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Effect of Pore size and Porosity on Contact angle of Ceramic membrane for Oil-in-water Emulsion Separation

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ABSTRACT

The main objective of this work is to study the effect of pore size and porosity on contact angle of ceramic membrane (CM) for Oil-in-water (O/W) emulsion separation. This would include using commercially produced unmodified CM pore size 6000nm and 15nm. The Archimedes equation is used to measure the overall porosity of 6000 and 15nm pore size ceramic membranes and the porosity of the interconnecting pores. Subsequently, the contact angle for the ceramic membranes is measured using Attention Theta Lite Optical Tensiometer to test for the hydrophilicity. The average contact angle of 6000 and 15nm CM over a 20 second period at 50 frames per seconds (FPS) were 67.7^0 and 76.6^0 respectively. The porosity of CM1 (6000nm) & CM2 (15nm) were 23 and 21% respectively. From the Porosity and contact angle result, it is observed that porosity and pore size have influence of contact angle or hydrophilicity of a CM. the higher the pore size and porosity of a CM, the higher the hydrophilicity of the CM. This means contact angle of a higher porosity and pore size CM is expected to be closer to zero degree in contact angle. The proximity of contact angle results of CM 1 & 2 considering pore size might be due to dead end pores in CM1 (6000nm) which constitute 95% of pores making up the CM1 reducing porosity.

INTRODUCTION

The mixture of oil with water creates an emulsion which is now termed as oil-in-water (O/W) emulsion (Elanchezhiyan, Sivasurian et al. 2016) and this emulsion needs to be treated/separated before reuse or discharge into the environment. The existence and operational presence of the oil & gas, petrochemicals, pharmaceuticals, transportation, food, and metallurgical industries generates oil-in-water emulsions (O/W) daily in the world at large, making it the most famous environmental pollutant affecting living and non-living things (Almojjly, Johnson et al. 2019). Ceramic membranes (CMs) were carefully chosen as a technique for separation of O/W emulsion due to their numerous advantage which include mechanical stability, chemical inertness, thermal stability, ability to be regenerated, high flux, and compactness in design (Phan, McDonald et al. 2016). Before ceramic membrane is used for separation, it must be characterized for certain parameters such as porosity, contact angle and morphology to determine the effect of these parameters on separation and flux. In this study, the parameters examined for characterization are pore size, porosity, and contact angle. Contact angle is the measurement of the relative amount of liquid-to-solid (adhesive) forces acting on a liquid (Yoon, Kim et al. 2013). This measurement varies between the range of $\leq 0^0$ to $\leq 180^0$. Contact angle is because of mechanical equilibrium among the three surface tensions, the liquid, the solid, and the liquid– solid interfacial tensions (Law, Zhao 2015). Therefore, contact angle (θ) can be used to measure wettability of a solid surface to determine its hydrophilicity or hydrophobicity. In this study, the contact angle of unmodified commercial CM is measured for hydrophilicity. CM surfaces with large contact angle (near 180^0) are termed hydrophobic while surfaces with small water contact angle (near 0^0) are termed hydrophilic (Yuan, Lee 2013). This study will measure the porosity and pore size of CM using Archimedes principle and already measured pore size 6000nm & 15nm CMs respectively to determine the effects of these parameters on contact angle measurement using OneAttension Theta Lite Tensiometer for separation of O/W emulsion.

MATERIALS AND METHODS

Contact angle and water permeation rate of the CMs were determined using OneAttension Theta Lite Optical Tensiometer as seen in Figure 1. The CM samples were placed on sample stage. A drop of deionised water (4uL) was place on the sample with the help of syringe. Contact angle and permeation measurements were automatically calculated after setting the recipe at 50 Frames Per Seconds (FPS) using sessile drop method.

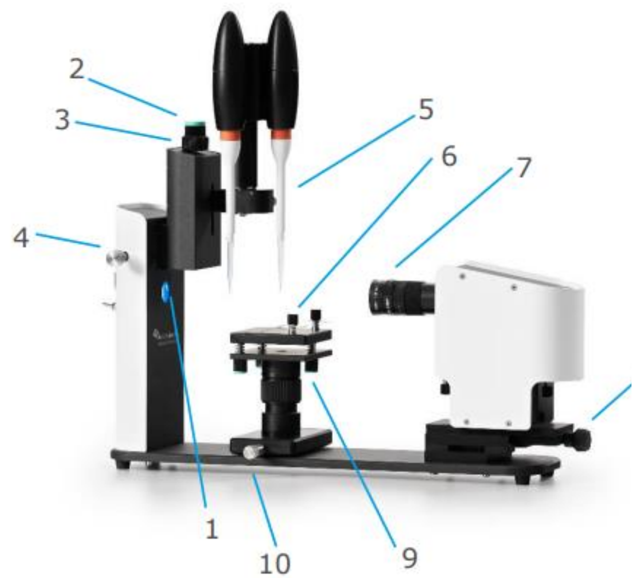

Fig. 1. Image of OneAttension Theta Lite Optical Tensiometer -adapted from Biolin Scientific Manual.

(1-LED light source, 2-syringe height adjustment, 3-manual dispenser adjustment, 4-syringe compartment adjustment, 5-syringe, 6-sample stage with sample attachment clips, 7-camera optics, 8-camera linear movement).

To determine the overall porosity (Ɛ) of unmodified CM1 & CM2, the dry weight was first measured using an analytical weighing balance. Subsequently, the membrane was immersed in deionized water allowed to reach equilibrium for 24 hours in a measuring cylinder and the wet weight was immediately measured using the same analytical weighing balance. Equation 1 was used to obtain the overall porosity of the membrane.

$$\varepsilon(\%) = \left(\frac{W_w - W_d}{d_w - V}\right) \times 100 \qquad (1)$$

Where W_w and W_d represents the wet and dry unmodified ceramic membranes (g) respectively; d_w indicates the pure water density at room temperature (g/dm^3), and V is the membrane volume (which includes membrane area (cm^2) $\times$ membrane thickness (cm). The interconnecting porosity and morphology of unmodified ceramic membrane was determined by the use Zeiss EVO LS10 scanning electron Microscope (SEM) and calculated with equation 2 where *I* represent interconnecting pores and D dead end pores. The SEM generated images of both outer and inner areas of the unmodified commercial ceramic membrane at 3000X magnifications

$$\frac{I}{D} \times 100\% \qquad (2)$$

RESULTS AND DISCUSSION

Both overall porosity and interconnecting porosity of CM1 and CM2 were measured using equation 1 and 2 respectively. The overall porosity was calculated to be 23% and 21% for CM1 and CM2 respectively. This result elucidates that there is a variation between CM1 and CM2 porosity, which is due to the pore size in the CMs as seen in fig. 2.

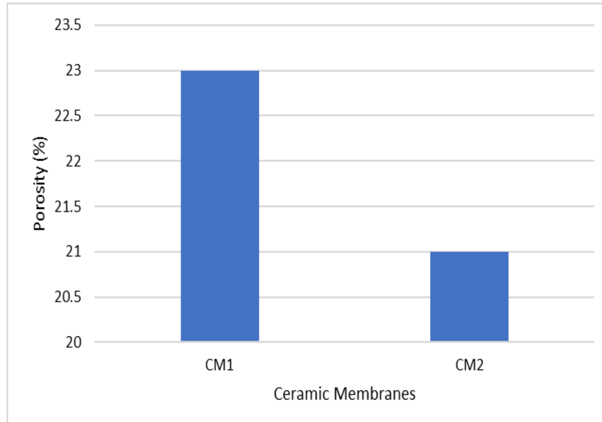

Fig. 2. Porosity of CM1 and CM2

There is the rule of thumb in contact angle that ties wettability of solid by liquid phase to contact angle less than 90^0 and non-wettability of solid by liquid to contact angle greater than 90^0. Wettability measures the contact relation between the solid and liquid phase. This is due to the interactions between intermolecular activities of both phases. Hence, the contact angle characterises the degree of wettability. For this study, a hydrophilic CM will have a contact angle close to zero and a hydrophobic CM will have contact angles close to 180^0. This indicates that in hydrophilic CM the water droplet will spread fast and permeate from the surface, while in hydrophobic CM the water droplet will spread less and permeate slowly.

From Fig.3 shows the contact angle of CM1 and CM2 respectively. The contact angle of CM1 in Fig. 3 is 67.7^0 which is higher than CM2 of 76.6^0. The means that CM1 is closer to zero compared to CM2. This is an indication that CM1 is more hydrophilic than CM2. This is a likely expected result considering porosity of both CM1 & 2 being 23 & 21 respectively, indicating the close figure between both contact angle result. This likely result is further underpinned by the early permeation rate with time of CM1 at 0.37milliseconds compared to CM2 which permeated fully in 20seconds as seen in fig.4. From the pore size of both CM1 & 2 should result in a wider contact angle result due to the large difference in pore size of CM1 and 2 being 6000 & 15nm respectively. This unlikely result considering pore size might be explained from the dead-end pores noticed CM1 (6000nm) when examined with Scanning Electron Microscope (SEM) as seen in figure 5. There are more dead-end pores in CM1 than interconnecting pores which allows the absorption of liquid and increase in porosity. Table 1 further explains the result that the higher the pore size and porosity of a ceramic membrane, the higher the hydrophilicity of the CM meaning that the contact angle is closer to zero with higher porosity and pore size. This explains that though contact angle is mainly determined by surface material of the solid sample as suggested by (Lu, Yu et al. 2009), the pore size and porosity of the CM also influences the contact angle or hydrophilicity.

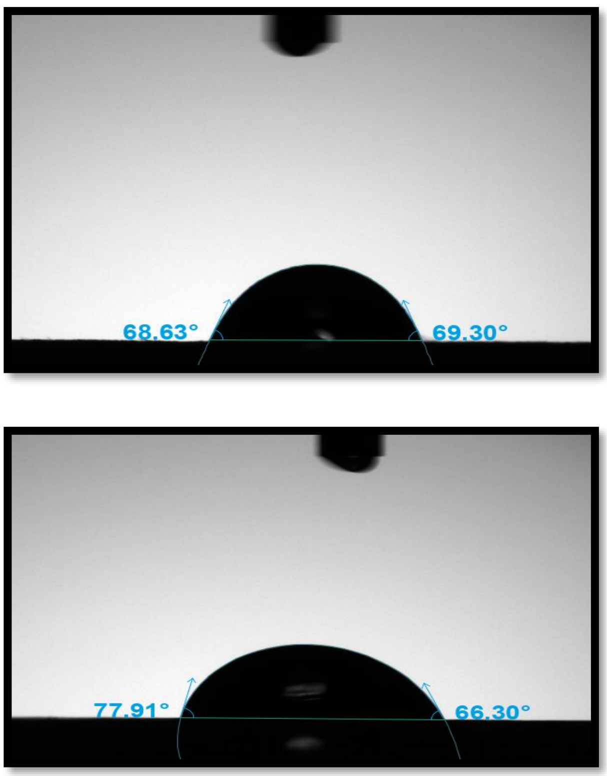

Figure 3: Contact angle image of CM1 (6000nm) & CM2 (15nm)

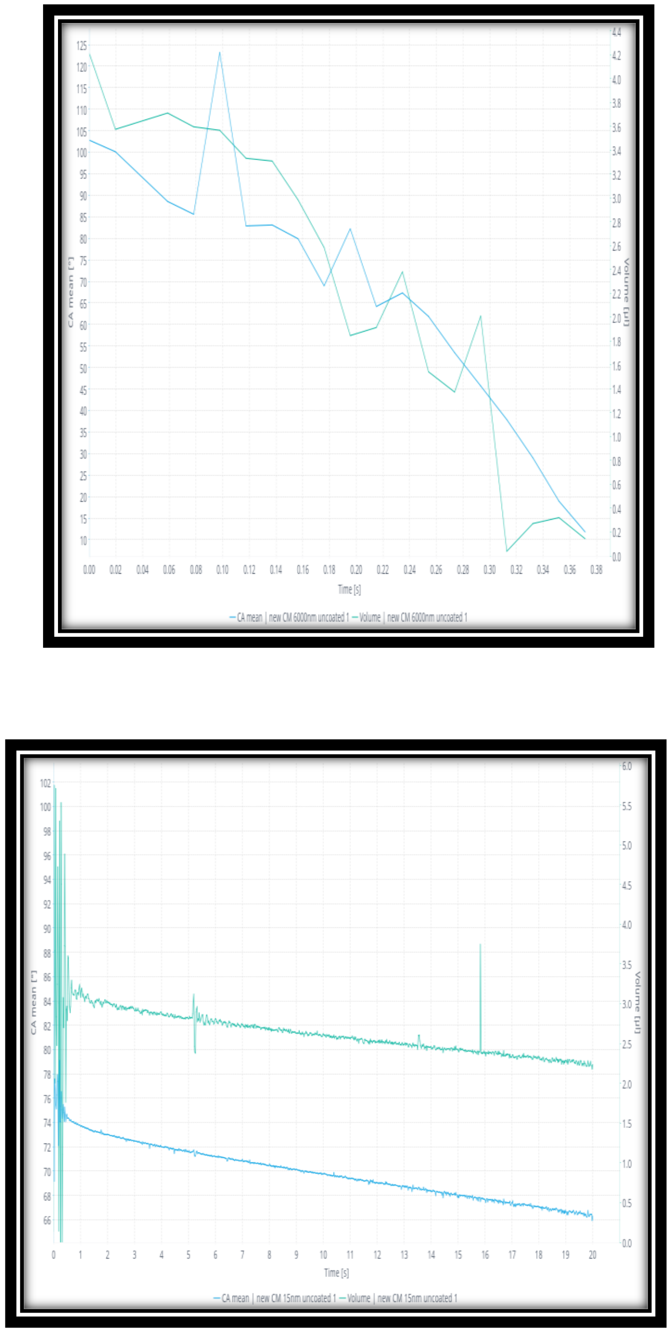

Figure 4: permeation rate and contact angle of CM1 & CM2 against time respectively

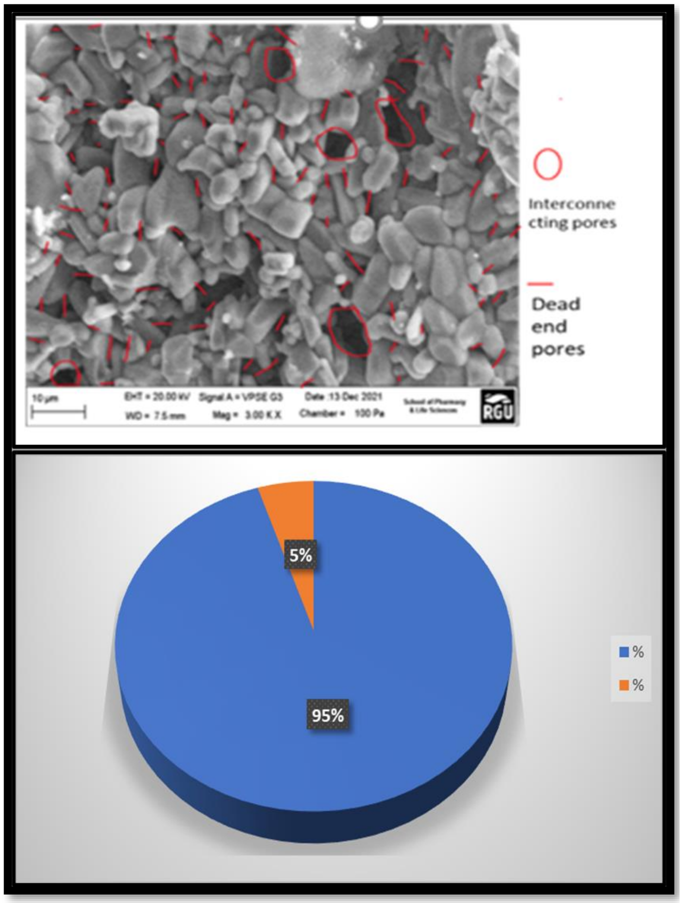

Figure 5: Dead-end and interconnecting pores in CM1 (6000nm)

Table 1: Comparison of pore size, porosity & contact

sample	Pore size (nm)	Porosity (%)	Contact angle $[^0]$
CM 1	6000	23	67.7
CM 2	15	21	76.6

CONCLUSION

Using already examine pore size of commercially produced CM1 & 2, the porosity and contact angle of CMs were measured using Archimedes principles and OneAttension Theta Lite Tensiometer for the determination of the effect of pore size and porosity on hydrophilicity oof CMs. From observation, it was concluded that the higher the pore size and porosity of CMs, the higher the hydrophilicity and contact angle measurement is closer to zero degree. Dead end pores in CM can restrict porosity thereby increasing contact angle measurement making it further away from zero degrees. Higher porosity and pore size of CMs can give higher permeation rates of liquids in CMs hence increase hydrophilicity.

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