Synthesis and Characterization of a Novel Modified ANA Zeolite Membrane

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ABSTRACT

A Novel modified Analcime (Na_{16} ($Al_{16}Si_{32}O_{96}$) $\cdot16H_2O$) zeolite with a new molar ratio have been successfully synthesized. In order to investigate the role of the template, Different samples were synthesized with and without Tetramethylammoniumhydroxide (TMAOH) template through hydrothermal method. Different synthesis times (24, 36 and 72 hours) and molar ratios have been utilized. The optimum sample with highest Crystallinity (95.2%) has been used as seed for synthesis of analcime membrane on α-alumina support via Seed-assisted crystallization method. The resultant analcime membranes were then modified by Cu^{+2} and Ni^{+2} by ion exchange method. Synthesis of these materials is confirmed by the XRD, EDX and SEM methods. The SEM results of modified membranes showed that the surface of the support is shielded with a continuous layer of Ni^{+2} and Cu^{+2} crystals and the analcime zeolite are not destructed. Also, the results of XRD patterns verified that the main diffraction peaks of synthesized zeolites are similar to the analcime zeolite component and ion exchange reactions have not disturbed the structure of zeolite. Furthermore, the purity of analcime zeolites and its orthorhombic structure has been established. It should be mentioned that the modified membrane can be merged as a potential material for many applications such as gas separation.

Keywords: Analcime Zeolite Membrane, α-alumina Support, Ion Exchange, Modification, Orthorhombic Structure.

1. Introduction

Zeolite components are microporous crystalline aluminosilicates with uniform and narrow pore size distribution pores [1]. In the recent decades, many efforts have been made to develop zeolite membranes for catalysis and separation applications due to their chemical and thermal stability and potentially high selective molecular sieving gas separations [2-6]. Generally, nano materials have many applications [7, 8].

The Zeolite analcime with formula of ($Na_{16}(Al_{16}Si_{32}O_{96})\cdot16H_2O$) has a complex and compact structure. The zeolite exhibits a typical microporous structure with irregular channels (0.42 × 0.16 nm) that formed by highly distorted 8-rings. The material because of their application in industrial processes. has been extensively studied. Researchers using Tetrapropylammonium hydroxide (TPAOH) organic template, with high silica formulation in gel at hydrothermal condition and at high temperature [9-11], have investigated synthesis of Analcime zeolite with compact structure. The most important points in this synthesis are using TMAOH instead of TPAOH,

higher achieved crystallinity than other researchers, and using low synthesis temperature in short time. Some of the recent studies tried to synthesize this type of zeolite from natural high silica zeolite and natural clinker [12, 13]. M. Tatlier et al. have used both microwave and conventional heating methods for synthesis of Analcime zeolite with high silica molar ratio gel formulations (160 and 220) and prepared maximum 95.3% crystallinity by conventional heating method at 180 °C [9].

The preparation of zeolite membranes has attracted a lot of attention in recent years because of their inimitable molecule-selective separations and their higher thermal, mechanical and structural stabilities and High chemical resistance [2, 14-16]. Like the application in catalytic membrane reactors, the insertion of catalytically active guests such as transition metal ions is an example of the potentialities of such membranes. The presence of different framework ions such as V and Ti in the MFI zeolite membrane has an enormous effect on its chemical, physical and catalytic properties.

Jiang et al.[17] tried that Cu-ZSM-5 zeolite membrane catalyzes the oxidation using aqueous hydrogen peroxide as an oxidant. It has been found that these membranes exhibit good catalytic properties. Jacobs et al [18] have tried to prepare Ti-MCM-41 zeolite membrane and expoxidate 1-octene catalyzed by the synthesized membrane. The applicability of Platinum complexes supported in zeolite KLTL as catalyst for CO oxidation was studied by Joseph D. Kistler et al. [19]. This catalyst were synthesized from $[Pt(NH_3)_4]$- $(NO_3)_2$, oxidized at 633 K and is stable at high temperatures. This zeolite alone lacked measurable catalytic activity at temperatures up to 423 K. As a result, it was activated with platinum metal. Recent studies

have shown the first site-isolated platinum catalyst with the locations of the Pt atoms were synthesized and successfully applied for CO oxidation. Lu et al. [20] proposed a new method for identification of the active complex using formation of $Ir/MgAl_2O_4$ on single atoms which provides different reactions mechanism and high activity for low-temperature CO oxidation.

Analcime is a common zeolite occurring in cavities of altered mafic volcanic rocks, possibly as a primary phase in some under saturated volcanic rocks, a digenetic mineral replacing various materials in both open and closed hydrologic systems, a common product of burial metamorphism, precipitates from strongly alkaline waters, and in low temperature hydrothermal veins.

The determination of the structure of analcime zeolite by Taylor et al [21] was a milestone in zeolite mineralogy. Not only was it the first zeolite structure to be solved, but the discovery that (Si,Al) O_4 tetrahedra are in a framework arrangement became the basis for a new definition of zeolite [22]. Taylor et al. (1930) determined the structure in the cubic space group Ia3d.

The analcime framework consists of singly connected 4-rings, arranged in chains coiled around tetrad screw axes (Fig. 1). Every 4-ring is a part of three mutually perpendicular chains, each parallel to a crystallographic axis. Cages, which contain the water molecules and sodium-cations, occur near where chains interconnect, and each T-site is a part of 3-cages. In the cubic space group, every T-site is equivalent to every other T-site, and Al, Si distribution among these sites. Sodium-cations are in the center of these cages, but there are 24 cages in the unit cell. The Na^+ must also be randomly distributed among the cages. Water
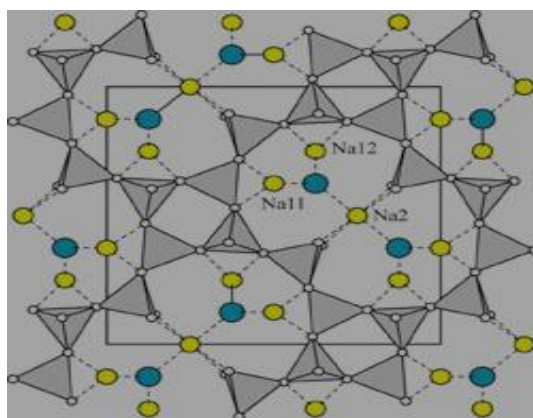

Fig. 1- Structure of analcime zeolite [23].

molecules fully occupy the 16 sites in the unit cell. Any excess water molecules must be randomly distributed in unoccupied sodium sites. Structure of the analcime zeolite is shown in Fig. 1 [23].

One of the modification methods of zeolites is Ion exchange, and exchange should be tunable by the proper choice of the ion. Both diffusion and adsorption properties should be affected by exchange. Single component and mixture permeances were measured to determine the effects of ion exchange.

A few researches have been carried out on the ion-exchanged zeolite membranes. Jafer and Budd [24] ion- exchanged NaA zeolite membranes with K., but no significant change in pervaporation performance was observed. Kusakabe et al. [25] ion exchanged NaY zeolite membranes with K^+, Li^+, Ca^{+2}, Ba^{+2} and Mg^{+2}. N_2 and CO_2 single gas permeances changed with exchange, though gas permeation rates and selectivities were not directly related to the size of cations. This zeolite membrane had a CO_2/N_2 separation selectivity of 19.6 at 40 °C. When Na ion was exchanged with K ion, the N_2 permeance decreased and the carbon dioxide permeance increased, so the CO_2/N_2 selectivity increased to 30.3. When Na ion was exchanged with Li ion and N_2 permeance increased almost an order of magnitude, the CO_2/N_2 separation selectivity decreased to 3.5. To observe the effects of ion exchange, membranes must have a low concentration of non-zeolite pores [26].

In this study, we used 24, 36 and 72 hours for synthesis of analcime zeolites. The optimum sample with highest Crystallinity that was synthesized without template was used for synthesis of analcime membrane. The resulting membrane was then modified by Cu^{+2} and Ni^{+2} ion-exchanged method and then characterized with XRD, EDX and SEM methods.

2. Experimental Section
2.1. Materials

Fumed silica (Aerosol 200, 12 mm) as silica source, Merck grade sodium aluminate ($NaAlO_2$) powder as aluminum source, Merck grade sodium hydroxide (NaOH) and potassium hydroxide (KOH) for sodium and potassium sources and Merck grade tetramethylammonium hydroxide (TMAOH) as the organic template were used for gel preparation. Also, Merck grade Nickel (II) nitrate [$Ni(NO_3)_2.6H_2O$] and Aldrich grade Copper Chloride ($CuCl_2$) were supplied for membrane modification.

2.2. Synthesis of analcime zeolite

The zeolite analcime was synthesized via hydrothermal process with some modification of work reported by Ghobarkar et al. [11]. In order to investigate the template effect, seven samples of analcime zeolite were synthesized. Different molar ratio and other conditions used for gel formulation are shown in Table 1. Three different synthesis times for analcime zeolites were used, (24, 36 and 72 hrs). The optimum samples resulted with 72 hrs. The optimum sample was ANA-1 with highest crystallinity of 95.2%.

Suitable amount of sodium aluminate was dissolved in distilled water. Suitable amount of silica source and sodium hydroxide were dissolved in distilled water and then mixture of two solutions was made homogeneous by stirring for 24 hrs. The resulting mixture was then transferred to a stainless steel liner. The liner was placed in an autoclave and the latter was sealed. The autoclave was then placed in an electric furnace; the temperature was maintained at 180 °C at autogenous pressure. Crystallization at this temperature and pressure was tried for 72 hrs. At the end of each run, product so formed was washed repeatedly with double

Table 1- Different synthesis conditions and gel formulations used for zeolite preparation

Time (hrs)	Temperature (°C)	TMAOH (mol)	H$_2$O (mol)	Na$_2$O (mol)	SiO$_2$ (mol)	Al$_2$O$_3$ (mol)	Samples Name
72	180	0	4800	33	50	1	ANA-1
72	180	3	500	0.312	5	1	ANA-2
72	180	4	4800	33	50	1	ANA-3
72	180	3	500	1.3	5	1	ANA-4
72	180	8	4800	33	50	1	ANA-5
36	180	2	4800	33	50	1	ANA-6
24	175	0	830	15.2	20	1	ANA-7

distilled water and then dried in an air-oven for 24 hrs at 80 °C.

2.3. Synthesis of analcime membrane

ANA-1 sample that was synthesized without template as optimum sample was used for synthesis of analcime membrane. Porous α-Al$_2$O$_3$ plate was used as support material [27-28]. At first, we prepared a 2%-Aqueous solution of ANA-1 powder and then mixed at ultrasonic probe for 3 minutes. Alumina support was cleaned at ultrasonic bathroom for 20 minutes and then for complete Seed-assisted crystallization, Alumina support deposited at this solution for 30 seconds. The resulting support was dried for 15 minutes at 60 °C. At the next step, an ANA-1 gel was prepared according to the same conditions mentioned above (Table 1) and then resulting support inserted at the gel and were placed in an autoclave (to prevent material being deposited on the support surface, the resulting support is placed in the holder and vertically shifted into the autoclave) and kept at 180 °C for 24 hrs. Finally, the resulting membrane was repeatedly washed with deionized water and dried at 80 °C for 24 hrs. The resulting membrane was named mANA-1.

2.4. Modification of analcime membrane

The m-ANA-1 was modified with ion-exchange method. At first, we prepared a 0.025 M Solution of Cu^{+2} and Ni^{+2} from their chlorides. For ion exchange, the synthesized membrane was tied to a magnetic stirrer with Teflon tape and placed at the bottom of a flask with a reflux system. The membranes were stirred at 200 rpm in each exchange solutions at 100 °C for 3 hrs. They were then rinsed with deionized water and finally dried in vacuum at 80 °C for 2 hrs. The modified membranes with Cu^{+2} and Ni^{+2} were named mANC-1 and mANi-1, respectively.

2.5. Characterization

The structures of resulting samples were identified by X-Ray diffraction (XRD) on a Philips 1830 diffractometer with Cu- Kα radiation source. SEM (PHILIPS XL30) was used to study the product morphology. The surface and cross-section morphologies of the resulting samples were examined by means of scanning electron microscopy (SEM-EDX, JEOL JSM-T330A) operating at 20 kV. In order to reduce specimen charging, a sample was first mounted onto a specimen stub with conductive adhesive and then sputter-coated with Au prior to measurement. The Si, Al, and Na concentrations on the surface of membranes were measured by means of energy dispersive X-ray analysis (EDX).

3. Results and discussion

XRD analysis is an important tool that can be used to evaluate structural aspects of a crystalline material. It is verified that the number of crystalline phases present in a sample. The powder X-ray diffraction patterns of ANA-1 and mANA-1 samples are shown in Fig. 2. These patterns for ANA-1 zeolite show a novel crystalline phase with reflections in the 2θ = 16, 26, 30, 32 and 33 the characteristic of analcime zeolite [10-11]. Formation of high crystallinity ANA zeolite is confirmed by XRD analysis. Crystallinity of the synthesized powder can be calculated via dividing the summation of the intensities related to three maximum peaks by the summation of the intensities of the three maximum peaks summarized in the standard [9]. Crystallinity of the synthesized ANA-1 zeolite phases is 95.2%.

The XRD pattern of mANA-1 sample shown the main diffraction peaks and relative diffraction intensities of this sample were at 2θ = 16, 26, 30, 32 and 33 and it was found to be the same as the standard data for this component but at diffraction

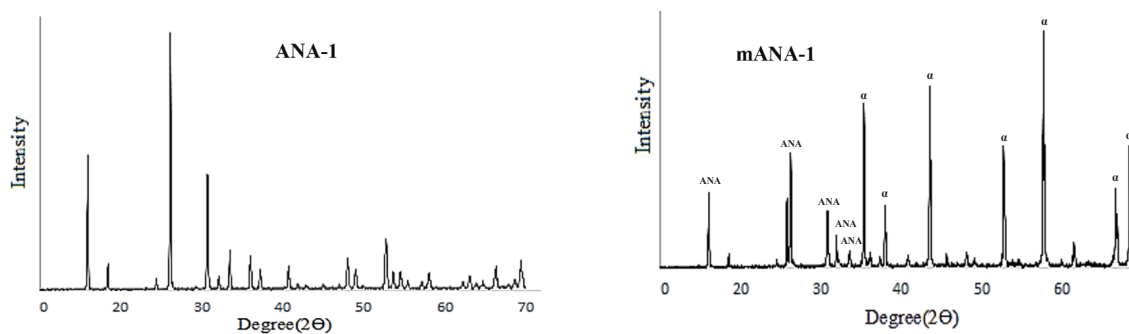Fig. 2- XRD patterns of the synthesized ANA-1 and mANA-1 samples (α: α-Al$_2$O$_3$).

angles >40 have increase intensity related to XRD peaks of α-Al$_2$O$_3$ that was used as support material.

Fig. 2. XRD patterns of the synthesized ANA-1 and mANA-1 samples (α: α-Al$_2$O$_3$).

The SEM images of the ANA-1 and mANA-1 samples are shown in Fig. 3 and 4. As is clear in these figures, the synthesized zeolite is well crystallized particles with trapezohedral morphology and range in size

FTIR spectra of ANA-1 and mANA-1 matrix are provided in Fig. 5. The broad band at 3200 - 3800 cm^{-1} can be assigned to the presence of -OH groups in the FTIR spectrum of ANA-1.The absorption bands at 450, 620, and 740 cm^{-1} are attributed to T–O–T (T = Si or Al) symmetrical stretching mode. The band at about 940 cm^{-1} is due to internal vibrations of the TO4 tetrahedral of ANA-1, whereas the band at about 1100 cm^{-1} is due

to vibrations related to external linkages between tetrahedral. There is an important assignment in the range of 1100–940 cm^{-1} with in the literature for the characteristic bands between 1250 and 950 cm^{-1} asymmetric stretching vibrations for all the zeolitic materials [30-31]. All the characteristic reference IR bands of the zeolite Analcim are observed for the hydrothermally synthesized sample of labeled as ANA-1 which proves the zeolite Analcim formation.

In the α-Al$_2$O$_3$ matrix the Al–O stretching mode in tetrahedron and symmetric bending of Al–O–H and the Al–O stretching mode in octahedral structure appear at 715 cm^{-1} and 1072 cm^{-1} and bands around 450-650 cm^{-1}, respectively [32]. However, the broad peaks of ANA-1 probably mask these peaks in the spectrum of mANA-1.

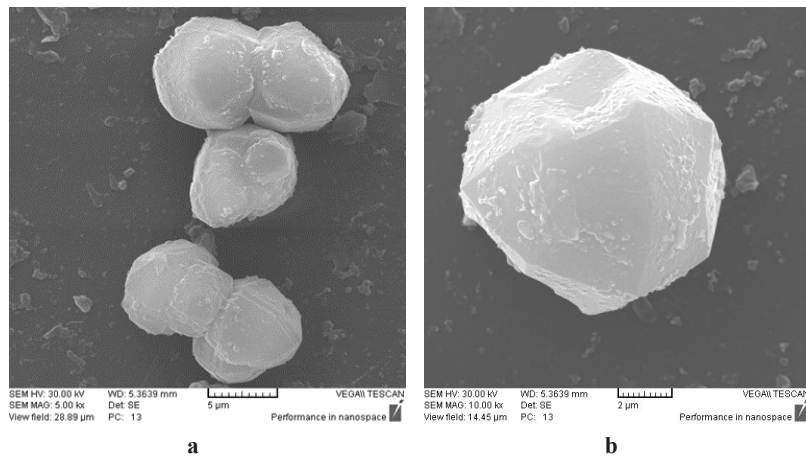The powder X-ray diffraction patterns of

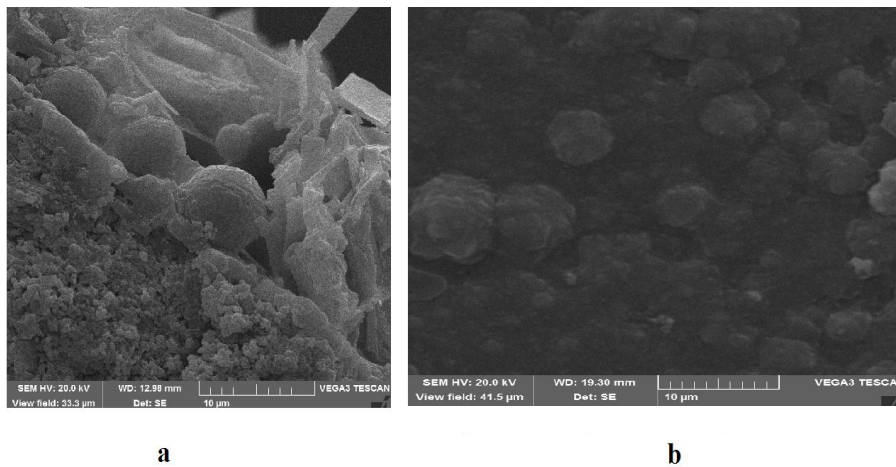Fig. 3- SEM images of the synthesized ANA-1 sample (a,b).

Fig. 4- SEM images of the synthesized mANA-1 membrane (a,b).

modified zeolites are shown in Fig. 6. The results of patterns show that the main diffraction peaks of synthesized zeolites are the same as the zeolite analcime component and ion exchange reactions have not disturbed the structure of zeolite analcime. It must be noted that the mANC-1 and mANi-1 maintained the peaks of the XRD pattern with reduced intensity compared with that for ANA-1. The crystallinity of mANC-1 and mANi-1 were 90% and 88%, respectively. The reduce intensities might be due to the partial damage of the orthorhombic structure.

SEM images of the modified membranes are shown in Fig. 7. The results of SEM of the modified membranes show that the surface of the support is covered with a continuous layer of Ni^{+2} and Cu^{+2} crystals and the analcime zeolite is not disturbed and imperceptible changes were observed in zeolite crystal sizes (ca. 5 to 15 μm for both modified and original membranes).

The powder EDX analysis of prepared zeolites membrane mANA-1 and modified membranes are shown in Figs. 8, 9 and 10. The results of Fig.8, shows that the mANA-1 contained Na, Si, O, Al and Fig.9, shows that the modified zeolite mANC-1 contained Na, Si, O, Al and Cu^{+2} which confirms that the ion exchange reaction is carried out successfully. Also, in Fig.10, the EDX spectra detected the presence of Ni ions and Na, Si, O, Al which has confirmed that the ion exchange reaction is carried out.
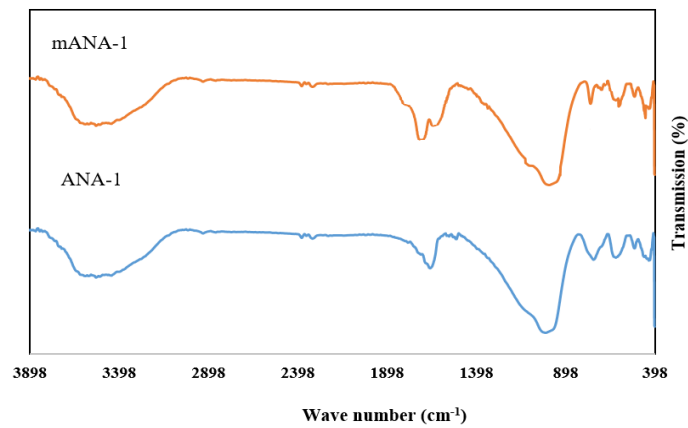

Fig. 5- FT-IR spectra patterns of the ANA-1 and mANA-1 samples.
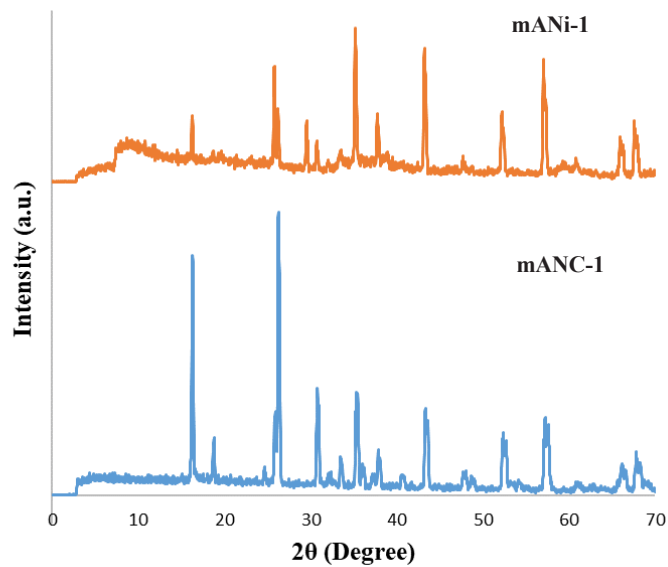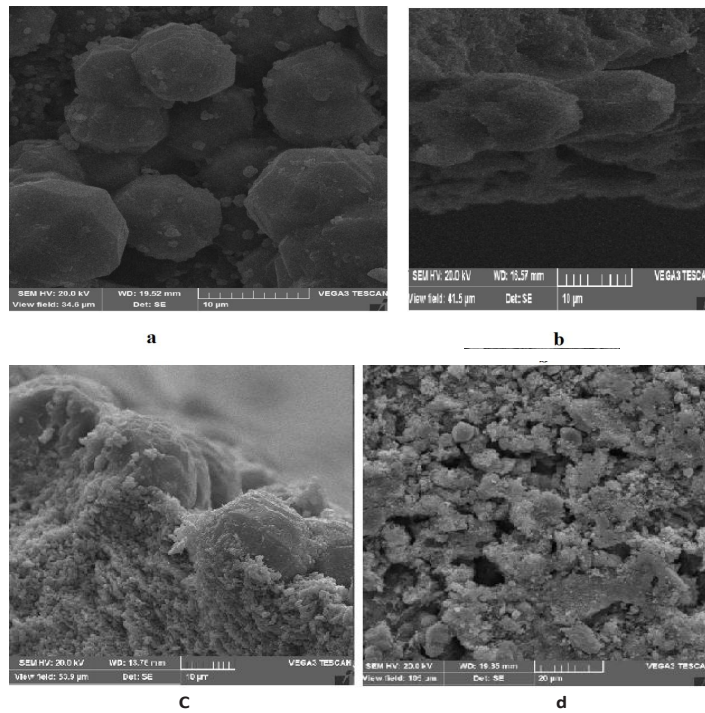

Fig. 6- XRD patterns of the mANC-1 and mANi-1 samples

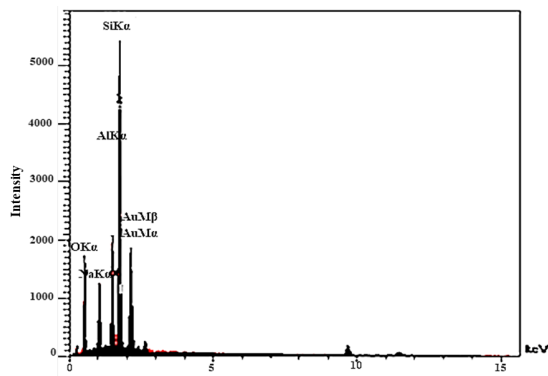Fig. 7- SEM images of the mANC-1 (a,b) and mANi-1 (c.d) samples.

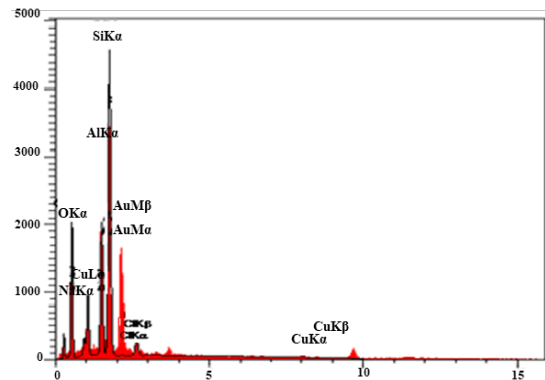Fig. 8- EDX spectra of mANA-1 sample.

Fig. 9- EDX spectra of mANC-1 sample (peaks related to Cu component are observable).
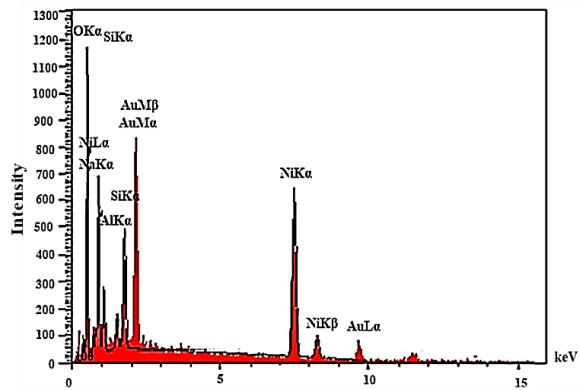

Fig. 10- EDX spectra of mANi-1 sample (peaks related to Ni component are observable).

4. Conclusions

In this study, in order to investigate the template effect, time effect and molar ratio of gel formulation effect, different samples of analcime zeolite were synthesized. ANA-7 with a new molar ratio was synthesized. Three different synthesis times for analcime zeolites (24, 36 and 72 hrs) and different molar ratios and other conditions are examined. The optimum samples resulted within 72 hrs. The optimum powder sample was ANA-1 with highest crystallinity of 95.2%. The ANA-1 as optimum sample which is synthesized without template is used for membrane synthesis in contact with a α-alumina tubular support by Seed-assisted crystallization method. The resulting analcime membranes were then modified by Cu^{+2} and Ni^{+2} ion exchanged with Na and characterized by the XRD, SEM and EDX methods. The results show that the synthesized Analcime zeolite has orthorhombic structure and is highly pure. The modified membrane is a potential material for many applications such as gas separation.

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