1. INTRODUCTION

Separation of aerosol particles from fluids is needed in many industrial processes and ceramic membranes are wildly used for this purpose.

Ceramic membranes are granular membranes and they are made from inorganic materials such as $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{ZrO}_2$, $\text{SiO}_2$, etc. or combination of these materials [1]. Recently, Sadigzadeh et al. has produced micro porous ceramic membrane filters by compressing and sintering of pyrex powder [2]. In contrast with polymeric membranes, ceramic membranes have excellent thermal and chemical stability which makes them usable in high temperature membrane operations and aggressive environments. Also they are very stable mechanically and bio inert which made them ideal materials for many pharmaceutical industries or in water and wastewater processing [3-5].

Performance of membranes is determined with energy consumption and the efficiency of system to particles capture. Therefore the permeability and separation are the two most important factors of a ceramic membrane. For porous ceramic membranes, these factors are typically governed by pore size and surface porosity [1]. When a membrane has a high porosity, its pressure drop is low. A membrane with narrow pore size, on the other hand, can remove smaller particle from the fluid. So that ceramic filter media must have high porosity and narrow pores size distribution [6]. Pore size of ceramic membranes is decreased by granules which are been in the pore, as shown in Figure 1. (Figure 1(a) shows a large pore. Figure 1(b) shows this pore that its size is decrease by granule). It is obvious that by this approach, porosity of ceramic membranes is decreased considerably by reduction of pore size in them and it is an important problem in these membranes because their pressure drop and energy consumption are increased significantly. It is better that we use fibres with narrow diameter instead of granules, as shown in Figure 1 (c) because of three causes:

1. Porosity of membrane doesn't change considerably.
2. Each original pore becomes a lot of small pores.
3. Because of the small diameter of fibres, efficiency of membrane must decrease.
On the other hand, the theoretical expression for the capture efficiency of the aerosol particles (E) by a granular bed is a function of its depth (L) and porosity (ε), as well as the diameter (D) and the total single collector efficiency (ηt) of spherical collectors [7].

If we neglect the interaction between the different collection mechanisms, electrostatic and sieve effect; ηt is obtained by adding the contribution of individual collection mechanisms: sedimentation (ηs), inertial impact (ηimp), direct interception (ηi) and diffusion (ηd). Consequently; ηt = ηs + ηimp + ηi + ηd [8].

Because of the large diameter of granules if they were used for reduction of pores size, efficiency of membrane must decrease, as shown in Eq. (1).

$$E = 1 - \exp \left( -\frac{3D - 6\eta_{i}}{2\eta_{d}} \right)$$  \hspace{1cm} (1)

It is concluded that carbon nanotube (CNT) can be a good material for this purpose because of the narrow diameter and large aspect ratio of them.

CNTs have considerable aspect ratio and specific surface area, so that they are suggested as a new material, which may be applied for hydrogen storage, gas absorption, filtration and separation [9]. Some researchers have investigated use of CNTs in filtration. For example Vander Wall and Hall [10] and Johnson et al. [11] synthesized directly CNTs upon a metal mesh screen and also Prak and Lee improved performance of micron-sized fibrous metal filters by direct growth of CNTs on them [12]. Srivastava et al. made a filter which was entirely composed of CNTs. This filter could remove micron- to nanoscale contaminants from water and heavy hydrocarbons from petroleum [13]. Because this filter is entirely composed of CNTs, its pressure drop is considerably high and its scale-up is limited [12].

In this study, we used a novel approach to reduce pore size of Pyrex ceramic membranes but porosity of them decreases a little. For this purpose CNTs were synthesized in pores of borosilicate Pyrex membranes by chemical vapour deposition (CVD) method.

2. EXPERIMENTAL PROCEDURE

Our experimental processes were done in two stages. Initially porous membranes were produced by sintering of Pyrex and cobalt powder mixture. In second stage, CVD process was applied to these membranes and nanotubes were grown on them. Details of these stages are described as follows:

2.1. Tablet Preparation

In this study we used Pyrex powder with size distribution between 60-70 micrometer which prepared by grinding of borosilicate glass (7740, Corning Inc.). Cobalt powder with different percent was homogeneously mixed with the Pyrex powder as shown in Table 1.

In order to produce row membranes, 0.5 gr of each of these mixtures were compacted in the form of tablet by use of a uniaxial cold press and in a stainless steel mould. The applied pressure and mould diameter was 1 ton and 1 cm respectively. These row tablets were sintered at different temperature in an electric furnace to produce Pyrex membranes. The sintering temperature profile is shown in Figure 2.

<table>
<thead>
<tr>
<th>sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co W (%)</td>
<td>2.267</td>
<td>1.167</td>
<td>0.566</td>
</tr>
</tbody>
</table>

Table 1 Co weight percent in different samples
2.2. Nanotube Synthesis

In second stage thermal chemical vapour deposition (TCVD) method was used to grow nanotubes within pores of the membranes.

The membranes were placed on a quartz plate and loaded into reaction zone of a thermal chemical vapour deposition apparatus operated at atmospheric pressure. Our CVD set up was a horizontal electrical furnace which has a quartz tube with 5 cm diameter and 1 m length for controlling the atmosphere.

Argon and ammonia were used as carrier and reactive gas respectively and acetylene was used as the carbon feedstock. The CVD apparatus temperature was increased to 750 °C, in Ar atmosphere at flow rate of 100sccm. When the temperature was reached 750 °C, a NH<sub>3</sub>/Ar (8:10) mixing gas with a 180 sccm flow was introduced to the samples for 15 min. Then C<sub>2</sub>H<sub>2</sub> at flow rate of 20 sccm was added to previous gases in order to grow CNTs. The growth time of CNTs was 20 min. At the end of this period the furnace was turned off and cooled to room temperature in an Ar flowing environment.

The morphology of synthesized samples was analyzed by Scanning Electron Microscopy (SEM).

3. RESULT AND DISCUSSION

Figure 3 shows the SEM images of the tablets (membranes) after sintering and before CVD process. Figure 3 (a) to (c) are corresponded to samples 1 to 3 respectively. The images indicate that tablets have porous structure with homogeneous porosity. This shows that the applied sintering temperature was correct. The pore size of these tablets distributed from 5 to 30 micron.

The purpose of this research was reduction of these Pyrex membranes pore size by growth of nanotubes on them. Therefore CVD process was applied to these tablets.

These membranes after CVD process are shown in Figure 4 and Figure 5. Figure 4 illustrates that membranes are porous yet but CNTs are grown in the form of bush like colonies on the surface of them after CVD process. Distribution of these structures in sample 1 which have higher catalyst percentage is denser than sample 2 and 3.

Also CNTs are grown into the pores and reduced pores diameters as shown in Fig. 5.

From Fig. 4 we can see that in sample 1 (with 2.267% catalyst), nanotubes were grown in the most of the pores and it seems that we can make a Pyrex membrane which its pores size are controlled with nanotubes.

Also SEM images illustrate that in sample 3 (which has lower catalyst) most of the pores were clogged after CVD process because CVD temperature was 50° more than sintering temperature of Pyrex therewith Pyrex powder were melted and clogged the pores. This problem didn't occur in samples 1 and 2 which have higher catalyst and most of their pores remained open because catalyst particles situated between Pyrex powders and didn’t allow them to weld to each other.

Because a good Pyrex membrane has high porosity and narrow pores size, it seems that the sample No. 1 is better than other samples because it is very porous and its pores were decreased by nanotubes too. With our developed method, the Pores size was decreased but total porosity of the membrane was not changed considerably after
growth of nanotubes because of the large aspect ratio of CNTs. Thereby, membranes with high porosity and fine pores were fabricated. It is expected that membranes pressure drop does not change considerably but nanoparticles can captured by CNTs, so that the filtration...
efficiency may be improved. It suggests a novel application of CNTs in filtration.

4. CONCLUSION

In this study, CNTs were grown directly in the pores of conventional micro porous Pyrex membranes by thermal chemical vapour deposition method. The CNTs were grown in the form of bush like structures and reduced the pore-size of membranes. By growth of nanotubes each of micro-pores became a lot of sub-micron pores but porosity of membrane was not change considerably because of the large aspect ratio of CNTs. Thereby it is expected that membranes pressure drop does not change considerably but nanoparticles may be captured by CNTs and the filtration efficiency may be improved. It suggests a novel application of CNTs in filtration.

5. ACKNOWLEDGEMENT

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REFERENCES


Fig. 5. SEM images of pores after growth of nanotubes. Figs a to c, corresponds to the samples given in table 1 and Figs d to f, belong to the samples produced at different conditions of CNTs growth regarding the feed and carrier gas flow.