



Effect of additives on morphology and performance of mullite-alumina microfiltration membranes

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Abstract

In this research, effects of hydraulic pressure (200,400,600 bar), content of α -alumina (25, 30, 35 and 40%) and additives on flux and porosity of microfiltration membranes (MF) were investigated. To complete mullite phase formation, α -alumina was added to Kaolin clay. CMC (Carboxymethyl cellulose), PVA (Polyvinyl acetate) and PEG (Polyethylene glycol) were also added to increase porosity and permeation flux of the membranes. Many experiments were carried out to understand the effects of different parameters. In order to determine the best operating conditions, full factor method was used. MF membranes containing 40% alumina and 1.5 % w/w PVA were shaped under 400 bar pressing pressure and sintered at 1200 °C for 5 h. Water permeation flux and porosity of these membranes were evaluated as 345.2 kg/m².h and 29.6%, respectively.

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1. Introduction

Membrane separation technology has been developed due to its applications in different industries having thermodynamic or safety restrictions. On the other hand, these processes are not mainly more economical compared with other separation technologies. This produces materials with higher purity and is cleaner in comparison with other conventional processes of separation. Many worldwide researches are carrying out to improve current membrane processes and materials and/or introduce new processes and materials to this technology. Membrane materials are ranged from polymeric to minerals (ceramics, metals and glasses) in different modular forms. Each of them has their own advantages and disadvantages including low cost and good process ability for polymeric and high mechanical and thermal strengths and nearly uniform pore size distribution for inorganic membranes. Disadvantages include non-uniform pore size distribution, operating temperature limit and tradeoff between permeability and selectivity for polymeric membranes and low specific surface area in module and high cost for ceramic membranes.[1,2] Ceramic membranes are used instead of polymeric membranes in a number of industrial fields because of their outstanding chemical, thermal and mechanical strength where more cost for ceramic membranes than polymeric membranes is

compensated by their superior properties. In addition, pore size in these membranes can be better controlled and as a consequence their pore size distribution is generally very narrow and their long life and desired, antifouling, ion exchange and catalytic properties should be added to these superior properties. Various techniques can be used to prepare ceramic membranes with some important ones being: sintering, sol/gel, anodic oxidation, extrusion, centrifugal deposition and isostatic pressing. [7]

Mullite, which is the only stable crystalline phase in the SiO₂-Al₂O₃ system at normal pressure, is formed as the result of thermal decomposition of alumina silicates. Among the extensively studied processing routes for mullite formation, sol-gel, hydrothermal and solution co-precipitation are essentially synthesis routes [16]. Conversely, conventional processing routes starting from high purity conventional raw materials such as quartz, amorphous silica, alumina and kaolinite are also being studied with the aim to produce more economical mullite for wider range of applications. Mullite and mullite based composites using chemical processing routes with Hexamethyldiamine were prepared [3]. The kaolinite and alumina sintering reactions were also performed at range of 980 – 1600°C with various amount of alumina resulted economically practical routes to produce mullite. [4]

In kaolinite and alumina system, kaolinite is first dehydrated at 500 – 600°C during heating and metakaolinite is created and it goes through a series of reactions at about 980°C, resulting in mullite crystal (primary mullite), and silica. Secondary mullite formation in a high purity kaolinite - α -alumina system has been reported in details. Porous mullite bodies which retain porosity at elevated temperatures and are used as crystal supports and contact materials were also prepared [5, 6].

MF is a membrane process which most closely resembles conventional coarse filtration. Pore size of MF membranes is in the range of 0.05 to 10 (μm), making the process suitable for retaining suspensions and emulsions. [9, 12]

MF membranes may be prepared from a large number of different materials based on either organic materials (polymers) or inorganic materials (ceramics, metals and glasses). Frequently, inorganic membranes are used instead of polymeric membranes because of their outstanding chemical and thermal resistance. In addition, pore size in these membranes can be better controlled and as a consequence their pore size distribution is generally very narrow [15]. The membranes are made of (α or γ)-alumina, but other substances like carbon, mullite and porous acetyl are also used. [7, 13]

In this study, the aim was to produce a kind of mullite MF membrane from kaolin clay via sintering reaction, with high strength and suitable porosity and permeation. In the experiments, the effects of calcinations temperature, hydraulic pressure, and alumina content and different additives on the membrane porosity, membrane permeation flux were investigated.

2. Experimental

2.1 Material

In this research, MF membranes were prepared from Kaolin clay. The kaolin material used in this stage (SL-KAD grade) was obtained from Zenooz mine in Marand, Iran. In this work, mullite – alumina MF membranes were synthesized from kaolin clay and α -alumina powder. The Chemical analysis of the kaolin is listed in Table 1. CMC, PVA and PEG solution and α -alumina with 99% purity (Merck with mean particle size $<150 \mu\text{m}$) were used to prepare the mullite – alumina membranes.

2.2 Membrane preparation

The first step is to produce powder mixtures consisting alumina (25-30-35-40%), CMC, PVA or PEG solution (3% wt) and kaolin (the rest). Three times sieving by 270 meshes ensures making homogeneous mixtures. The second step is pressing the powder mixtures with pressures of 200, 400 and 600 bar in a hydraulic jack. After that, sintering was performed at 1200 °C for 5 h with heating and cooling rates of 3 °C/min. Alumina is active only in formation of mullite, hence the minimum temperature must be suitable for breaking α -alumina

crystals. Therefore, 1150 °C was selected as the lowest temperature to ensure the mullite formation.

2.3 Porosity measurement

Porosity of the membrane was measured according to water saturation route based on the weight of absorbed water by the membrane. Porosity was obtained using the volume difference caused by floating of the membrane saturated with water in water [17].

2.4 Permeation measurement

Distilled water permeation flux was also measured. Pressure and temperature are important factors in flux measurements. They were kept constant during all experiments. Experiments were carried out at a temperature of 25°C and a pressure of 3 bar. Each experiment was run for 10 min and repeated 2 times. The results are presented on average with maximum standard deviation of 10 Kg/m².h.

2.5 Membrane Characterization

Phase structures of the membranes were determined by X-ray diffraction (XRD, Philips PW3710) using Cu K α radiation and Ni filter with 2θ varying from 20 to 80°, scan rate of 1°/min, and 2θ intervals of 0.02°. XRD was performed by Philips-PW3710 (Figure 5) with radiation of CuK α . Membrane surface morphology was also studied by Scanning Electron Microscopy (SEM) by nonospace Co. (Figure 1, 2).

3. Results and discussion

Variance analysis was used to distinguish effects of all parameters. This was performed to determine whether changes in the results are caused by change in the parameters values or related to the accidental errors of measurements. Fig.5 shows XRD analysis of the sample containing 30% Al and 2% SiO₂ sintered at 1200°C. Free silica was removed from the sintered membranes. Removal of this free silica increases porosity of the microporous ceramic membranes. The results show that mullite and alumina crystalline phases are present and this means that silica phases are eliminated. In other words, the amount of alumina is excess.

3.1 Effect of alumina content and additives

As expected, by adding alumina to the mixture, porosity and permeation of the synthesized membranes increase. This is due to the fact that the size of alumina particles is bigger compared with the size of kaolin particles. Also, alumina prevents formation of a mild liquid phase flowing through the pores and blocking them after getting cold. Alumina reacts with the liquid phase and changes to mullite. As a result, the highest alumina content of 40% was selected.

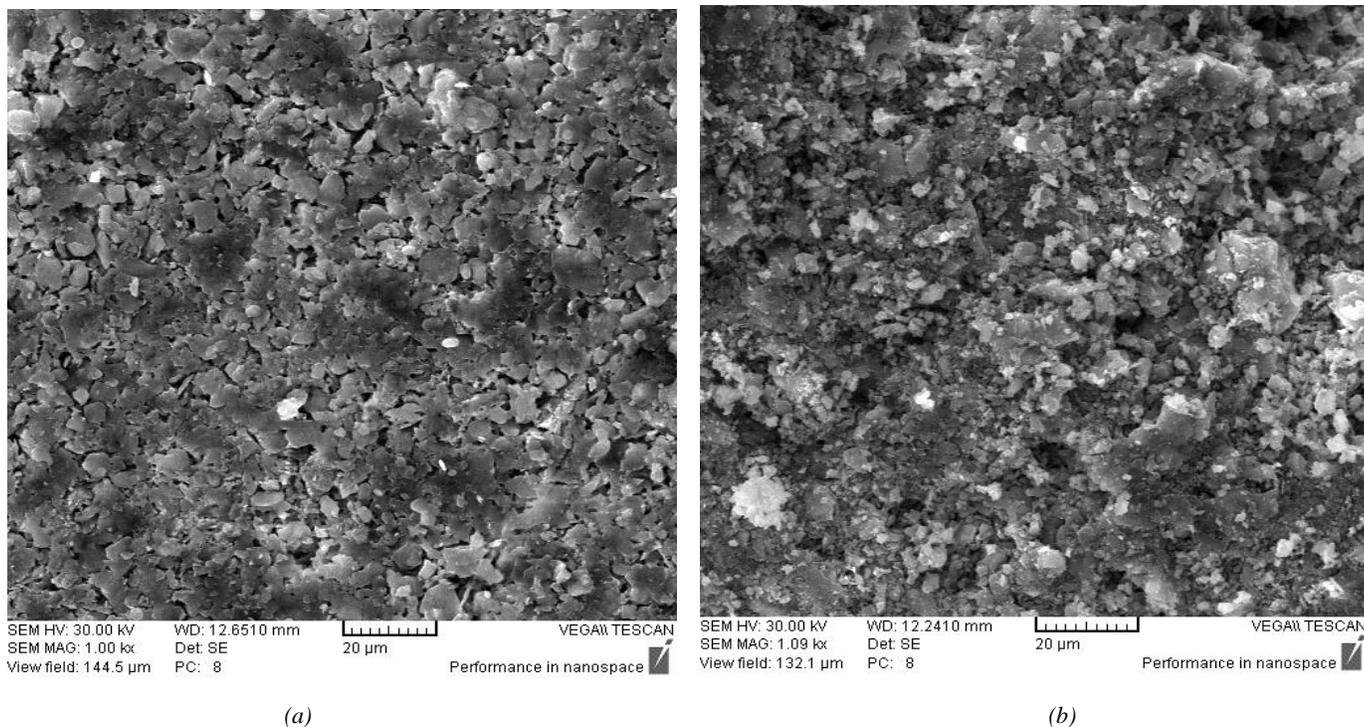


Figure 1: SEM of the membrane, (a) no additive, (b) PVA Al content = 40% Sintering temperature = 1200 °C Pressure = 400 bar

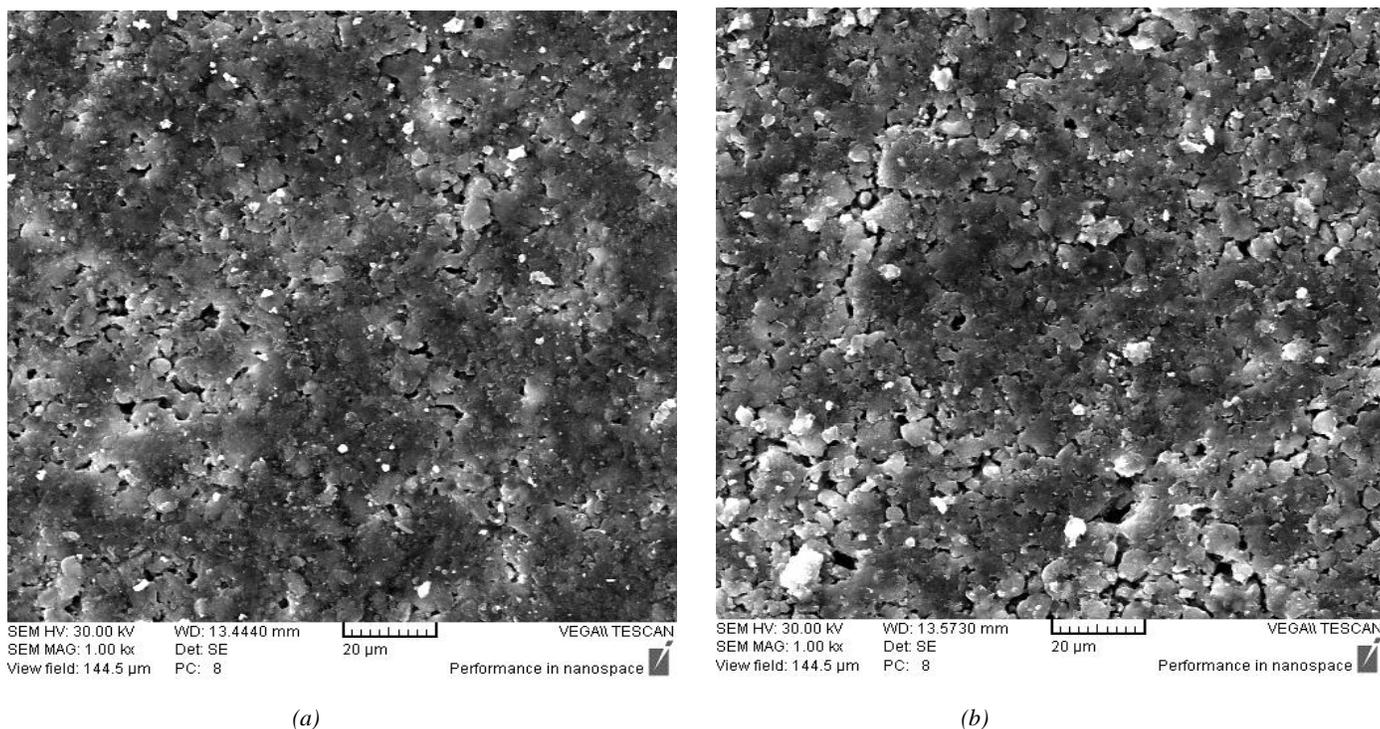


Figure 2: SEM of the membrane, (a) No additive, (b) PVA Al content = 40% Sintering temperature = 1250 °C Pressure = 600 bar

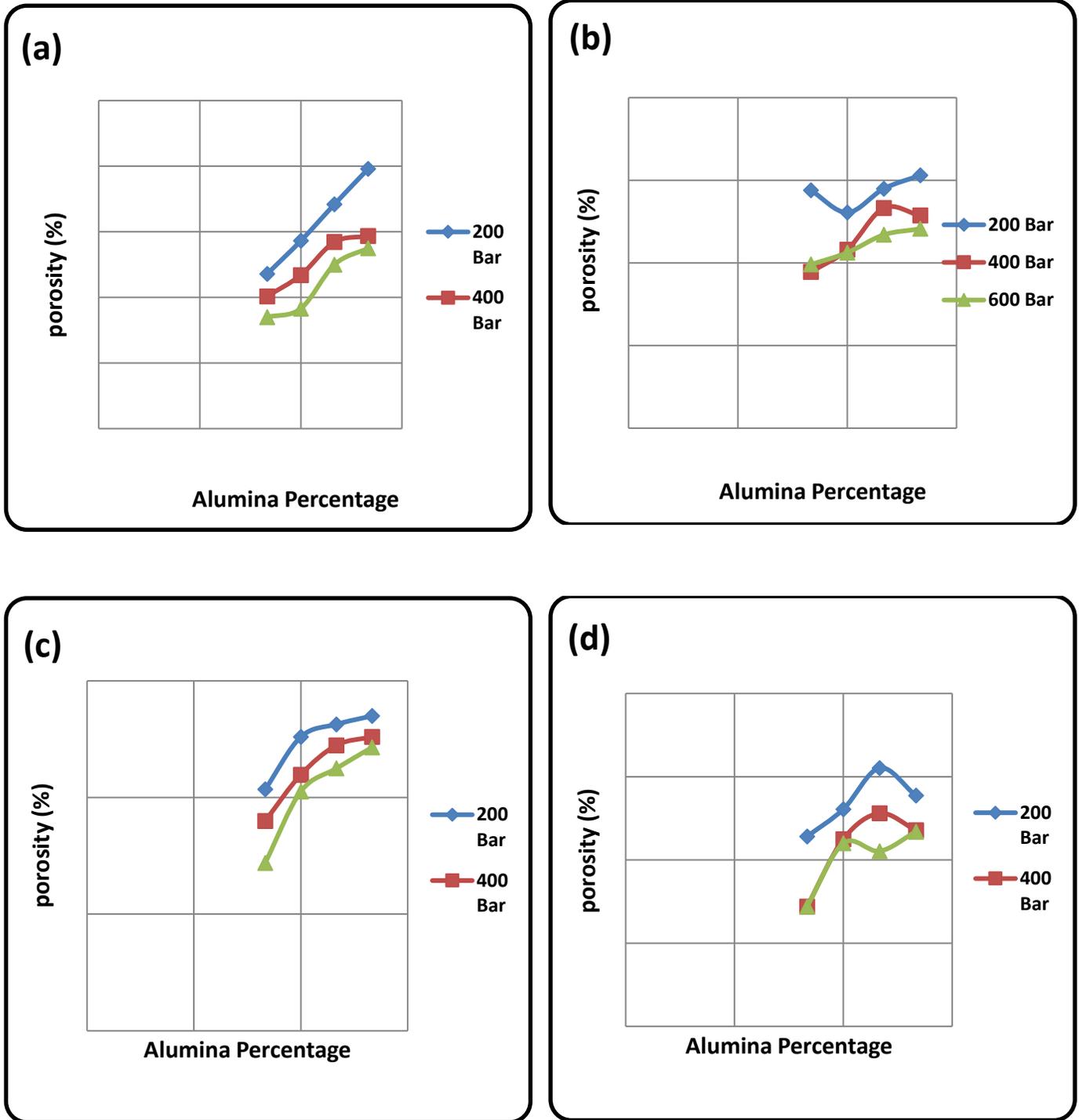


Figure 3: Effect of hydraulic pressure and alumina percentage on porosity in different additive at $T=1200^{\circ}\text{C}$,
 (a) PVA, (b) PEG, (c) CMC, (d) Without additive

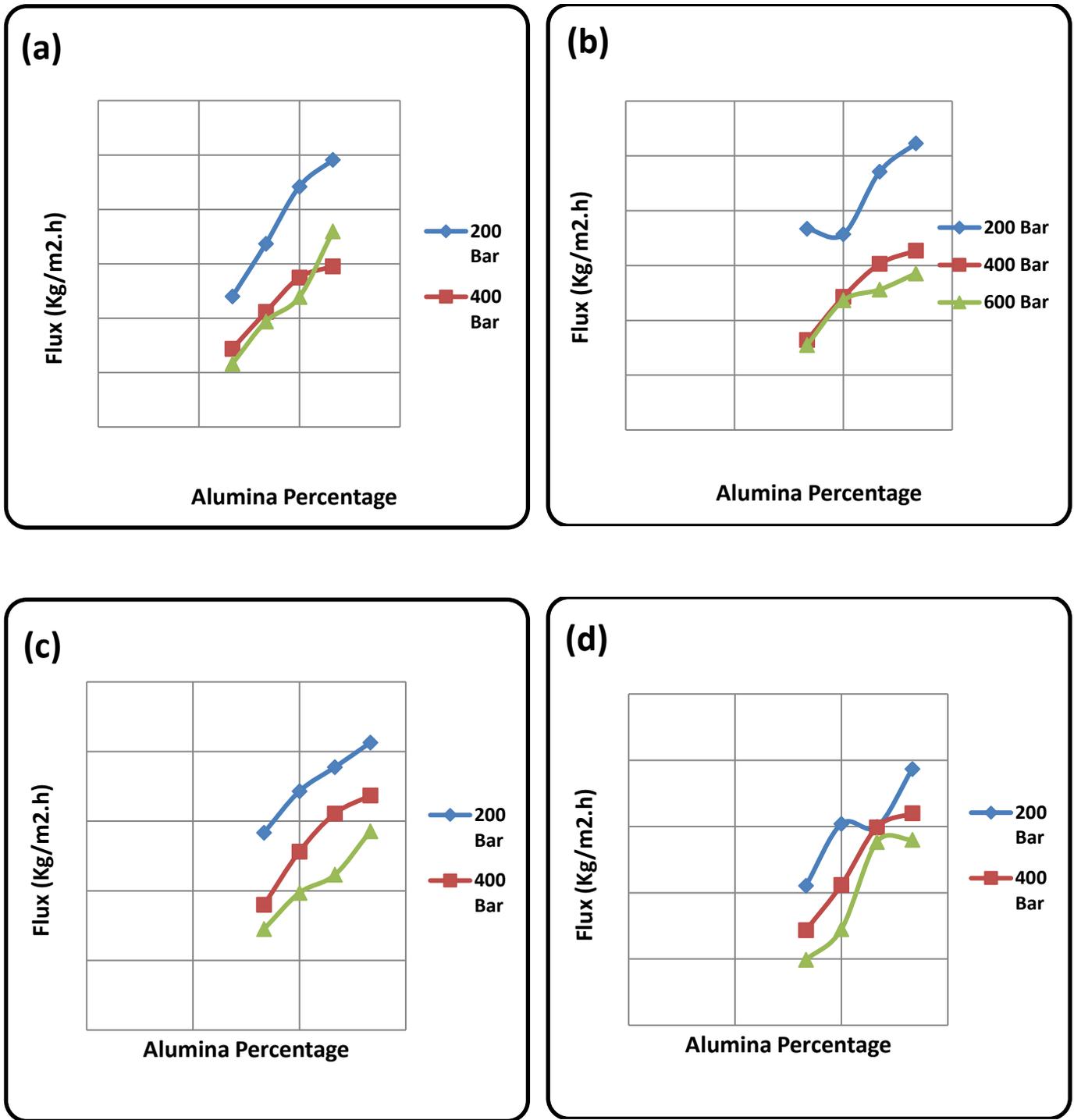


Figure 4: Effect of hydraulic pressure and alumina percentage on porosity in different additive at $T=1200^{\circ}\text{C}$, (a) PVA, (b) PEG, (c) CMC, (d) Without additive

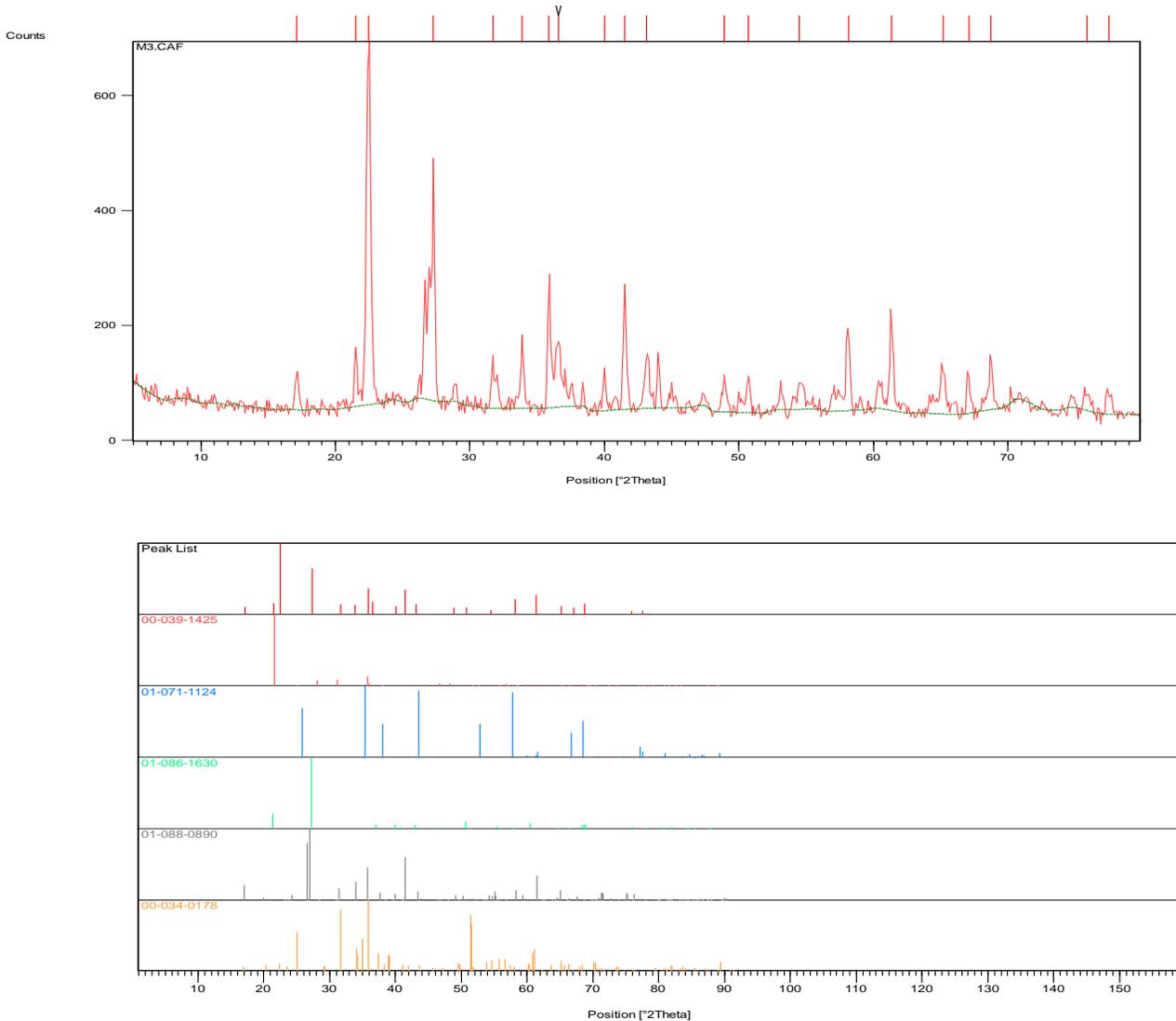


Figure 5: XRD of Sample containing 30% Al
(Plot of identified phases)

Enhancement of membrane porosity and permeation was observed due to the effect of PVA in comparison with other additives (PEG and CMC) as shown in Figs .3 and 4, PVA was removed from the sintered membranes, Formation and molecular structure of removed PVA made larger hollow than removed PEG and CMC which enhanced percentage of porosity and permeation. As seen, Membrane porosity and permeation were enhancing with increasing PVA content. As observed, the presence of PVA in the membrane powder enhances porosity and permeation more significantly compared with PEG and CMC.

3.2 Effect of hydraulic pressure

Figs. 3 and 4 show effects of pressing pressure on membrane permeation and porosity. Increasing hydraulic pressure results

in more compression and denser membrane. As result, porosity and permeation decrease with increasing hydraulic pressure. The result revealed that the optimum hydraulic pressure to prepare MF membrane of mullite and α -alumina is 400 bar.

4. Conclusion

Addition of alumina to kaoline enhances formation of mullite phase and enhances mechanical strength and permeation flux of the membranes significantly. Impurities of kaolin provide seeds, which are necessary for crystal growth. Increasing temperature leads to formation of glassy phases, which can block the pores and reduce permeation flux of the membranes. The results revealed that all three additives (PVA, PEG and CMC) improve permeation flux and porosity of the

membranes. As can be seen, effect of PVA presence is more dominant compared with the others. In addition, with increasing hydraulic pressure, porosity and permeation flux of the membranes decrease.

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