Development and Characterization of Alumina-Based Membranes for Water Purification

B A Ahmed*, F Ahmed, K Ali and J B Shabbir

Department of Mechanical Engineering, College of Electrical and Mechanical Engineering, National University of Sciences and Technology (NUST), Islamabad, Pakistan, 46000

*banjumahmed@gmail.com

Abstract. High energy ball milling (HEBM) and pressure less sintering technique were performed to achieve a homogenous powder mixture and porous ceramic membranes of $\alpha$-Al$_2$O$_3$/2%MWCNTs. A uniaxial powder compaction press was used to compress the powder mixture into circular green pellets (27 mm in diameter, 3-4 mm thickness) at three different pressure values of 100 MPa, 250 MPa and 400 MPa, followed by sintering at three different temperature values of 1200 ºC, 1250 ºC and 1300 ºC under argon gas atmosphere. The effect of process parameters on the pore distribution and phase change was characterized by employing Field Emission Scanning Electron Microscopy (FESEM) and X-Ray Diffraction (XRD) respectively. Process parameters were found to have a strong influence on the characteristics of the developed membranes like diametrical strength, water permeability and porosity. Water flow rates varied from 950 l/m²·hr to 42 l/m²·hr, porosity decreased from 48.57% to 28.87% and diametrical strength increased from 0.95 MPa to 11.06 MPa as compaction pressure was increased from 100 MPa to 400 MPa and sintering temperature was increased from 1200 ºC to 1300 ºC.

1. Introduction

Human activities are the major cause of water pollution around the globe[1]. In agricultural and industrial zones, fertilizers are observed to react in the soil to produce heavy metals as by products which further accrue in the soil and water[2]. The main pollutants in these waste are nitrates, nitrites, cations, anions such as Ag$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, HCO$^3$ and toxic metals like iron mercury, cadmium, lead, chromium, arsenic, nickel, cobalt, copper, zinc and magnesium[3, 4]. Adsorption based filtration technique has cemented its status as one of the economic and efficient way for removing heavy metals from wastewater. Many reported studies focus on the use of low-cost adsorbents for removing heavy metal ions from waste waters. Bhattacharyya and Gupta used kaolinite and montmorillonite to remove heavy metals from waste water[5]. Investigation have also been conducted for possibility of heavy metal removal through industrial by-products such as lignin, diatomite, clino-pyrrhotite, lignite, aragonite shells, natural zeolites, clay, kaolinite and peat[6–12]. In addition, some other industrial waste by-products such as fly ash, waste slags and titanium oxide were also studied due to the economic benefits[13, 14]. Alumina has also found its way as an adsorbent in the water filtration industry thanks to its favorable characteristics like thermal stability, mechanical strength and adsorption capabilities. Because of its high porous structure and surface area, it is also used as a matrix to hold other materials for making of composites[15–17]. Furthermore, carbon nano tubes (CNTs) are well-known for the heavy metal removal capability[18–20]. This outstanding ability
of CNTs for the water purification applications stems from its inherent characteristics of highly porous structure, large specific surface area, strong affinity towards toxic pollutants, high thermo-chemical stability and excellent mechanical strength[21–24].

Thereby, preparation of porous ceramic membranes by using alumina matrix and CNT reinforcement seems to be a wise approach to achieve greater heavy metal removal efficiency. Most of the previous studies on alumina-CNT composites has been focused around dense composites primarily for the improvement in thermo-mechanical, electrical and tribological properties, however little work has been carried out towards the synthesis of porous alumina-CNT ceramic membranes[25–28]. The most commonly used technique to develop CNT based ceramic membranes is chemical vapor deposition (CVD), wherein CNTs are grown on ceramic substrates. Altalhi et al. developed CNT based membranes, wherein multiwalled CNTs were grown on alumina-polyamide substrate[29]. In another study Parham et al. developed porous alumina-CNT membranes by employing thermal pyrolysis technique[30].

Traditional ceramic powder processing method that involves formation of green pellets followed by sintering have been commonly employed to develop porous ceramic substrates having sufficient mechanical strength for ceramic membranes[31]. The final characteristics of the synthesized membranes are greatly influenced by the raw materials, processing methods, parameters and sintering techniques[32]. Not only this but the amount and type of binder used, initial compaction load and sintering cycle can also affect the physical and mechanical characteristics of the synthesized membrane[33, 34].

In the present work, powder metallurgy technique was utilized to develop alumina-MWCNT porous ceramic membranes for their intended use in water purification applications. Alumina-2wt.%MWCNT powder mixture was prepared using high energy ball milling technique followed by compaction using uniaxial pressing and further consolidation via solid state pressure less sintering. Effect of processing parameters namely compaction pressure and sintering temperature on the porosity, water permeability and mechanical strength of the synthesized membranes was investigated. Optimal processing parameters required to develop alumina-2wt.%MWCNT porous ceramic membrane having sufficient porosity with appropriate mechanical strength was identified.

2. Experimental procedure

α-alumina having a particle size of ~0.5 μm, procured from Buehler, Illinois, USA was used as the starting powder for the matrix. Multi-walled carbon nanotubes (MWCNTs) having a purity of 90% were procured from Times Nano, China, with an outer diameter of 10-20 nm and average length of 10-30 μm. Poly vinyl alcohol (PVA) was used as the binding agent during the compaction process. High energy ball milling (HEBM) was used for the preparation of alumina-MWCNTs powder mixture (2% loading of MWCNTs were added into 98% alumina matrix). The balls used in HEBM were made from zirconia with a weight ratio of one to twenty (for 1g of powder mixture 20 g of zirconia balls were used). Ethanol was used as a mixing media to attain proper mixing of alumina and MWCNTs. The mixture was prepared through HEBM at 3000 rpm for three hours. After three hours of mixing, the powder mixture was dried at 100 °C for about twenty-four hours in vacuum oven. Alumina-2%MWCNTs mixture was compacted into disc shaped pellets using a uniaxial powder compression machine with a holding time of about two minutes at three different pressures of 100 MPa, 250 MPa and 400 MPa. A stainless-steel die having a diameter of 27 mm was used for compaction. This resulted in green pellets of approximately 2.5-3 mm thickness and 27 mm diameter. The pellets were then taken out of the die with the help of a hydraulic press. The green pellets were then sintered at temperatures of 1200 °C, 1250 °C and 1300 °C so that the effect of variation of temperature could be studied on the synthesized membranes. Sintering was carried out in argon atmosphere to prevent oxidation of CNT at temperature values greater than 800 °C. During the sintering cycle, the heating rate was set at 5 °C/min and temperature was held constant at 500 °C for 4 hours followed by isothermal sintering for a period of 4 hrs at the respective sintering temperatures. The first batch of experiments included three green pellets compressed at 100 MPa followed by sintering at 1200 °C, 1250 °C and 1300 °C. Similarly, the next two batches were compressed at 250 MPa and 400 MPa and then sintered at the aforementioned temperatures.
Field emission scanning electron microscope (Lyra 3, Tescan, Czech Republic) was utilized to examine the microstructure of the initial powder mixture and the synthesized membranes. FESEM micrographs were acquired at an accelerating voltage of 20 kV in order to evaluate the effect of process parameters on the grain size of alumina matrix, size and distribution of the pores. Phase analysis was performed using X-ray diffraction (XRD), (Rigaku MiniFlex X-ray diffractometer, Japan). The diffractometer was operated at a wavelength, current and voltage of 0.15416 nm, 10 mA, and 30 kV respectively. Scan rate of 2°/min for 2 theta of 20° to 80° was used to analyze the crystal structure of the synthesized membranes for changes, if any. Water flux measurements were determined with the help of a custom designed test bench where the transmembrane pressure across the membrane housing was varied in the range of 1-4 bar. Water permeability of the membranes (l/m².hr) was calculated by \( J = \frac{V}{A \times t} \), where \( A \) represents the cross-sectional area of the membrane, \( V \) represents the amount of water that flowed through the membrane in liters (l) and \( t \) is the time. The porosity of the membrane was measured as per the ASTM standards for porous ceramic materials (ASTM c373-14a). Suspended weights, dry weights and saturated weights were experimentally calculated using a Mettler Toledo kit with distilled water as the media. The porosity was calculated using the equations

\[
\text{Volume} = \text{saturated weight} - \text{suspended weight} \\
\text{Porosity} = \left[ \frac{(\text{saturated weight} - \text{dry weight})}{\text{volume}} \right] \times 100
\]

The mechanical strength of the membrane was evaluated using diametrical compression test. This test was used to estimate the strength of porous ceramic membranes. In this test, the membrane was placed in vertical position between the two flat plates of compression testing machine and the tensile stresses developed within the membrane caused the failure of the membrane into two pieces. The crack traversing through the middle of the sample is an indication of successful completion of the test. The diametrical strength of membrane was calculated using the following equation.

\[
\sigma = 2 \times \frac{(\text{Applied Load})}{(\pi \times \text{Diameter} \times \text{Thickness})}
\]

Here \( \sigma \) is the amount of stress that the membrane can bear before permanent fracture. This is a useful value as it helps in determination of suitable membrane for practical applications with specific strength requirements.

### 3. Results and discussion

FESEM was performed for the starting alumina and raw MWCNT powders as well as the HEBM powder mixture of alumina/2wt.%MWCNT. Figures 1a and 1b show the FESEM micrographs of the as received alpha alumina and MWCNTs respectively. Figure 1c depicts FESEM micrographs of HEBM powder mixture. The comparison of the as received powders and HEBM powder mixture reveal that the alpha alumina particle size decreased from ~500 nm to ~270 nm due to HEBM. Furthermore, the clots of MWCNTs were observed to have opened up and fairly homogenous distribution of MWCNTs in the alumina matrix was evident. Figure 1d represent the XRD pattern of raw MWCNTs, starting alumina and HEBM powder mixture. The hump representative of MWCNTs was not observed in the XRD spectrum of HEBM powder mixture primarily due to the low weight % of CNTs in the mixture i.e. 2wt% (below the detection limit of XRD). Figure 1e presents the XRD patterns of HEBM powder mixture and the membranes synthesized at 1300 °C-100 MPa, 250 MPa and 400 MPa. In all the samples, alpha alumina peaks were seen to reside at the same 2-theta angles indicating that there wasn’t any chemical reaction between the starting materials (alumina and MWCNTs) or that of the starting materials with the surrounding atmosphere.
Figure 1. FESEM micrographs of (a) alpha alumina starting powder, (b) MWCNTs and (c) HEBM powder mixture of alpha alumina/2wt.% MWCNT. (d) XRD pattern of (i) MWCNTs, (ii) Alumina, (iii) HEBM powder mixture (98% alumina-2wt% CNTs) and (e) XRD pattern of (i) HEBM powder mixture (98% alumina-2wt% CNTs), (e) alumina/MWCNT disks sintered at 1300°C and compacted at
(ii) 100MPa, (iii) 250 MPa, (iv) 400MPa.

Figures 2a and 2b represent the FESEM micrographs of the membranes sintered at 1200 ℃. The membranes depict a porous and loosely fused morphology of alumina grains at low compaction pressure of 100 MPa that seems to improve further with the increase in the initial compaction load of 400 MPa (Figure 2b). Figures 2c and 2d show the micrographs of the membranes sintered at 1250 ℃. The morphology of alumina particles appeared to be more compact with relatively lesser porosity as compared to the samples sintered at the lower temperature. The apparent porosity as well as the loosely held appearance of the of the matrix particles was observed to decrease with the increase in the initial compaction load from 100 MPa to 400 MPa. Figures 2e and 2f depict the micrographs of the samples sintered at 1300 ℃. Grain growth of alumina particles at the expense of smaller grains is quite evident even at the lowest compaction pressure of 100 MPa. It is observed that with the increase in compaction pressure alumina particles fused well into each other and the apparent porosity is much less as compared to the samples prepared at the lower temperatures and compaction loads. As reported in the literature, the morphological evidence revealed that increasing the pressure caused the alumina particles to pack closely together which resulted in strong network development [35]. The greater contact area of grains allows the grains to fuse together more profoundly at higher compaction pressure as compared to lower compaction pressures.
By increasing the temperature, porosity of the samples was observed to decrease. For 100 MPa samples, increasing the temperature from 1200 to 1250 to 1300 °C, the porosity was observed to decrease from 48.57% to 45.06% to 39.95% respectively. Similarly, the percentage porosity decreases with the increase in compaction pressure. Similar trend was observed for 250 MPa samples where the porosity decreased from 43.67% to 39.91% to 31.89% with the increase in sintering temperature. Further increase in compaction pressure to 400 MPa resulted in a relatively lesser reduction in porosity of 39.25% to 35.16% to 28.87%. Generally, for all the sintering temperatures, the reduction in porosity was more evident with the increase in compaction pressure from 100 MPa to 250 MPa followed by a relatively lesser decrease in porosity as the compaction pressure was increased from 250 MPa to 400 MPa.

Diametrical compression strength is the stress that a membrane can withstand under the application of a transmembrane pressure. The variation in diametrical strength of the synthesized membranes as the initial compaction pressure was increased. As it is already mentioned that the porosity decreased with the increase in initial compaction pressure. The growth of alumina grains as well as the fusion of grains was quite evident both at high sintering temperature as well as higher compaction load. The diametrical strength showed an increasing trend with the increase in the values of the process parameters. The measured strengths of the membranes prepared in the current study are well in agreement with the previously reported literature on diametrical compression strengths of CNT based membranes. The effect of process parameters (compaction loads and sintering temperatures) on the porosities and diametrical strengths of the synthesized membranes are summarized in table 1.

Table 1. Physical and mechanical properties of the synthesized membranes against respective process parameters.

| S. No | Sample ID | Compaction Pressure (MPa) | Sintering Temp. (°C) | Porosity (%) | Diametrical Strength (MPa) |
|-------|-----------|---------------------------|---------------------|-------------|---------------------------|
| 1     | 130100    | 100                       | 1300                | 37.95       | 5.35                      |
| 2     | 130250    | 250                       | 1300                | 31.89       | 7.59                      |
| 3     | 130400    | 400                       | 1300                | 28.87       | 11.07                     |
| 4     | 125100    | 100                       | 1250                | 45.06       | 2.87                      |
Figures 3 a-c represent the water permeability data of the synthesised membranes with reference to the process parameters of sintering temperature and initial compaction loads. The water flux values of these membranes were determined for transmembrane pressure in the range of 1-4 bar. Increasing the transmembrane pressure result in an increase of water flux for all the membranes. As porosity and flow rates follow a direct relationship, thereby with increase in the sintering temperature (for same compaction load) the flow rates of the membranes decreased. With regards to the processing conditions, membranes synthesised using the compaction load of 100 MPa and sintering temperature of 1200 ℃, high flow rates were recorded. The maximum flow rate of about 950 l/m²·hr was achieved for the membrane processed at 100 MPa and 1200 ℃. The membranes synthesized in the current study exhibited higher flow rates as compared to the CNT based membranes developed through CVD method reported in literature[36].

![Figure 3](image)

Figure 3. Effect of compaction pressure on water permeability for the membranes sintered at (a) 1300 ℃, (b) 1250 ℃ and (c) 1200 ℃.

4. Conclusion
In this work alumina/2wt.% MWCNT powder mixture was prepared using high energy ball milling process. The powder mixing process helped in achieving homogenous powder mixture of the alumina matrix and the MWCNTs. The process parameters, such as pressure (100 MPa, 250 MPa and 400 MPa) and sintering temperature (1200 ℃, 1250 ℃ and 1300 ℃) were found to greatly affect the physical and mechanical characteristics of the developed membranes. Water flow rates varied from 950 l/m²·hr to 42 l/m²·hr, porosity decreased from 48.57% to 28.87% and diametrical strength increased from 0.95 MPa to 11.06 MPa when compaction pressure was increased from 100 MPa to 400 MPa and sintering temperature increased from 1200 ℃ to 1300 ℃. Membrane synthesized at 1200 ℃, compacted at an initial load of 100 MPa, being able to withstand the transmembrane pressure of up to 4 bar and having the highest water permeability would now be subjected to assess the arsenic heavy metal removal capability.

5. References
[1] Mark J. Hammer, *Water and Wastewater Technology*, 5th ed. Prentice Hall, 2004.
[2] D. P. Li and Z. J. Wu, “Impact of chemical fertilizers application on soil ecological environment,” *Chinese Journal of Applied Ecology*. 2008.
[3] A. Q. R Ullah, RN Malik, “Assessment of groundwater contamination in an industrial city, Sialkot, Pakistan,” *African J. Environ. Sci. Technol.*, vol. 3, no. 12, 2009.
R. A. Sial, M. F. Chaudhary, S. T. Abbas, M. I. Latif, and A. G. Khan, “Quality of effluents from Hattar Industrial Estate.,” *J. Zhejiang Univ. Sci. B.*, 2006.

K. G. Bhattacharyya and S. Sen Gupta, “Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review,” *Advances in Colloid and Interface Science*. 2008.

X. Gu and L. J. Evans, “Surface complexation modelling of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) adsorption onto kaolinite,” *Geochim. Cosmochim. Acta*, 2008.

S. A. Al-Jilil and F. D. Alsewilem, “Saudi Arabian clays for lead removal in wastewater,” *Appl. Clay Sci.*, 2009.

S. J. Köhler, P. Cubillas, J. D. Rodríguez-Blanco, C. Bauer, and M. Prieto, “Removal of cadmium from wastewaters by aragonite shells and the influence of other divalent cations,” *Environ. Sci. Technol.*, 2007.

D. Mohan and S. Chander, “Removal and recovery of metal ions from acid mine drainage using lignite-A low cost sorbent,” *J. Hazard. Mater.*, 2006.

A. Lu, S. Zhong, J. Chen, J. Shi, J. Tang, and X. Lu, “Removal of Cr(VI) and Cr(III) from aqueous solutions and industrial wastewaters by natural clino-pyrrhotite,” *Environ. Sci. Technol.*, 2006.

G. Sheng et al., “Adsorption of Pb(II) on diatomite as affected via aqueous solution chemistry and temperature,” *Colloids Surfaces A Physicocem. Eng. Asp.*, 2009.

M. Betancur, P. R. Bonelli, J. A. Velásquez, and A. L. Cuikerman, “Potentiality of lignin from the Kraft pulping process for removal of trace nickel from wastewater: Effect of demineralisation,” *Bioresour. Technol.*, 2009.

K. Ishizaki and M. Nanko, “A hot isostatic process for fabricating porous materials,” *J. Porous Mater.*, 1995.

V. K. Gupta, M. Gupta, and S. Sharma, “Process development for the removal of lead and chromium from aqueous solutions using red mud - An aluminium industry waste,” *Water Res.*, 2003.

I. Nettleship, “Applications of porous ceramics,” *Key Eng. Mater.*, 1996.

Y. C. Sharma, V. Srivastava, S. N. Upadhyay, and C. H. Weng, “Alumina nanoparticles for the removal of Ni(II) from aqueous solutions,” *Ind. Eng. Chem. Res.*, 2008.

M. J. Santos Yabe and E. de Oliveira, “Heavy metals removal in industrial effluents by sequential adsorbent treatment,” *Adv. Environ. Res.*, 2003.

K. Pillay, E. M. Cukrowska, and N. J. Coville, “Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution,” *J. Hazard. Mater.*, 2009.

N. A. Kabbashi, M. A. Atieh, A. Al-Mamun, M. E. Mirghami, M. D. Z. Alam, and N. Yahya, “Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution,” *J. Environ. Sci.*, 2009.

H. Wang, A. Zhou, F. Peng, H. Yu, and J. Yang, “Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb(II),” *J. Colloid Interface Sci.*, 2007.

N. M. Mubarak, J. N. Sahu, E. C. Abdullah, and N. S. Jayakumar, “Removal of heavy metals from wastewater using carbon nanotubes,” *Sep. Purif. Rev.*, 2014.

G. P. Rao, C. Lu, and F. Su, “Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review,” *Sep. Purif. Technol.*, 2007.

V. K. K. Upadhyayula, S. Deng, M. C. Mitchell, and G. B. Smith, “Application of carbon nanotube technology for removal of contaminants in drinking water: A review,” *Science of the Total Environment*. 2009.

X. Ren, C. Chen, M. Nagatsu, and X. Wang, “Carbon nanotubes as adsorbents in environmental pollution management: A review,” *Chemical Engineering Journal*. 2011.

J. W. An, D. H. You, and D. S. Lim, “Tribological properties of hot-pressed alumina-CNT composites,” *Wear*, 2003.

L. Kumari et al., “Thermal properties of CNT-Alumina nanocomposites,” *Compos. Sci. Technol.*, 2008.
[27] S. I. Cha, K. T. Kim, K. H. Lee, C. B. Mo, and S. H. Hong, “Strengthening and toughening of carbon nanotube reinforced alumina nanocomposite fabricated by molecular level mixing process,” Scr. Mater., 2005.

[28] F. Inam, A. Heaton, P. Brown, T. Peijs, and M. J. Reece, “Effects of dispersion surfactants on the properties of ceramic-carbon nanotube (CNT) nanocomposites,” Ceram. Int., 2014.

[29] T. Altalhi, M. Ginic-Markovic, N. Han, S. Clarke, and D. Losic, “Synthesis of carbon nanotube (CNT) composite membranes,” Membranes (Basel), 2010.

[30] H. Parham, A. Kennedy, and Y. Zhu, “Preparation of porous alumina-carbon nanotube composites via direct growth of carbon nanotubes,” Compos. Sci. Technol., 2011.

[31] P. Maarten Biesheuvel and H. Verweij, “Design of ceramic membrane supports: Permeability, tensile strength and stress,” J. Membr. Sci., 1999.

[32] M. Fukushima et al., “Microstructural characterization of porous silicon carbide membrane support with and without alumina additive,” J. Am. Ceram. Soc., 2006.

[33] T.Mohammadi, A. Pak, Z. Nourian, and M. Taherkhani, “Experimental design in mullite microfilter preparation,” Desalination, 2005.

[34] K. Shafiei, M. Kazemimoghaddam, T. Mohammadi, and S. Ghanbari Pakdehi, “An investigation on manufacturing of alumina microfiltration membranes,” Desalin. Water Treat., 2015.

[35] H. K. Shahzad, M. A. Hussein, F. Patel, N. Al-Aqeeli, M. A. Atieh, and T. Laoui, “Synthesis and characterization of alumina-CNT membrane for cadmium removal from aqueous solution,” Ceram. Int., 2018.

[36] M. Ahmadzadeh Tofighy and T. Mohammadi, “Nickel ions removal from water by two different morphologies of induced CNTs in mullite pore channels as adsorptive membrane,” Ceram. Int., 2015.

Acknowledgements
The authors would like to acknowledge the support provided by the Higher Education Commission (HEC) of Pakistan through the Startup Research Grant Program (SRGP) for funding this work through project No:21-2415/SRG/ R&D/HEC/2019. The authors would also like to acknowledge the support provided by Dr. M. Shoaib for his help in the preparation of the ceramic membranes and Dr. Abbas Saeed Hakeem for his support in the characterization of the synthesized membranes.