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# Ceramic membrane synthesis based on alkali activated blast furnace slag for separation of water from ethanol

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ABSTRACT

The main purpose of this research is synthesis of zeolite ceramic membranes based on alkali activated blast furnace slag for pervaporation separation of ethanol/water mixture (90 wt%). A new and simple method was applied to fabricate these ceramic membranes. In addition, gross waste of steel industry (blast furnace slag) was firstly used as the main starting material for making the membranes. In this study, for making the zeolite ceramic membranes, some experiments were conducted with water levels of 38, 40, 42 and 44 wt% of the blast furnace slag and NaOH levels of 4, 4.2, 4.4 and 4.6 wt% of the blast furnace slag. At first, for making the membranes, a primary geopolymer gel was prepared. Afterward the membranes were cast at 25 °C for 24 h. In order to form the zeolite layer, the membranes after geopolymerization process were kept at 90 °C for 24 h. The maximum value of selectivity (2579.48) was obtained for separation of water from ethanol using the synthesized membrane with 42 wt% water and 4 wt% NaOH.



## 1. Introduction

Today, membrane separation processes are taken into consideration as important techniques and have found wide applications in various fields. Each membrane separation process uses a membrane, thereby selectively separates one component from the other. This separation is due to the differences in physical and chemical properties of the membrane and the permeable component. In fact, permeation through the membrane occurs due to a driving force. The driving force can be pressure, concentration, temperature and electrical potential gradient. Pervaporation (PV) as one of the membrane processes was introduced by Kobber in 1917 [1,2]. Separation mechanism in pervaporation is solution-diffusion, compared with boiling point difference in distillation which is economically less affordable [1,3,4].

Pervaporation is a membrane process in which a liquid is in direct contact with a membrane (feed side). In most cases, partial pressure is reduced in permeate side by creating a vacuum or using a carrier gas. In fact, this process is a method for separating a mixture of liquids by partial evaporation through a porous or non-porous membrane. This process is often used for dehydration of hydrocarbons to obtain a high purity product, such as ethanol [5], isopropyl alcohol [6] and ethylene glycol [4,7–9].

Different membranes can be used in pervaporation, including ceramic [10] polymeric [11] and composite [2,12] membranes. Ceramic membranes have attracted more interest because of their chemical and thermal stability, applicability in high pressure operation, durability and mechanical stability [13–15]. Ceramic membranes are usually made of alumina, titania, zirconia and synthesized via extrusion, slip casting and sol gel [2,16].

Ceramic membranes are being made as microfiltration [16], ultrafiltration [2,3], nanofilteration [2], and zeolite [5,10] membranes. Purpose of pervaporation is mainly removal of water from organics, therefore in order to achieve an effective separation, zeolite membranes can be used. Zeolites contain small and uniform pores in molecular size. As a results, it can be expected that zeolite membranes are suitable for dehydration of alcohols.

Zeolite membranes can be formed from zeolite layers coated on microporous inorganic supports. Zeolite layers can be prepared via growth of zeolite crystals by means of methods like sol gel [17], microwave [18] and hydrothermal synthesis [19]. Actually, zeolite membranes are some kinds of microporous ceramic materials consisting of aluminosilicates with different ratios of aluminum to silicium. In other words, zeolites are crystal materials with porous structures that are very different from amorphous porous silica.

One of the traditional zeolite membrane production methods is hydrothermal synthesis. In this method, depending on the zeolite

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type, seeded supports and zeolite gels are kept in autoclaves for a few hours or even a few days at specified temperatures. At the end of procedure, zeolite layers are formed on surface of the supports [19]. The aim of seeding, is to speed up zeolite membrane formation and also to form uniform zeolite layer [20]. Researchers have used different formulations for synthesis of zeolite membranes so far and mentioned that seeding support is an effective and swift method for zeolite membrane synthesis [18,20,21].

Zeolite membrane synthesis methods have their own complexity and as a result defect free membranes are hard to be obtained. The main weakness of the zeolite membrane synthesis is that the synthesis processes are costly and not reproducible. Achieving a new method for zeolite synthesis is a target to obtain cheap and reproducible membrane suitable for dehydration. It must be mentioned that using environmentally friendly waste materials reduces synthesis costs and makes the process economically efficient. In this study, fabrication of zeolite membranes via geopolymerization of waste blast furnace slag (BFS) as the base material is investigated. This method is very simple in comparison with the other usual methods.

Geopolymers are a type of mineral polymers that are formed through reactions between hydroxide/silicate of alkaline metals and aluminosilicate sources. These mineral polymers are defined as amorphous to semi-crystalline three dimensional silico-aluminate of polysialate (-Si-O-Al-O-) or polysialate siloxo (-Si-O-Al-O-Si-O-) [22]. Molecular structures of geopolymers are very similar to that of zeolites and aluminosilicate gels. In other words, zeolites are crystalline shape of geopolymers [17,23].

Synthesis processes of geopolymers are more similar to those of zeolites or molecular sieves. For preparation of geopolymer materials, metakaolin [24], granulated slag [22] and fly ash [25,26] are used as the base material of geopolymer gel. Low temperature range of thermal treatment (25 °C) and simplicity in preparation of geopolymers using different aluminosilicate sources could eliminate the leading challenges in synthesis of the other materials.

In this article, formation of ceramic membranes via geopolymerization of waste BFS is reported. Also, separation factor and permeate flux of the membranes with different formulations in pervaporation process will be discussed.

## 2. Materials and methods

### 2.1. Materials

The primary material was rapidly water-cooled blast furnace slag prepared from Zob-Ahan industries (Esfahan-Iran) with desire Blain fineness of 3000 ($cm^2/g$) by further grinding in a ball mill. Chemical composition of the slag was determined according to standard ASTM C311 as presented in Table 1. According to the chemical composition, this type of slag is neutral and has a basic coefficient of 1.04 ($K_b=(CaO+MgO)/(SiO_2+Al_2O_3)$).

Alkali activation solution for geopolymerization process was prepared from sodium hydroxide (NaOH, Merck 98%) and distilled water.

### 2.2. Gel preparation

Chemical compositions of the applied activators are presented in Table 2. To prepare activators, the required distilled water and sodium hydroxide were weighted. The activator was simply prepared by dissolving the sodium hydroxide in distilled water. Then it was kept in a sealed place to reach room temperature ($24 \pm 1$ °C). To prepare fresh gel, BFS was added to the activator and mixed for 5 min to obtain a uniform and homogenous gel.

**Table 2**
Alkali activator solutions used to produce geopolymer samples.

| Mix no. | Sodium hydroxide (wt% of BFS) | Distilled water (wt% of BFS) |
|---|---|---|
| 1 | 4 | 38 |
| 2 | 4 | 40 |
| 3 | 4 | 42 |
| 4 | 4 | 44 |
| 5 | 4.2 | 38 |
| 6 | 4.2 | 40 |
| 7 | 4.2 | 42 |
| 8 | 4.2 | 44 |
| 9 | 4.4 | 38 |
| 10 | 4.4 | 40 |
| 11 | 4.4 | 42 |
| 12 | 4.4 | 44 |
| 13 | 4.6 | 38 |
| 14 | 4.6 | 40 |
| 15 | 4.6 | 42 |
| 16 | 4.6 | 44 |

### 2.3. Preparation of zeolite membranes

The prepared gel was cast into a polytetrafluoroethylene (PTFE) self-made disc mold (Fig. 1) using vibration with power of 25 W. The PTFE mold was built from two removable parts. The part 1 is a solid square plate and the part 2 is a square plate with 4 circular hollow sections each has a diameter of 25 mm and a thickness of 3 mm.

Then the cast gel was kept in an environment with more than 95% relative humidity at temperature of $24 \pm 1$ °C for 24 h. After this period, hardened geopolymer discs were removed from the mold and hydrothermally cured in an autoclave for 24 h at temperature of $90 \pm 1$ °C. During this process, zeolite crystals grow on the membrane surfaces. The synthesized membranes were then removed from the autoclave and evaluated in pervaporation process.

### 2.4. Membrane characterization

Structure and morphology of the synthesized zeolite membranes were evaluated using SEM, XRD, and PV experiments. The XRD pattern was recorded using a powder diffractometer machine (Siemens, 40 kV, 30 mA, Cu K α). The analysis was performed for 2 h in a range of 5–75° at a scanning rate of 2°/min, with a deliverance slit of 1°, an anti-scatter slit of 1°, and a receiving slit of 0.01 mm.

Microstructure of the synthesized zeolite membranes was investigated using an electron microscopy device (KYKY, EM 3200, 30 kV). For preparation of SEM images, selected samples were coated with a 100 Å- thick layer of gold via physical vapor deposition using a coating device (sputter coater KYKY, SBC12). Then the coated samples were placed in the electron microscopy device.

The PV experiments were conducted using a feed solution of

**Table 1**
Chemical composition of the blast furnace slag powder (wt%).

| **Oxide** | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $TiO_2$ | $K_2O$ | $Na_2O$ | $SO_3$ | $V_2O_5$ | MnO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **wt%** | 36.06 | 9.16 | 0.70 | 36.91 | 10.21 | 3.5 | 0.70 | 0.48 | 1.15 | 0.10 | 1.46 |