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RESEARCH ARTICLE

INVESTIGATION OF CARRIER GAS TRANSPORT THROUGH SILICA MEMBRANE FOR ETHYL LACTATE SEPARATION AND VOC EMISSION APPLICATIONS

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ABSTRACT

Ethyl lactate has played a major role in daily living and chemical industry including fragrance, lubricant, additives and plasticizers. The esterification process of lactic acid and ethanol is an equilibrium limiting reaction. The selective removal of the products from the reaction mixture can be enhanced using a membrane. This work presents the carrier gas permeation behaviour with silica membrane for ethyl lactate separation and VOC applications. The experiment was carried out at the gauge pressure of 0.10 – 1.00 bar and 100 °C (373 K). Helium (He), argon (Ar), nitrogen (N<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) were used as the carrier gases. The membrane dip-coating process was carried out twice. The carrier gas flow rate was found to increase with increase in gauge pressure. The order of the gas molecular weight with respect to the gas permeance at 0.5 bar was He > Ar > N<sub>2</sub> > CO<sub>2</sub>. The gas permeance was found to decrease with respect to gauge pressure confirming the mass transfer limitations. The order of the gas permeance with respect to gauge pressure was He > N<sub>2</sub> > Ar > CO<sub>2</sub>.

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INTRODUCTION

The focus in chemical industries over the years has shifted towards the improvement and application of integrated methods that combines both the separation and the reaction into one single process (Buchaly *et al.*, 2007). In the past few years, organic solvents including chloroform, carbon tetrachloride and benzene have shown a lot of environmental and health problem. This resulted in their removal from general use as petrochemical solvents because of their carcinogenic and toxic effect. Volatile organic compounds (VOCs) including toluene and hexane, have been implicated in the production of photochemical smog whereas chlorofluorocarbons (CFCs) due to its ozone-depleting effects has also been removed from their general use. However, a lot of research effort has been made on the replacement of VOCs and chlorinated solvents (Clark and Tavener, 2007). There has been great concern in the emission of VOC from oil and process industries in recent years. Light hydrocarbons like methane, ethane and propane are considered to be a part of these volatile organic compounds (Ghoshal and Manjare, 2002). Methane is considered a greenhouse house gas with global warming potential (GWP) that is 21 times greater than that of CO<sub>2</sub>. Other non- methane VOCs (NMVOCs) like

ethane, propane, butane, pentane and hexane can react with nitrous oxide to form ground level ozone which is detrimental to both plants and humans. Different countries in the world have regulations in place that tightly regulate these emissions. The US Environmental Protection Agency proposed the air quality standards of a maximum 3 h concentration of hydrocarbon content not to exceed  $1.6 \times 10^{-4} \text{ kgm}^{-3}$  (0.24 ppm) (Clark and Tavener, 2007). The European community has a limit set not to exceed 35 g of total organic compounds (TOC) per cubic meter gasoline loaded. The Gothenburg Protocol that was adopted by the EU in 1999 to abate acidification, eutrophication and ground level ozone sets emission levels for sulphur, nitrous oxide, VOCs and ammonia hence, when fully implemented it is expected that European VOC emission will be cut down by 40% when compared to 1990 levels [Derwent *et al.*, 2010]. In many countries emissions of VOCs and NMVOCs are not subject to control, hence loss of hydrocarbons into the atmosphere can cause severe environmental pollution and great monetary loss. These gases are highly flammable; therefore emission during loading and unloading operations can also be a safety hazard. There are various measures in place for the abatement of VOC that are emitted from operations at oil terminals. Ethyl lactate (EL) has shown a lot of promise as a powerful non-toxic replacement for petroleum-based solvents that have dominated U.S and the world market over the years (Asthana *et al.*, 2005). The production of EL from the esterification process of lactic acid

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with the respective alcohol in the presence of a catalyst suffers the major drawback of purity and low conversion due to chemical equilibrium. In order to obtain a high yield of the ester, different methods have been used including introducing more of the alcohol to the reaction and increasing the temperature (Rattanaphanee, 2010; Khajavi *et al.*, 2010). The use of membranes to selectively eliminate water from the reaction product during esterification of lactic acid is yet another important application that has attracted a lot of attention. Over the years, membrane reactors have received a lot of attention because of their excellent advantages in liquid-phase reaction. These advantages include close contact with the reactant, improvement of selectivity usually with respect to one of the reactant species, combination of both the reaction and separation in one system, and enhancement of reaction conversion. Membranes may be classified into organic and inorganic membranes and the membranes maybe dense, porous or composite (Mulder, 1996). Currently, ceramic porous inorganic membranes have been widely employed in different fields such as petrochemical, bioengineering, and environment engineering (Jiang *et al.*, 2013). Compared to other membranes, ceramic membrane can withstand the effect of thermal, mechanical and chemical stability. In spite of these advantages, the major drawback of porous membrane is the low selectivity offered by some mesoporous materials for gas separations (Smart *et al.*, 2013). This membrane can be categorised into different types depending on the pore size including microporous with the pore size < 2nm, mesoporous 2-50nm, macroporous > 50 nm (Li, 2007). Materials such as zirconia, zeolite, metals, glass, alumina and carbon are used as commercially porous inorganic membrane (Ismail and David, 2001).

Inorganic membrane can be prepared using different separation methods including sol-gel, sintering, chemical deposition and dip-coating methods (Mulder, 1996). Generally the conventional dip-coating process involves two major steps: support dipping and support withdrawal (Zhu *et al.*, 2011). The gas transport through porous ceramic membrane can be explained using different mechanism of transport including surface diffusion, viscous flow, molecular sieving, Knudsen diffusion and capillary condensation (Pandey and Chauhan, 2001). In Knudsen diffusion mechanism, gas molecules diffuse through the pores of the membrane and then get transported by colliding more frequently with the pore walls (Lee and Oyama, 2002). Molecular sieve occurs when the diameter of the gas molecule is roughly the same as the pores of the membrane. Viscous flow occur if the pore radius of the membrane is larger than the mean free path of the permeating gas molecule, in this case more collision will take place between the molecules than the pore wall of the membrane. Surface diffusion mechanism enables diffusion in such a way that the gas is strongly adsorbed on the on the pores of the membrane (Lee and Oyama, 2002). In capillary condensation mechanism of transport, partial condensation within the pores occurs as a result of low vapour pressure. However, the condensed gas diffuses faster through the pores of the membrane resulting in separation (Basu *et al.*, 2004). The carrier gas permeation through silica membrane will be investigated for ethyl lactate separation and VOC emission applications.

## Experimental

The four gases used for the carrier gas permeation include; nitrogen (N<sub>2</sub>), argon (Ar), helium (He) and carbon dioxide (CO<sub>2</sub>). The gases were supplied by BOC, UK. The permeation test was carried out at the feed pressure of 0.10 – 1.00 bar and at 373 K. The membrane support was modified twice before the permeation analysis. The effective length of the membrane was 36.6 cm, while the inner and outer radius of the membrane was 7 and 10 mm respectively. The support modification process was carried out based on the procedure developed by (Gobina, 2006).

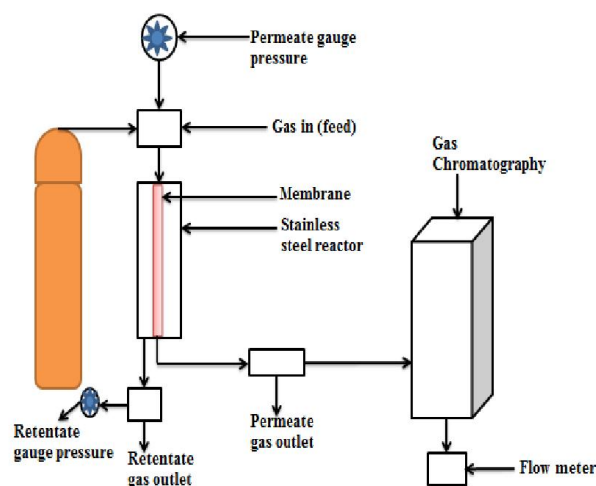


Fig. 1. Schematic diagram of gas permeation setup

Figure 1 shows the carrier gas transport permeation setup through inorganic ceramic membranes. The membrane thickness was calculated using the formula:

$$L = \frac{W_2 - W_1}{A\rho(1 - \varepsilon)} \quad (1)$$

Where L = membrane thickness (m), A = membrane area (m<sup>2</sup>),  $\rho$  = theoretical density of silica (3.95 x 10<sup>-3</sup> kgm<sup>-2</sup>), W<sub>1</sub> = initial weight of the alumina support (g),  $\varepsilon$  = membrane porosity (%), W<sub>2</sub> = total weight of the support and membrane (g) (Zhu *et al.*, 2011).

## RESULTS AND DISCUSSION

Figure 2 shows the relationship between the gas flow rate (mols<sup>-2</sup>) and the feed gauge pressure (bar). From figure 2 it can be seen that the flow rate of the four gases increases with respect to gauge pressure. CO<sub>2</sub> (44 g/mol), N<sub>2</sub> (28 g/mol) and Ar (40 g/mol) with a higher molecular weight showed a lower permeation rate in contrast to He (2 g/mol) gas with the least molecular weight indicating a Knudsen type mechanism of transport. It is also observed that Ar, N<sub>2</sub> and CO<sub>2</sub> shows non-Darcian flow whereas He flow increased continuously without any inertial contribution. Figure 3 depicts the relationship between the gas flow rate (mols<sup>-2</sup>) and the gas kinetic diameter (Å) at 0.8 bar gauge feed pressure. From Figure 3, it can be seen that Ar and N<sub>2</sub> gas with the lower kinetic diameter showed a higher permeance in contrast to CO<sub>2</sub> and He gases. Generally,

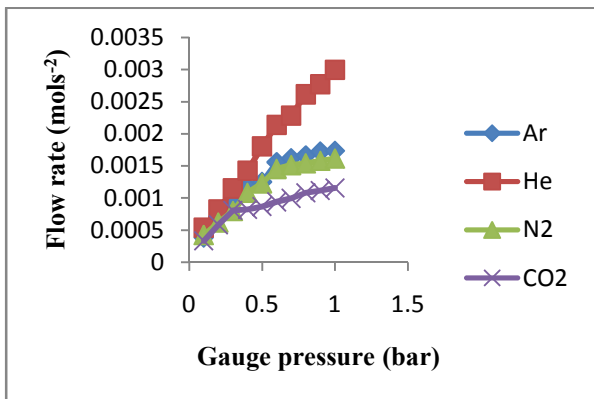


Fig. 2. Gas flow rate (mols<sup>-2</sup>) against gauge pressure (bar) at 373 K

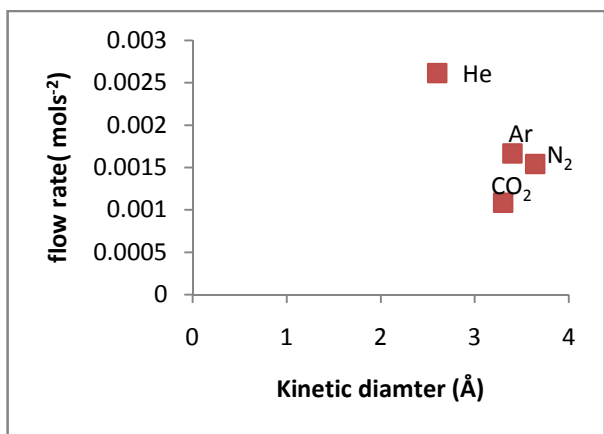


Fig. 3. Gas flow rate (mols<sup>-2</sup>) against Kinetic diameter (Å) at 0.8 bar and 373 K

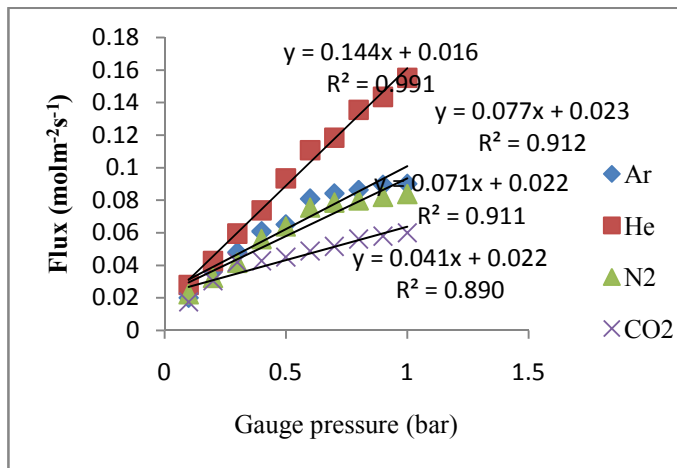


Fig. 5. Gas flux (mols<sup>-2</sup>) against gauge pressure (bar) at 373 K

Ar and N<sub>2</sub> and with the higher kinetic diameter would have exhibited the lower flow rate to explain the molecular sieving transport mechanism. He (2.65 Å) with a lower kinetic diameter permeated faster than N<sub>2</sub> with the highest kinetic diameter (3.64 Å) indicating a molecular sieving contribution. The increasing order of the gas kinetic diameter is N<sub>2</sub> (3.64 Å) > Ar (3.40 Å) > CO<sub>2</sub> (3.30 Å) > He (2.65 Å) as shown in table 1. Table 1 shows the gas molecular weight, Kinetic diameter, gas viscosity and the calculated activation energy of the four gases. Figure 4 shows the relationship between the gas permeance (molm<sup>-2</sup>s<sup>-1</sup>Pa<sup>-1</sup>) and the inverse square root of the gas molecular weight. From Figure 4, it was found that Ar and N<sub>2</sub> gas exhibited almost the same permeance and the gas pressure of 0.50 bar. It was also found that the silica membrane exhibited a linear proportionality on the inverse square root of Ar, N<sub>2</sub> and CO<sub>2</sub> gases confirming Knudsen flow as the dominant mechanism.

Table 1. Gases, Molecular weight, Kinetic diameter, Viscosity and calculated Activation Energy

Gases	Molecular weight (g/mol)	Activation Energy (K J mol) at 0.5 bar	Kinetic diameter (Å)	Viscosity (Pas <sup>-1</sup> )
He	2	-2.49x10 <sup>-9</sup>	2.65	20
Ar	40	-8.31x10 <sup>-9</sup>	3.40	17.81
CO <sub>2</sub>	44	-4.98x10 <sup>-9</sup>	3.30	22.7
N <sub>2</sub>	28	-8.31x10 <sup>-9</sup>	3.64	15

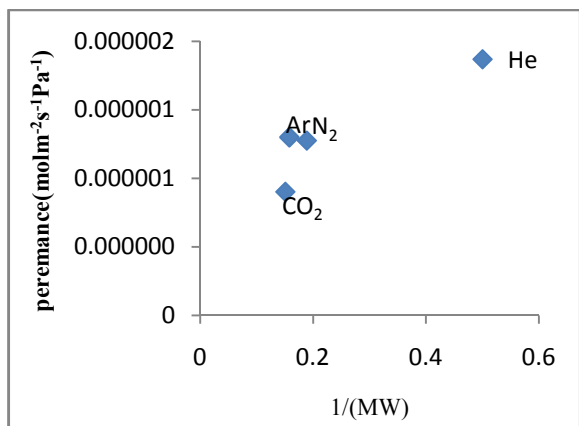


Fig. 4. Gas permeance against inverse square root of molecular weight at 0.5 bar and 373 K

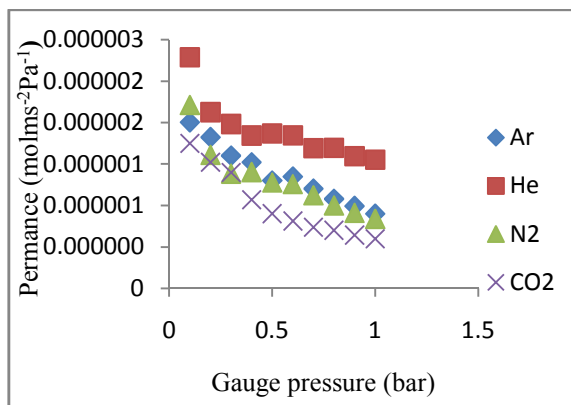


Fig. 6. Gas permeance (molm<sup>-2</sup>s<sup>-1</sup>Pa<sup>-1</sup>) against gauge pressure (bar) at 373 K

It was suggested that He gas was controlled by another flow mechanism at 0.5 bar and at 373 K, although it showed a higher permeability. From Table 1, it was found that the calculated activation energy of the gases with the membrane was low. It was suggest that the lower activation energy could indicate the lower diffusion rate of the gases through the membrane. Figure 5: shows the relation between the gas flux (mols<sup>-2</sup>) against the gauge pressure at 373 K and fitted with a least sequence line. It can be seen from Figure 5 that CO<sub>2</sub>

exhibited the least  $R^2$  value (0.8901) with a low gradient (0.041) compared to He gas with  $R^2$  and gradient of 0.9912 and 0.144 respectively, indicating that  $\text{CO}_2$ ,  $\text{N}_2$  and Ar are strongly influence by inertia forces. These forces are in the order;  $\text{Ar} > \text{N}_2 > \text{CO}_2$ .

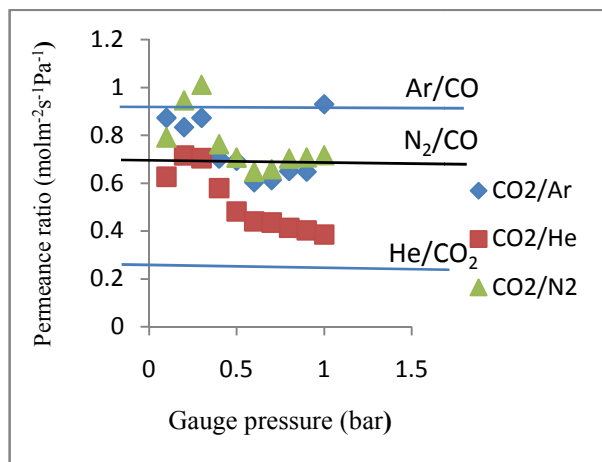


Fig. 7. Permeance ratio of  $\text{CO}_2$  over Ar, He,  $\text{N}_2$  gas ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) against gauge pressure (bar) at 373 K

The gas flux was calculated using the equation:

$$J = \frac{Q}{A} \quad (2)$$

Where  $J$  = flux ( $\text{mol m}^{-2}\text{s}^{-1}$ ),  $Q$  = flow rate of the gases ( $\text{mol s}^{-1}$ ),  $A$  = membrane surface area ( $\text{m}^2$ ). Figure 6 depicts the relationship between the permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) of the four gases and the gauge pressure (bar) at 373 K. From figure 6, it was found that the membrane exhibited the permeance in the range of  $10^{-6} - 10^{-7} \text{ molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ . It was also found that the permeance of the various gases decreases with respect to the gauge pressure at 373 K indicating Knudsen mechanism. It also found that  $\text{CO}_2$  and Ar decrease more rapid between 0.10 – 0.30 bar but subsequently more or less stabilised after 0.4 bar. Additionally, He gas showed a slight increase at 0.10 bar although it was not as pronounced as that of Ar gas. This irregularity was suggested to arise as a result of mass transfer limitation between the silica membrane and the permeating gas molecules and the pores of the membrane.

The gas permeance was calculated using the formula:

$$\bar{P} = \frac{J}{\Delta P} \quad (3)$$

Where  $\Delta P$  is the pressure drop across the membrane (bar),  $J$  = flux ( $\text{mol m}^{-2}\text{s}^{-1}$ ) and  $\bar{P}$  is the permeance ( $\text{mol m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ). Figure 7 presents the relationship between the selectivity of the Ar, He and  $\text{N}_2$  over  $\text{CO}_2$  between the gauge pressure range of 0.10 -1.00 bar and 100 °C. From figure 7, it can be seen that the experimental selectivity values of  $\text{CO}_2/\text{Ar}$ ,  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{He}$  at 373 K were slightly higher than the theoretical Knudsen selectivity of  $\alpha_k \text{Ar}/\text{CO}_2$  (0.95),  $\alpha_k \text{He}/\text{CO}_2$  (0.30) and

$\alpha_k \text{N}_2/\text{CO}_2$  (0.79) which suggest that the gas flow was based on Knudsen mechanism of transport.

## CONCLUSION

The investigation of carrier gas transport through silica membranes for ethyl lactate separation and VOC emission applications has been studied. Ar,  $\text{CO}_2$  and  $\text{N}_2$  showed a linear dependence with the inverse square of the gas molecular weight exception of He gas. The permeance of the four gases with respect to their kinetic diameter showed molecular sieving mechanism. Helium gas with least molecular weight permeated faster compared to other gases. The gas permeance decreases with respect to gauge pressure confirming mass transfer limitations across the membrane.  $\text{CO}_2$  gas exhibited a low  $R^2$  value of 0.8901. The experimental selectivity of Ar, He and  $\text{N}_2$  were greater than the theoretical Knudsen selectivity. The gases exhibited low activation energy with the silica membrane.

## REFERENCES

- Asthana, N., Kolah, A., Vu, D.T., Lira, C.T. and Miller, D.J. 2005. A continuous reactive separation process for ethyl lactate formation. *Organic process research and development*. 9(5):599-607.
- Basu, A., Akhtar, J., Rahman, M. and Islam, M. 2004. A review of separation of gases using membrane systems. *Petroleum Science and Technology*. 22(9-10):1343-1368.
- Buchaly, C., Kreis, P. and Górak, A. 2007. Hybrid separation processes—Combination of reactive distillation with membrane separation. *Chemical Engineering and Processing: Process Intensification* 46(9):790-799.
- Clark, J.H. and Tavener, S.J. 2007. Alternative solvents: shades of green. *Organic process research and development*. 11(1):149-155.
- Derwent, R.G., Witham, C.S., Utembe, S.R., Jenkin, M.E. and Passant, N.R. 2010. Ozone in Central England: the impact of 20 years of precursor emission controls in Europe. *Environmental Science and Policy*. 13(3):195-204.
- Ghoshal, A. and Manjare, S. 2002. Selection of appropriate adsorption technique for recovery of VOCs: an analysis. *Journal of Loss Prevention in the Process Industries*. 15(6):413-421.
- Gobina, E. 2006. *Apparatus and method for separating gases*.
- Ismail, A.F. and David, L. 2001. A review on the latest development of carbon membranes for gas separation. *Journal of Membrane Science*. 193(1):1-18.
- JIANG, H., MENG, L., CHEN, R., JIN, W., XING, W. and XU, N. 2013. Progress on Porous Ceramic Membrane Reactors for Heterogeneous Catalysis over Ultrafine and Nano-sized Catalysts. *Chinese Journal of Chemical Engineering*. 21(2):205-215.
- Khajavi, S., Jansen, J.C. and Kapteijn, F. 2010. Application of a sodalite membrane reactor in esterification—Coupling reaction and separation. *Catalysis Today*. 156(3):132-139.
- Lee, D. and Oyama, S.T. 2002. Gas permeation characteristics of a hydrogen selective supported silica membrane. *Journal of Membrane Science*. 210(2):291-306.
- Li, K. 2007. *Ceramic membranes for separation and reaction* : John Wiley and Sons.

- Mulder, M. 1996. *Basic Principles of Membrane Technology Second Edition*. : Kluwer Academic Pub.
- Pandey, P. and Chauhan, R. 2001. Membranes for gas separation. *Progress in Polymer Science*. 26(6):853-893.
- Rattanaphanee, P. 2010. Factorial design of experiments for comparative study of lactic acid esterification with ethanol and n-butanol. Factorial design of experiments for comparative study of lactic acid esterification with ethanol and n-butanol. *Chemistry and Chemical Engineering (ICCCE), International Conference on: IEEE; 2010*. p. 1-5.
- Smart, S., Liu, S., Serra, J.M., Diniz da Costa, J.C., Iulianelli, A. and Basile, A. 2013. 8 - Porous ceramic membranes for membrane reactors. In: Basile A, editor. *Handbook of Membrane Reactors*. : Woodhead Publishing. p. 298-336.
- Zhu, J., Fan, Y. and Xu, N. 2011. Modified dip-coating method for preparation of pinhole-free ceramic membranes. *Journal of Membrane Science*, 367(1):14-20.

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