to pure propylene was proposed in 1994. Experimental results demonstrated that most membrane recovery cases were significantly boosted by exposure to
propylene and it was confirmed that this chemical is effective in removing absorbed groups. During regeneration, the adsorbed compounds were easily removed from the carbon due to the weak interaction forces on the pore wall of the carbon membrane (47). Besides functioning as regeneration agent, propylene can also be used for storage purpose of the carbon membranes as suggested by Menendez and Fuertes (45). However, the systematic studies on the stability and durability of the derived carbon membranes are still not sufficient to be used as a reference.

1.4.3. Sorption of trace components

In general, carbon surface are hydrophobic but micropore of carbonized membrane wall are partially covered with oxygen-containing functional groups in giving the membrane a hydrophilic character (48). It has been reported that the selectivity of a typical membrane decreases as the amount of sorbed water has increased. This is primarily due to the fact that water vapor can be found in a large number of process streams. One of the approaches to this problem is coating method with highly hydrophobic polymer to develop carbon composite membrane (49). The composite membranes were designed to have high resistance to water vapor to prevent decreasing in permeation flux. Kai et al. (50) reported that the problem of separation performance decline under humid conditions was improved by incorporation of Cesium (Cs) in polymeric precursor solution. The separation performance was evaluated using a CO$_2$/N$_2$ gas mixture with controlled relative humidity at 40 °C and at atmospheric pressure. The results showed that the Cs-incorporated carbon membranes had a higher CO$_2$ permeance and separation factor under humid conditions.

Membrane performance losses in terms of selectivity and flux were severel and occurred with feed stream concentrations of organics as low as 0.1 ppm. Carbon membranes have limited stability in some gases (CH$_4$, H$_2$, CO$_2$, O$_2$) at relevant temperatures and appeared less feasible for precombustion decarbonization processes (51). Therefore, the modification of the carbon membrane in terms of surface properties is the important aspect in developing carbon membranes with high performance stability.

2.0 METHODS OF CARBON MEMBRANE PREPARATION AND CHARACTERIZATION - DESIGN OF CARBON MEMBRANE MODULES

2.1. Introduction

Carbon membranes considered as one of the most popular topic among the membrane researchers due to its spectacular separation performance. However, an intensive research and development work should be carried out to ensure the reality of carbon membranes in industry. This section briefly discusses the process taken in the preparation, characterization, and the membrane module design of carbon membrane. Generally, the preparation of carbon membranes
involves three important processes, including precursor selection, precursor membrane preparation, and heat treatment process. Simultaneously, there are several factors that need to consider in order to ensure the success of each process (39, 40).

2.2. Precursor selection concepts

In polymeric precursor materials selection, thermal and chemical stability is not the only features that need to be consider. The promising combination of required permeability and selectivity and good mechanical properties of the final carbon membrane were also required. Many researchers had fabricated carbon membranes from a wide range of polymeric precursors. The used polymer precursor should satisfy a number of criteria such as high aromatic carbon content, high glass transition temperature, $T_g$, chemically stable and provide superior separation properties (14, 32, 39, 52).

Frequent used polymers are polyimides and derivatives, phenolic resin, polyacrylonitrile (PAN), polyfurfuryl alcohol (PFA), polyetherimide (PEI), polyphenylene oxide (PPO), polyvinylidene chloride (PVDC), and polyphthalazinone ether sulfone ketone (PPESK). Many studies reveal that the pore dimensions and the distribution in the microstructure carbon membranes are dependent on the selection of polymer precursors. As reported by Tin et al. (53), the chemical composition of polymer precursor is the crucial factor which determines the pore population created in the carbon matrix. Table 2.1 shows the summary of several potential candidates of polymeric precursors for carbon membranes previously studied in the literature. Detail reviews on these polymeric precursors can be found elsewhere (39, 40, 54, 55).

2.3. Precursor membrane preparation

In flat sheet membrane preparation, the polymer solution is poured onto the top surface of a glass mirror and cast by a casting knife. The solvent is then allowed to evaporate until the membrane is fully vitrified, which is determined by a change in the appearance of the membrane. The resulting polymeric film then removed by lifting the edge of the film with a razor blade to ease the film off of the surface. If the film is complicated to come off, a few drops of water is squirted under the exposed edge, which causes the film to lift off of the glass plate. The polymeric film will be dried at room temperature to remove any residual solvent and water. Any areas which have visual stress points will not using for permeation experiments (55). Flat sheet membrane also can be fabricated as supported membrane by depositing polymer solution onto the inorganic support (81).

In the fabrication of hollow fiber membrane, the process are more complicated than flat sheet and cannot be approached by the same method that led to the successful casting of the flat sheet configuration. In hollow fiber membrane fabrication, spinneret is the most important device
that would be utilized to form hollow fiber. Figure 2.1 illustrates the side view and cross section of the spinneret that have been used in the spinning process (82)

### Table 2.1: Summary of polymer precursor selection

<table>
<thead>
<tr>
<th>Polymer precursor</th>
<th>Properties</th>
</tr>
</thead>
</table>
| Polyimide (12,14,17,19,23,33,56-61) | - Widely used by previous researchers  
- Limited (expensive and need to synthesize manually in the laboratory)  
- Good for H₂/CH₄, CO₂/N₂, O₂/N₂, CO₂/CH₄, N₂/CH₄, and C₂H₆/C₃H₈ separation  
- Gas transport through the membrane occurs according to the molecular sieving mechanism  
- Commercially available polyimide; Kapton, Matrimid, and P84 copolymer (BTDA-TDI/MDI) |
| PEI (20,62-64) | - Good chemical and thermal stability  
- Impressive separation factors  
- Give high carbon yield  
- Good for CO₂/CH₄ separation |
| PAN (27,39) | - Conquer nearly 90% of all worldwide sales of carbon fibers  
- Low O₂/N₂ selectivity |
| Phenolic resin (13,22,44,65) | - Inexpensive polymers  
- Good separation of hydrocarbon gas mixtures such as alkenes/alkanes and n-butane/iso-butane |
| PFA (25,29,31,66) | - Simple molecular structure and formation mechanism  
- Only can be used for preparing supported membrane  
- Good for O₂/N₂ separation |
| PPO (67,68) | - Excellent mechanical properties |
| PVDC (24) | - Exhibit molecular sieve properties similar to Zeolite 5A  
- Good for O₂/N₂ separation |
| Polypyrrolone (69) | - Involved two step of synthesis  
- Exhibit high permeability |
| PPESK (70-73) | - Exhibit high H₂, CO₂, and O₂ permeability |
- Good for H₂/N₂, CO₂/N₂, and O₂/N₂ separation
- Membrane performance can be improved by manipulating sulfone over ketone units molar ratio (S/K)

<table>
<thead>
<tr>
<th>Polymer blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>(26,64,71,74-80)</td>
</tr>
</tbody>
</table>

- Blending of two polymers with different thermal properties is preferably used (eg: PPO/polyvinylpyrrolidone (PVP), polyimide/polyethylene glycol (PEG), PEI/PVP, PAN/PVP, polyimide/PVP, polybenzimidazole (PBI)/polyimide)
- Blending polymer with inorganic materials (zeolite, silica, and carbon nanotube) (eg: polyimide/multiwall carbon nanotubes (MWCNTs), PEI/MWCNTs, PPESK/zeolite, polyimide/silica)
- Increased the mesoporous volume
- Enhanced the gas permeability

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**Figure 2.1:** Schematic diagram of (a) side view and (b) cross section of the spinneret (82)

Two methods were used for the preparation of essentially defect-free asymmetric hollow fiber membranes by the phase inversion process, which is by wet spinning process and dry/wet spinning process. The dry/wet phase inversion process is commonly used in the literatures (12, 18, 52, 59, 68, 83). In this process, dense skin is created due to the solvent in the casting solution desolvates rapidly into the coagulation bath and relatively little nonsolvent diffuses into the casting solution at the point when the casting solution and nonsolvent come into contact. The thickness of the skin layer increased gradually until the diffusion of solvent from the sublayer solution through the dense skin layer into the coagulation bath is restrained. On the other hand, the wet spinning process predominated when the length of air-gap is zero. This would produce the outer skin layer with big pores owing to the lack of coalescence (84, 85). In coagulation bath, both the inside and the outside of the polymer solution were in contact with a nonsolvent for the polymer. An exchange of solvent and nonsolvent caused the polymer to precipitate and a structure with a certain degree of porosity is formed.

### 2.4. Heat treatment process
Further study on the preparation factors are crucially needed in order to obtain reproducible carbon membrane with high separation efficiency. Many researchers agreed that the heat treatment conditions impose strong effect on the pore population created in the carbon matrix as well as their gas permeation properties of the final carbon membranes. Table 2.2 summarized the heat treatment conditions that recently applied into carbon membrane preparation by various researchers along with the types of precursor and configuration.

2.4.1. Stabilization Process

Stabilization or pre-oxidation process is one of the steps involved in the fabrication of carbon membrane and carried out before the carbonization process. Most of the prepared high performance carbon membranes were successfully stabilized in air atmospheres between 150 and 460 °C, depending on the type of polymer precursor used. It is believed that greater stability membranes were obtained after stabilization under air atmosphere mainly due to the contribution of oxygen in the dehydrogenation reaction. In fact, oxygen mainly acts as a dehydrogenation agent in the conversion of C-C bonds to C=C bonds and generates oxygen-bearing groups in the polymer backbone, such as –OH and C=O. These groups promote intermolecular crosslinking of the polymer chains and provide greater stability to sustain high temperature in the subsequent carbonization process. If the stabilization process is not completed throughout the entire membrane cross section, a significant weight loss can occur at higher temperature (62).

Table 2.2: Heat treatment condition used by previous researchers

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Configuration</th>
<th>Stabilization and Carbonization Condition (Temperature, Heating rate, Thermal soak time)</th>
<th>Atmosphere</th>
<th>Ref(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>Hollow fiber</td>
<td>250 °C, 5 °C/min, 0.5 h 500 - 800 °C, 3 °C/min, 0.5 h</td>
<td>Air</td>
<td>(31)</td>
</tr>
<tr>
<td>PAN</td>
<td>Flat sheet</td>
<td>450 - 950 °C, 1 °C/min, 2 h</td>
<td>N₂/Ar</td>
<td>(86)</td>
</tr>
<tr>
<td>PEI/PVP</td>
<td>Hollow fiber</td>
<td>300 °C, 3 °C/min, 0.5 h 650 °C, 3 °C/min, 0.5 h</td>
<td>Air</td>
<td>(87-89)</td>
</tr>
<tr>
<td>PFA</td>
<td>Flat sheet</td>
<td>100°C, 5 °C/min, 1 h 400 - 800°C, 5 °C/min, 2 h</td>
<td>Ar</td>
<td>(25)</td>
</tr>
<tr>
<td>PFR</td>
<td>Tube</td>
<td>150°C, 0.5 °C/min, 1 h 850°C, 0.5 °C/min, 1 h</td>
<td>Ar</td>
<td>(90)</td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>Tube</td>
<td>700 – 1000 °C, 10 °C/min, 1 - 8 h</td>
<td>Vacuum</td>
<td>(22)</td>
</tr>
<tr>
<td>6FDA / BPDA-</td>
<td>Flat sheet</td>
<td>550 °C, 2 h</td>
<td>Vacuum, Inert</td>
<td>(91)</td>
</tr>
</tbody>
</table>
The stabilization process also offers the potential to prevent the melting and fusion of the polymeric membranes. This is to avoid excessive volatilization of carbon element in the subsequent carbonization process (73). As a result, the final carbon yielded from the precursor can be maximized (39). Moreover, Zhang et al. (71) suggested that the stabilization process should be conducted in order to maintain the morphological structure of the thermoplastic polymer precursor in the resultant microporous carbons after heat treatment. Stabilization of the thermoplastic polymers in the air allows oxygen bridges to be created between aromatic molecules that inhibit the rearrangement and growth of aromatic crystallites during carbonization step. Thus, a porous structure with more open pores can be formed in the resultant carbon membranes (72).

The stabilization process variables can significantly affect the performance of the resulted carbon membrane. These variables include stabilization temperature, heating rate and thermal soak time. The effect of stabilization temperature and thermal soak time was reported frequently in the literature because an excess oxidation abruptly expands the pore size and decreases permselectivity for permeants larger than 0.4 nm. A number of studies also been done to optimize this condition process in order to obtain carbon membrane of good performance (44, 62, 71-73). The gas permeability and selectivity of the stabilized membranes were increased in the magnitude compared to the precursor membranes. This was due to the formation of pore structure by crosslinking and volatilization of small gaseous molecules produced by minor thermal degradation during stabilization. Additionally, as the stabilization temperature increased, the degree of decomposition and crosslinking in the membrane increased, which resulted in different micropore structures of the carbon membranes that can be used to tune gas separation properties of the derived carbon membranes.

The stabilization process perform in carbon membrane preparation is also similar to the stabilization process that carried out in carbon fiber preparation. Basically, during the stabilization process, the precursor undergo numbers of physical and chemical changes due to a variety of exothermic chemical reactions, including decomposition, cyclization, dehydrogenation, oxidation, crosslinking and fragmentation. The cyclization reactions that
convert PAN into an infusible stable ladder polymer are of most importance in PAN fibers (95). The stabilization reaction involved in the precursor polymer could be estimated quantitatively by means of FTIR spectroscopy. For PAN polymer, the reactions such as cyclization, crosslinking and dehydrogenation were indicated by the observation of a new band at 1595 cm\(^{-1}\). This band represented the combination vibration of C=C and C=N stretching, and NH in-plane bending of the ladder-frame structure of the stabilized PAN. Another band that contributed to the stabilization of PAN fiber was at 1718 and 1660 cm\(^{-1}\) due to the oxygen uptake reactions. Additionally, the 1595 cm\(^{-1}\) band corresponding to cyclization became distinct only after PAN fiber was heated for 30 min in air atmosphere (96, 97). It was concluded that the effective stabilization reaction can occur at certain temperatures under certain time of exposure in air environment.

However, there are no further explanations and description on the scientific studies concerning the mechanism of the stabilization reaction during the stabilization step in the preparation of polymer based carbon membranes in the literature. Most of the studies focus on the effect of stabilization parameters on the gas permeation properties of the carbonized membranes, in terms of permeability and selectivity rather than on the chemical point of views. For instance, the mechanisms and kinetics of the stabilization reaction involved in PAN based carbon fiber have been studied. Therefore, similar studies on the mechanism of the stabilization occurred in the preparation of stabilized polymeric precursor membrane need to be conducted to have further understanding on carbon membrane formation process.

2.4.2. Carbonization Process

Carbonization process is the heart of carbon membrane fabrication and considered as compulsory process. Generally, the carbonization process takes place after stabilization process. At the initial stage of carbonization process, most chemical reaction and volatile emission occurred. Typical volatile byproducts that have been produced are ammonia (NH\(_3\)), hydrogen cyanide (HCN), methane (CH\(_4\)), hydrogen (H\(_2\)), nitrogen (N\(_2\)), carbon monoxide (CO), and carbon dioxide (CO\(_2\)). The hydrogen evolution was indicated by the formation of graphite like structure. The evolution of byproducts is dependent on the type of polymer used and generally causes a large weight loss (39, 98).

During the carbonization process, part of the heteroatoms originally presented in the polymer structure was eliminated while leaving behind a crosslinked and stiff carbon matrix. As a result of the rearrangement of the molecular structure starting from the polymeric precursor, amorphous microporous structure of carbon membranes was created by the evolution of gases (63). The pore structure that formed during the carbonization process determines the separation properties of carbon membrane. These pores were non homogeneous and consist of relatively wide openings with few constrictions. In general, the pores vary in size, shape and degree of connectivity depending on the chemistry of the carbonization step and the polymer precursor
morphology. The microstructure of carbon membranes (pore size, pore volume, and pore distribution) could be tailored by controlling the conditions of carbonization process. The carbonization temperature that known as final temperature (25, 64, 83, 93), heating rate (22, 62), thermal soak time (12, 31, 83), and carbonization atmosphere (59, 60, 91) are the factors that influences the carbonization process. Therefore, it is necessary to optimize the parameters in order to gain the best carbon membranes for gas separation.

Carbonization is carried out typically from 500 to 1000 °C, between the decomposition and graphitization temperature of the precursor and at a wide range of heating rate of 1 to 13 °C/min. The increasing temperature of carbonization will produce carbon membrane with higher compactness, more turbostratic, higher crystallinity, higher density and smaller average interplanar spacing between the graphite layers of the carbon (99, 100). Meanwhile, thermal soak time during the carbonization process can be different depending on the final carbonization temperature (22, 101). Thermal soak time is the period of time taken to hold the membrane at a constant carbonization temperature before the membrane is cooled down to room temperature. Previous studies reported that selectivity of carbon membrane would increase at high thermal soak time (98, 100). Carbonization process can be applied either in vacuum, inert atmosphere (He, N₂, or Ar) or oxidative atmosphere (CO₂). The chemical damage and undesired burn off of the polymer precursor membrane during carbonization can be avoided by controlling the carbonization atmosphere. Vu and Koros (83) postulated that the inert gas environment accelerates the carbonization reaction by increasing the gas phase heat and mass transfer to form a more open porous matrix. The carbonization under CO₂ environment showed a more permeable and exhibited high permselectivity than those carbonized in N₂. In this section, it can be concluded that the application of a reactive media could result in carbon structures with higher microporosity, total volume of pores and BET specific surface area (59).

2.5. Membrane characterization

Few techniques on characterization commonly used in carbon membrane preparation are shown in Table 2.3. The techniques included thermogravimetry analysis (TGA), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), adsorption and sorption experiments, and elemental analysis.

2.6. Membrane performance

Gas permeation measurement is the most comprehensive tool to assess performance of the membranes. The two important quantities which can be determined by permeation measurement are the gas permeability, which is a measure of the amount of permeate that passes through a certain membrane area in a given time for a particular pressure difference, and the selectivity which is a measure of the membrane quality. The performance of the carbon
membranes are depending largely on the nature of pore structure and pore size in the concerned porous carbon membranes. The pore size distributions of the resultant carbon membrane are normally obtained from the N\textsubscript{2} adsorption isotherms.

Carbon membranes have a well-developed ultramicropore network that can separate small gas pairs with minor difference in diameter, thus exhibit higher gas permeability and selectivity than polymeric membranes. The separation mechanism that normally take placed in the carbon membrane is listed in the Table 1.2. The pore structure of carbon membrane is mainly composed of the disordered inter-connective nano-channels formed by the intergranular holes (supermicropores) packed by the turbostratic carbon microcrystals and the space (ultramicropores) existed between the carbon sheets. The disordered inter-connective nano-channels in the pore structure of the carbon membrane result in high diffusion resistance of the gas molecules penetrating through the membrane, thus lead to low gas permeability of the carbon membranes. As such, how to further enhance the gas permeability of carbon membranes remains a challenge, and it must be tackled to help speed up the commercial applications (102).

Before carry out the gas permeation test, the hollow fiber membranes were potted at both ends to form a bundle consisting of 5 to 10 fibers. One end of the fiber bundle is sealed into a stainless steel tube, while the other end is fully potted with the epoxy resin. Loctite E-30CL epoxy adhesive is used as a potting resin. Figure 2.2 shows the results of typical carbon hollow fiber membranes that has obtained.

### Table 2.3: Membrane characterizations

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Descriptions</th>
</tr>
</thead>
</table>
| TGA         | - To determine weight loss of a substance as a function of process temperature  
- To observe the thermal decomposition behaviors of the precursor membranes |
| SEM         | - To observe the morphological structure of the membrane (surface, skin layer and cross section)  
- To determine the overall quality of the selective layer, the presence of any macroporous/mesoporous cracks or pinholes  
- To evaluate the apparent changes in membranes dimensions as a result of the heat treatment process |
| FTIR        | - To detect the change of the functional groups and elemental in the membranes when they were heated from room temperature to carbonization temperature |
| XRD         | - To determine the crystalline structure of polymers  
- To estimate the interplanar distance (d-spacing) in the membrane matrix by the well known Bragg equation  
- The most relevant peaks when examining polymer-based carbon are
the (002) and (100) peaks. The (100) peak is commonly used to
determine the crystal length while the (002) peak is related to the
distance between carbon atoms on the same plane

<table>
<thead>
<tr>
<th>Adsorption and sorption experiments</th>
<th>• To determine the pore size distribution of the carbon membrane by the HK (Horvath and Kawazoe) method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental analysis</td>
<td>• To measure the percentage composition of carbon, hydrogen, nitrogen and oxygen in the carbon membrane as a function of process temperature</td>
</tr>
</tbody>
</table>

**Figure 2.2:** Typical carbon hollow fiber membranes (103)

This bundle is then inserted in a stainless steel module. All fittings and nuts that used are of Swagelok type to get a better prohibition of leakage during the gas permeation test. A simple bubble flow meter was used to obtain the permeation properties of the gas owing to its suitability for the measurement of small and wide range of flow rate (56). In the single gas permeation system, pure gases are introduced into the system at feed pressures of 1 to 15 bars at ambient temperature. The permeate side of the membrane is maintained at atmospheric pressure. The permeance, \( P \) (GPU) and ideal separation factor (or selectivity, \( \alpha \)) of the carbon membrane are calculated from the permeation rate by using equations (2.1) and (2.2) respectively.

\[
\left( \frac{P}{l} \right)_i = \frac{Q_i}{\Delta p \cdot A} = \frac{Q}{n \pi D l \Delta P} \tag{2.1}
\]

\[
\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \tag{2.2}
\]
where $P/l$ is the permeance of the hollow fiber (cm$^3$ (STP)/cm$^2$.s.cmHg), $Q_i$ is the volumetric permeate flow rate of gas i at standard temperature and pressure (cm$^3$ (STP)/s), $\Delta p$ is the pressure difference between the feed side and the permeation side of the membrane (cmHg), $A$ is the membrane surface area (cm$^2$), $n$ is the number of fibers in the module, $D$ is an outer diameter of hollow fiber (cm) and $l$ is an effective length of hollow fiber (cm).

### 2.7. Membrane modules

In order to ensure the efficiency of a membrane process in a given application, the geometry of the membrane and the way it is installed in a suitable module is also important. The accomplish system of the membrane separation depends not only on the development of high performance membrane but also on the design and construction of an efficient and economical membrane module. For commercial applications of membranes, it is preferable to fabricate a module with an asymmetric structure and capillary or hollow fiber configurations in order to increase the rate of permeation of the products. In general, the characteristics of the modules that must be considered in all system designs are the cost of production, maintenance, and efficiency. The most challenging task that must be considered while fabricating these modules is improving the poor mechanical stability of carbon membranes. This is more crucial in hollow fiber carbon membranes, since they are self-supporting (39, 40).

Until today, only the laboratory scale tubular or hollow fiber membranes have been described in detail. Industrial scale applications of carbon membranes were hampered by the difficulty that involved in the large scale membrane production, poor mechanical stability of the membranes and the poor reproducibility of the membrane modules. The assembly of large scale modules described only in the patents by Soffer and coworkers (104-106). The only commercial modules are now available from Carbon Membranes Ltd (Israel) with a hollow fiber (small tubular) configuration with the packing density of 2000 m$^2$/m$^3$. Furthermore, the novel carbon membrane module of the Blue Membranes GmbH is based on “honey comb module” concept and has a high packing density of 2500 m$^2$/m$^3$ (107, 108). Selected examples of modules fabricated by various researchers are shown in Figures 2.3 and 2.4.
3.0 CARBON MEMBRANE PROCESSES & APPLICATIONS

3.1 Gas separation

At present, membrane processes are employed in a wide range of applications and the number of such applications is still growing. In order to compete with the conventional processes, the performances of membranes in the existing markets need to be improved and alternative materials must be developed. The utilization of membranes in industrial gas separations has undergone substantial growth in several areas since 1980 when the first large scale application was developed by Permea for H₂ separations (109). In 2007, there are 15 new gas plants around the world and this number jumped to 24 for 2008, indicating substantial new opportunities for membranes are available (110). It is expected that by 2020, the opportunities for new membrane installations in natural gas treatment will increase (109, 111). The increasing in the activities of carbon membrane research and a great separation performance of the carbon
membrane will be the motivation principles in future. In Table 3.1 below, the results of carbon membrane performance that have been reported by different investigators are shown.

In the literature, various reports on O$_2$/N$_2$ separation using carbon hollow fiber membranes and supported carbon membranes are available (12, 21, 22, 44, 58, 61, 64, 68, 69, 72, 76, 90, 113, 117). This gas pair separation can be applied in air separation, oxygen-enriched air for combustion processes, medical purposes and pure O$_2$ and N$_2$ production. Currently, the largest industrial gas separation application is the processing of natural gas. It is owing to the rising in the natural gas consumption worldwide and most of the membrane processes is applied towards the CO$_2$ removal. The total consumption of natural gas worldwide is approximately 95 trillion standard cubic feet a year and is expected to rise up to 182 trillion cubic feet in 20 years onwards due to the increasing demand for energy around the world (118).

Although polymeric membranes are able to compete successfully with other technologies, for example the amine scrubbing, improvement in membrane fabrication is necessary to grab the broader market opportunity for carbon membranes. This is because some of glassy polymeric membranes lose their selectivity and productivity in the presence of trace quantities of condensable heavy hydrocarbon. Moreover, the extremely high partial pressure of CO$_2$ can cause the plasticization in the skin layer of a membrane (119). Carbon membrane also has a potential to recover CO$_2$ gas from power plants that burn fossil fuel and to avoid its emission to the atmosphere. This application was recommended by Centeno and Fuertes (11), when they had successfully prepared carbon membrane with high selectivity of CO$_2$/N$_2$. Similar findings were also made in the studies of Fuertes and Menendez (44), Lua and Su (58), Powell and Qiao (120), Zhang et al. (79), Favvas et al. (59), Rao et al. (64) and Liu et al. (72).

In addition, the power plants combined with coal gasification processes need a H$_2$ separation step at about 300 to 500 °C. At high temperature operation, only a pressure driven membrane separation process can isolate the H$_2$ from other carbon compounds (CO$_2$, CO). In this case, organic polymeric membranes cannot resist very high temperatures and begin to decompose with certain components. Thus, carbon membrane that is chemically inert and thermally stable up to more than 500 °C is more suitable for this application (11, 20, 121). Carbon membranes can also be applied to the H$_2$ recovery from the gasification process without further compression of the feed gas, while rejecting a substantial portion of the hydrocarbons (122). Polymeric membranes incurred additional recompression costs because H$_2$, as a fast gas, exits the unit at the low pressure side (119).

<table>
<thead>
<tr>
<th>Precursor</th>
<th>O$_2$/N$_2$</th>
<th>CO$_2$/CH$_4$</th>
<th>CO$_2$/N$_2$</th>
<th>H$_2$/CH$_4$</th>
<th>H$_2$/N$_2$</th>
<th>He/N$_2$</th>
<th>C$_2$H$_4$/C$_2$H$_6$</th>
<th>Ref(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>~3.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(31)</td>
</tr>
<tr>
<td>PEI</td>
<td></td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(63)</td>
</tr>
<tr>
<td>PEI</td>
<td>3.9</td>
<td>17.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(64)</td>
</tr>
<tr>
<td>PEI/PVP</td>
<td>4.6</td>
<td>13.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(64)</td>
</tr>
</tbody>
</table>

Table 3.1: Results of carbon membrane performance reported by different investigators
Furthermore, the separation of light alkenes/alkanes and olefins/paraffins have been recognized as a key technology by the petrochemical industry (44, 100, 123). Carbon membranes are promising candidates for separating light alkenes/alkanes and olefins/paraffins, especially propene/propane separation and 1,3-butadiene/n-butane separation, respectively. Hayashi et al. (43, 124) reported that special carbonized membrane is capable of recognizing size differences between alkane and alkene molecules. It is expected more superior than other methods, such as distillation, adsorption and absorption-based on energy consumption. A recent study estimated that about 10,000 BTU of energy is used annually for olefin-paraffin distillation (119). It is also possible to employ carbon membranes to separate the isomers of hydrocarbons into normal and branched fractions (125).

3.2. Membrane reactor
A carbon membrane reactor constitutes one of the most promising applications of carbon membranes. The performance of a carbon membrane for the dehydrogenation of cyclohexane to benzene was examined by Itoh and Haraya (126). They reported that the performance of their carbon membrane reactor for dehydrogenation was fairly good compared with that of a normal reactor, i.e. functioning at equilibrium. On the other hand, Lapkin (127) used a macroporous phenolic resin carbon membrane as a contactor for the hydration of propene in a catalytic reactor. He found that the use of this porous contactortype reactor for his high-pressure catalytic reaction is practical. In 2003, Coutinho et al. (18) claimed that the PEI-based carbon membranes had a potential to be applied in catalytic reactor application.

The combination of reaction and separation at high temperature in a membrane reactor offers interesting new possibilities. In a membrane reactor, the separate product and feed compartments allow more ways to optimize selectivity and conversion (128). Zhang et al. constructed a carbon membrane reactor (CMR) for methanol steam reforming and found CMR gave a higher methanol conversion than the conventional fixed bed reactor (FBR) and produced a CO free hydrogen stream (129). Carbon membrane was prepared by spraying a DMF solution containing phenol formaldehyde novolac resin (PFNR) and polyethylene glycol (PEG) on a PFNR based green membrane support, the details of which are given elsewhere. The sprayed layer was then carbonized under an inert gas stream to 800 °C at a heating rate of 0.5 °C/min. As the catalyst for the steam reforming reaction, laboratory made Cu/ZnO/Al₂O₃ composite catalyst was used. The inner diameter of a tubular carbon membrane that used is similar with a stainless steel tube of FBR (6mm). The permeation mechanism through the membrane is by the sieve mechanism since the gas permeance decreased with an increasing kinetic diameter of the gas molecules. The steam reforming consists of the following chemical reactions:

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H}_2\text{O} &= \text{CO}_2 + 3\text{H}_2 & \text{endothermic reaction} \\
\text{CO} + \text{H}_2\text{O} &= \text{CO}_2 + \text{H}_2 & \text{exothermic reaction} \\
\text{CH}_3\text{OH} &= \text{CO} + 2\text{H}_2 & \text{endothermic reaction}
\end{align*}
\]

The first and the third reactions are highly endothermic and the second reaction is highly exothermic. The results showed that CH₃OH conversion increased with an increasing temperature. This is because; both CH₃OH conversion reactions (first and third reaction) are endothermic. Meanwhile, the CH₃OH conversion of CMR is higher than for FBR. This is because the equilibrium shifted to the right side in the first and the last reaction when H₂ is preferentially removed from the reactor through the membrane wall. It is practically no CO and methanol found in the permeate through the carbon membrane.

### 3.3. Pervaporation
Sakata et al. made porous carbon membrane plates (PCMP) to separate benzene/cyclohexane azeotrope by pervaporation (130). PCMPs were prepared from phenol resin powder (BELLPEARL S-870, Kanebo) by pressurize the powder in a hydraulic press. The disk was heated at 300 °C for an hour in the air stream and then carbonized at 800 °C in two different environments. The results showed that PCMPs prepared under N2 stream had only micropores, while PCMPs prepared under CO2 stream had both micro and mesopores. The separation factor (benzene/cyclohexane) of 2.8 was obtained by pervaporation at 60 °C. Flux of pure benzene and pure cyclohexane was 0.34 kg/m²h and 0.57 kg/m²h, respectively. Recently, Tanaka and coworkers (131) have produced supported carbon membranes through the carbonization of resorcinol/formaldehyde resin at relatively low temperatures ranging from 400 to 600 °C. Pervaporation separations for water/alcohol (methanol, ethanol, and i-propanol) and water/acetic acid mixtures were conducted to investigate the feasibility of using the microporous carbon membranes for pervaporation. The permeation flux and separation factor of about 0.23 kg/m²h and 4150, respectively, for 10 wt % water/i-propanol mixture at 70 °C were obtained. The membrane stability in acid was improved by the sulfonation treatment. It is indicated that for 10 wt % water/acetic acid mixture at 30 °C, the permeation flux and separation factor were stable 0.12 kg/m²h and 70, respectively, for 196 h.

3.4. Water treatment

Polyvinylidene chloride (PVDC) and polyvinyl alcohol (PVA) microspheres were carbonized on ceramic membrane to fabricate activated carbon membrane for coke furnace wastewater treatment (132). A ceramic tube was dipped into a polymer latex containing 70 wt % PVDC and PVA microspheres of 0.10 to 0.15 µm to form aggregates of polymeric microspheres on and within (within the pores of) the ceramic pipe. The precursor was heated at 300 °C and further to 750 °C for carbonization. Nitrogen adsorption applying Horvath and Kowazoe method, the membrane was found to have a bimodal pore size distribution with micropores of 0.7 to 0.8 nm in diameter and mesopores of 2 to 20 nm. The molecular weight cut off of the membrane at ca 10,000 Dalton. Coke furnace wastewater containing dissolved organic carbon (DOC) of 69 ppm and two peaks at the molecular weight of 400 and 10,000 Da was subjected to the filtration by the activated carbon membrane. The result indicated that 32 % of the COD is removed by the sieve mechanism. Most likely, the adsorption occurs in the micropores in the carbon particles while the filtration takes place where the pores formed as the interstitial space between the carbon particles.

The immobilization of biofilms on permeable membranes for the biodegradation of pollutants had drawn an increasing interest for applications, where conventional treatment technologies are difficult to apply. As one of such examples, Hu et al. demonstrated the usefulness of membrane aerated biofilm reactor (MABR) for the wastewater treatment (133); a
carbon membrane aerated biofilm reactor (CMABR) was constructed to remove organics and nitrogen containing compounds simultaneously in one reactor. The biofilm was occurred when the bacterial adherence to the membrane surface. Oxygen pumped into the lumen (left side) of the membrane passes through the membrane wall and is utilized by the bacteria within the biofilm to oxidize the pollutants as it penetrates into the biofilm. The reactor feed contained glucose and ammonium chloride as the sources of organic carbon and nitrogenous component. In addition, the feed contained a small amount of minerals as element nutrition. The experimental membrane bioreactor contained 16 carbon tubes of length 20 cm with an inner and outer diameter of 4.7 and 8.9 mm, respectively. The pore size was 2 µm.

The most important parameter in the operation of CMABR is the oxygen supply rate. If the excess oxygen is provided, heterotrophic bacteria will grow and the organic carbon for heterotrophic denitrification will be in short supply. On the other hand, if the oxygen supply rate is low, the heterotrophic bacteria will compete with nitrifying microorganisms. Therefore, the supplies of the oxygen need to be controlled for the optimum operation of CMABR. The oxygen transfer was controlled by changing the oxygen pressure. Under the aeration conditions, an assumption was made that all carbon and nitrogen in the feed water are oxidized into CO₂ and NO₃⁻. With this assumption, the maximum oxygen supply rate (OSR) at each run was evaluated to be around 1 to 6 g/day. Based on the analysis, the COD and NH₄⁺-N were removed effectively over a period of 121 days and a stable operation was achieved for COD removal within 8 days. However, a significant growth of biofilm from 68th day and the NO₃⁻-N concentration as well as TN concentration decreased considerably. It is revealed that the thickness of biofilm became as high as 3.3 mm, which starts to hinder the supply of oxygen through the biofilm.

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