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Research Article

Synthesis of Geopolymer-Based Phase-Pure Analcime and Cancrinite Zeolite via Simple Hydrothermal Method

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ABSTRACT

It is well-reported that the synthesis of Analcime and Cancrinite zeolites via hydrothermal process requires long treatment reaching up to several days, also, the resulting zeolite is commonly phase impure and has weak mechanical strength. In the current work, Analcime and Cancrinite zeolites were synthesized using a simple hydrothermal method, utilizing metakaolin-based geopolymer as a template and 1 M and 5 M aqueous solutions of sodium hydroxide as a media for the hydrothermal process. The effect of the time and the temperature of the hydrothermal treatment were investigated. Characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR) were employed to assess the synthesized Analcime and Cancrinite zeolites. It has been found that phase-pure Analcime and Cancrinite zeolites can be obtained via the treatment at a temperature of 240°C and 220°C respectively for only 6 hours in NaOH solution, Analcime records a compressive strength of 61 MPa and Cancrinite reaches a compressive strength of 56 MPa. The findings not only establish the viability of geopolymer as a starting material for Analcime and Cancrinite zeolites synthesis but also contribute valuable insights into the key factors influencing the process.

Keywords: Analcime, Cancrinite, Zeolite, Alkaline-hydrothermal method, Geopolymer.

1. INTRODUCTION

Zeolites are widely needed in many industries as catalysts, adsorbents, and ion exchangers due to their mesoporous and microporous structures [1], [2], they also have versatile applications such as environmental remediation, catalytic activity, biotechnological applications, gas sensing, and medicinal applications [3]. Since zeolite minerals are uncommon worldwide, more than 200 synthetic zeolites have been created utilizing either natural or chemical resources [4].

The relatively structured unit cells of Analcime, one of the most common and well-defined types of zeolites, are based on non-intersecting channels with four, six, and eight members of oxygen rings and 16 sites occupied by sodium in the smallest 24 cavities and by water molecules in the 16 largest channels. Analcime exhibits a compact structure, due to the presence of the smallest-pores, compared to other types of zeolites with an idealized unit cell of ($Na_{16}Al_{16}Si_{32}16H_2O$) [5]. Analcime presents practical importance nowadays in dental systems, nanoelectronic field, adsorption [4], [6], fertilizer in agriculture [7], and heterogeneous catalysis in the oil industry and gas separation [8], [9], [10]. Additionally, it can be utilized as an ion sieve and ion exchanger at ambient temperature; however, ion exchange is made easier by raising the temperature [8], [11].

Cancrinite (CAN) has several industrial uses because of its unique structural characteristics and notable stability at high temperatures and pressures. [12]. Two well-known examples of these applications are the storage of alkaline wastes and the treatment of radioactive wastes [13]. The standard chemical formula for CAN is $Na_6[Al_6Si_6O_{24}].2NaX.6H_2O$ where X can be OH^-, Cl^-, NO^{3-}, or $1/2CO^{2-}$ [14]. The hexagonal framework of CAN zeolite contains tiny ε-cages consisting of five 6-membered and six 4-membered rings. These give rise to enormous continuous channels made up of 12-membered rings with a free dimension of about 5.9Å [15]. Due to the substitution of Al^{3+} ions for Si^{3+} ions, the structure of CAN has cages and channels in its negatively charged frameworks [16], To neutralize the β- and ε-cages, positively charged species are required [14], These porous materials allow cations to enter in order to balance the charge of their structural frameworks [16]. In the early 1920s, CAN was synthesised by hydrothermally treating kaolinite in a NaOH solution [17], from that time and on, many studies were published devoted to the composition, crystallochemistry, and properties of CAN.

Numerous studies have reported the synthesis of Analcime and Cancrinite zeolites by hydrothermal method using various starting materials and conditions. However, in many cases phase-impure Analcime was obtained as reported by Seyed et al. [18], [19], Samar et al [20], Ma et al. [21], and Jin et al. [22] although long duration of treatment was used reaching up 3-12 days. And phase-impure Cancrinite was obtained as reported by Wang et al. [23], Qingyuan et al. [24], Jenika et al. [25] and Véronique et al. [26], although long duration of treatment was used varying from 1-21 days. On the other hand, many studies have reported the preparation of Analcime using different precursors including a mixture of aluminum black dross and waste glass [27], saline slag [28], coal fly ash [29], natural mineral [6], [30], [31], [32] and natural zeolites [33], [34]. Similarly, many studies have reported the preparation of Cancrinite using various precursors including natural bentonite [35], kaolin [36], glassy combustion residue [37], kaolinite and metakaolinite [38], fly ash [39], [40], [41], [42], [43], natural zeolite [44], aluminosilicate gels [45], natural diatomaceous earth [46], raw muscovite [47], zeolite A, zeolite X, and precipitated silica [48]. However, complex process and prolonged period of hydrothermal treatment were involved in these processes, moreover, obtaining phase-pure was not supported with evidence. Several studies involved incorporation of organic template, as organic structure directing agents, to obtain Analcime with specific shape and high degree of crystallinity, however, in addition to the environmental and cost issues related to the use of these templates, still very long time of treatment is required ranging from 1-13 days [19], [19], [49], [50], [51], [52], [53]. Utilizing the microwave treatment for 2 hours could reduce the time of the hydrothermal to 16 hours [54], however, such complex route makes it costly and difficult to industrialization.

The synthesis of zeolites within the geopolymeric framework has garnered significant attention in recent years, owing to the distinctive properties and diverse applications of these materials [55]. Also, the exploration of geopolymer-based zeolite synthesis has gained momentum due to its sustainable nature, utilizing industrial by-products and contributing to the advancement of green chemistry [56].

The current work reported a simple method to fabricate phase-pure and self-supporting Analcime and Cancrinite zeolites using the Geopolymer-Gels-Conversion (GGC) method, without using organic structure directing agents, utilizing natural metakaolin-based geopolymer as an economic and eco-friend aluminosilicate material.

2. MATERIALS AND METHODS

2.1. Materials

Kaolin clay was used as starting materials to synthesis Analcime and Cancrinite zeolites, it was supplied by Al-Mishraq company from the north of Iraq, the chemical composition of the kaolin is given in Table 1. Metakaolin was obtained by the calcination of the kaolin clay at 800˚C for 3 hours in air atmosphere using heating rate of 5°C/min. The activator solution was made using reagents of industrial grade including sodium hydroxide flakes (97.99%), sodium silicate solution, ($Na2O$ = 13.1-13.7%, $SiO2$ = 32-33%, and $H2O$ = 53.3-54.9%), and distilled water.

Table 1. Quantitative chemical composition of kaolin.

Oxides	SiO_2	Al_2O_3	Na_2O	K_2O
wt.%	54.46	33.68	0.22	0.3

2.2. Preparation of Geopolymer Samples

Geopolymer samples, with the formula $Na2O.Al2O3.3.6SiO2$, were synthesized according to our previous study [57]. The alkaline liquid utilized in this investigation is a mixture of sodium hydroxide and sodium silicate solutions. At the beginning, distilled water was placed in a beaker on a magnetic stirrer at a speed of 600 rpm, and the water was then mixed with sodium hydroxide. Sodium hydroxide was dissolved, and then sodium silicate was added to the mixture. At this time, the solution was heated up to 80°C and soaked at this temperature for 20 minutes, then, it was subsequently allowed to cool down to room temperature. The metakaolin was added to the solution and mixed using a mechanical mixer at a fixed speed of 3000 rpm for 5 minutes. Cylindrical molds made of polyvinyl chloride, with a diameter of 13 mm and a height of 26 mm, have been utilized for the molding of geopolymer pastes. The inner surface of the molds was lubricated with oil to prevent the geopolymer paste from sticking to the molds and to facilitate the demolding of the samples. The fresh paste was poured in the molds which was covered with plastic bags until the next day. The samples were left in the molds at room temperature for three days and afterward, they were demolded and left at room temperature for 28 days to be used in the preparation of Analcime and Cancrinite zeolites.

2.3. Synthesis of Analcime and Cancrinite zeolites

The Analcime and Cancrinite zeolites were synthesized via the hydrothermal process without prior activation steps. The hydrothermal treatment was performed in water, 1 M, and 5 M aqueous solution of sodium hydroxide at temperature of 160°C, 220°C, and 240°C. A sample of geopolymer weighing 4.5 g was placed in a Teflon-lined autoclave with 90 ml volume, 48.5 ml of the water/sodium hydroxide solution was added to the autoclave, and the autoclave was placed in an oven at the desired temperatures for 6 or 8 hours. At the end of each run, the samples so formed were left to cool down to room temperature. Subsequently, the samples were washed with distilled water several times, and eventually dried at 80°C for 6 hours.

3. CHARACTERIZATON OF MATERIALS

The particle size distribution of kaolin and metakaolin powder was tested using Laser Particle Size Analyzer (Bettersize 2000), before the test, a small quantity of the sample was mixed with 250 ml of water at room temperature under stirring and ultrasonic treatment. The phase analysis of the starting materials and the hydrothermally treated samples was performed by the X-ray diffraction (XRD) technique using Shimadzu-6000 diffractometer, Cukα X-ray was used as a source of radiation, with 30 mA and 40 kV, at a scanning speed of 5°/min over 2θ range 10-60° with a step size of 0.02°. Phase identification and the calculations of the amount of each phase present were carried out using Rietveld refinement method on X-Ray powder diffraction patterns using X'Pert HighScore Plus software using ICDD powder diffraction database and CIF files. FTIR spectra of the geopolymer and analcime were recorded at room temperature using FTIR spectrometer from Shimadzu (IRAffinity-1) over a range of 400–4000 cm-1 with a resolution of 2 cm−1 using KBr-pellets method. The microstructure of the geopolymer and hydrothermally treated samples were examined using scanning electron microscope (TESCAN-VEGA3), the samples were coated with copper by ion sputtering before imaging. Compression testing has been used to determine the mechanical properties of the hydrothermally treated and geopolymer samples, the test was performed at a rate of 0.5 mm/min along longitudinal axis of the specimen until failure is achieved, every sample was examined at 28 days of age. Archimedes' method has been used to assess the water absorption, apparent porosity, bulk density, and real density of the geopolymer and hydrothermally treated samples. The 28-day compressive strengths of geopolymer sample and hydrothermally treated samples were tested to confirm the self-supporting property.

4. RESULTS AND DISCUSSION

XRD patterns of the kaolin and metakaolin is shown in Fig.1, the kaolin clay is composed of kaolinite clay mineral and quartz according to the ICDD cards (96-901-5000) and (96-900-8093) respectively. Rietveld refinement method showed that there are 23% quartz and 77% kaolinite in the kaolin clay. When kaolin is calcined, the peaks that correspond to kaolinite disappear. This can be explained by heat treatment dihydroxylating the water molecules present in the kaolinite structure. [58], this produces metakaolin with both amorphous phase and quartz.

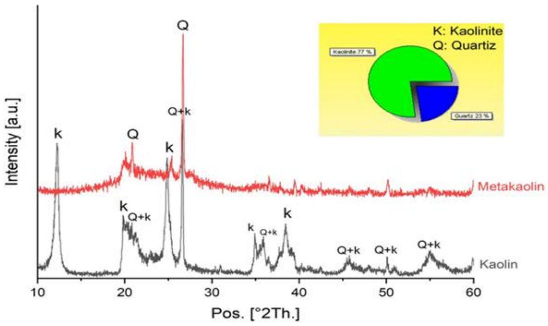

Figure 1. XRD patterns of kaolin clay before and after calcination.

The particle size distribution of the metakaolin is shown in Fig.2, the distribution is multimodal with D90 of ~49 µm, this indicates the formation of secondary particles during the test due to the aggregation of the primary particles of metakaolin.

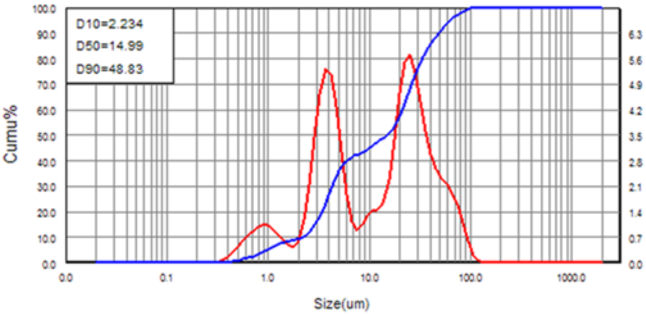

Figure 2. Particle size distributions of metakaolin powder.

Fig.3 shows the XRD patterns of the geopolymer and the hydrothermally treated geopolymer samples in a distilled water or 1M NaOH solution for 6 hours at different temperatures. It has been found that the geopolymer sample hydrothermally treated in water has an amorphous phase in addition to the quartz (96-900-8093), this finding was observed when the hydrothermal treatment was achieved at 160°C as well as 220°C, this indicates that the hydrothermal treatment is not sufficient to make a noticeable progress in the phase change in geopolymer. On the other hand, when the hydrothermal treatment is achieved in alkaline solution, phases of 37% of Analcime (96-900-8208), 35% of chesnokovite (96-901-3144), 15% nacrite (96-901-6424), 8% quartz (96-900-5025), and 5% cancrinite (96-900-4242) could be observed as these conditions promote nucleation and accelerate the crystallization process [59], these zeolite phases include, this indicates that the alkalinity of the solution is an essential requirement for the development of zeolite phases. As the time or the temperature of the process increase, a phase-pure Analcime is obtained, as shown in Fig4, based on the Rietveld refinement calculations, this suggests that the Analcime is the more stable phase in the conditions of the current treatment, while, the other phases of the zeolites obtained at the lower time or temperature are metastable phases.

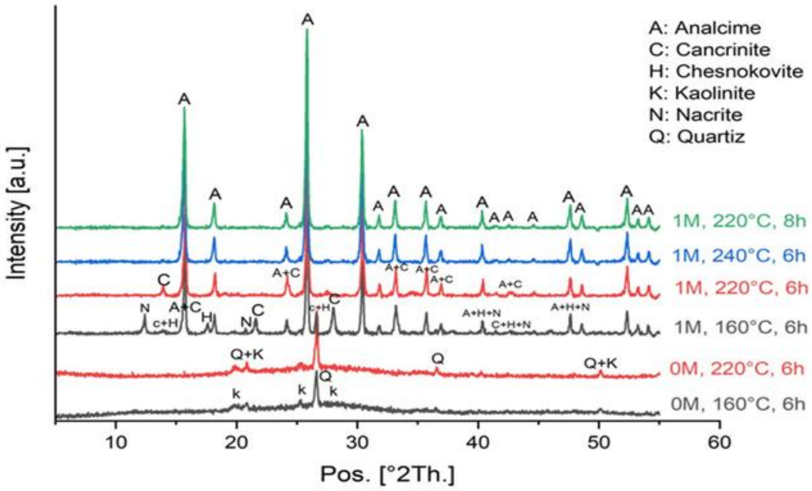

Figure 3. XRD patterns of zeolites synthesized at different hydrothermal temperatures.

Scanning electron microscopy was performed on the hydrothermally treated geopolymer samples to investigate the morphology of the prepared phases. As can be seen in Fig.5A, the geopolymer sample hydrothermally treated in water at 160°C is composed of a gel-like structure, this finding is matched with the XRD result. However, when the treatment is achieved at higher temperature of 220°C, the structure seems to composed of very fine particles and pores, as shown in Fig.5B, this indicates that a crystallization process was took place, however, this process seems to be in its initial stage as any new phases could not be detected by the XRD.

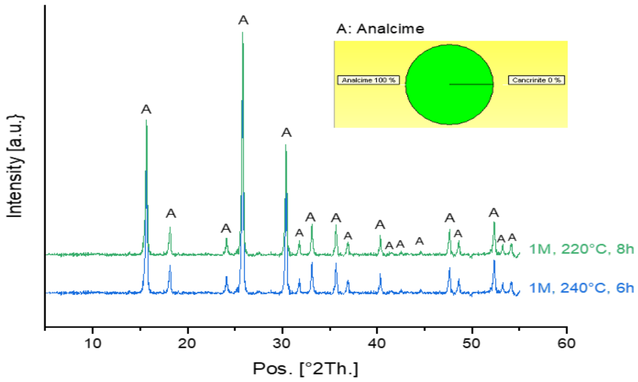

Figure. 4. XRD patterns of phase-pure analcime zeolite.

On the other hand, when alkaline solution is used, the main morphological feature observed is the spherical-shaped particles with minor fibrous phase among them, as shown in Fig.6A. As per the XRD results and the findings of the previous studies [32], [60], [61], these spheres are belonged to the Analcime zeolite as the main phase and the fibrous phase represents the other minor zeolites. When the hydrothermal treatment's temperature is raised from 160 to 220°C, the amount of these fibrous phase decreases, Fig.6B, 6C. A closer look to the surface of the analcime spheres shows that it composes of facetted crystals, Fig.6D. At a higher hydrothermal treatment temperature, the facetted crystals become more sharp, identical, and larger in size, Fig.6E, 6F, due to the progress of the crystallization and the subsequent growth process of Analcime zeolite.

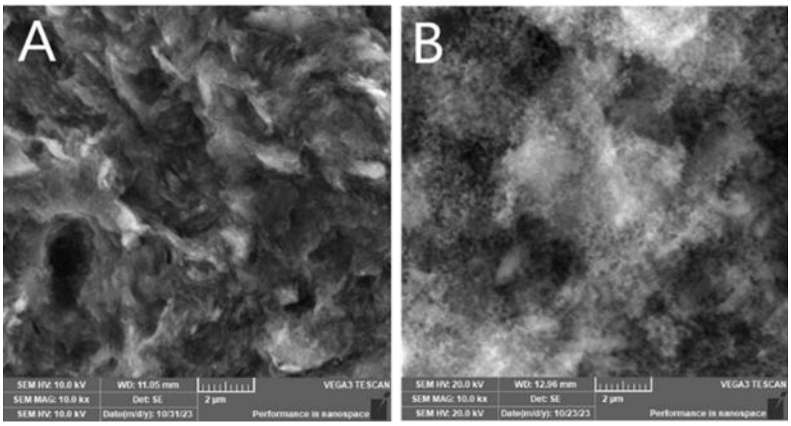

Figure 5. SEM micrographs of geopolymer after hydrothermal treatment in water for 6 hours at (A) 160°C and (B) 220°C.

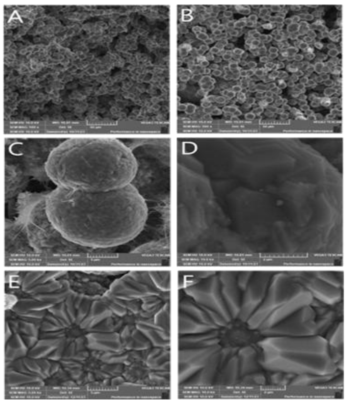

Figure 6. SEM micrographs of geopolymer after hydrothermal treatment in alkaline solution for 6 hours at 160°C, 220°C, and 240°C.

Fig.7 shows the XRD patterns of the geopolymer and the hydrothermally treated geopolymer samples in a distilled water for 6 hours at the hydrothermal temperatures of 160°C and 220°C. It has been found that the geopolymer sample hydrothermally treated in water has an amorphous phase in addition to the quartz (96-900-8093), this finding was observed when the hydrothermal treatment was achieved at 160°C as well as 220°C, this indicates that the hydrothermal treatment is not sufficient to make a noticeable progress in the phase change in geopolymer. On the other hand, when the treatment is achieved in 5 M NaOH at 160°C, the amorphous phase in the geopolymer sample decreases and Cancrinite phase is formed while quartz phase is still present, this suggests that the alkaline media enhances the transformation of the geopolymer in to zeolite. At higher temperature of 220°C, phase pure CAN zeolite is obtained at short time of 6 hours only as proved by Rietveld refinement calculations.

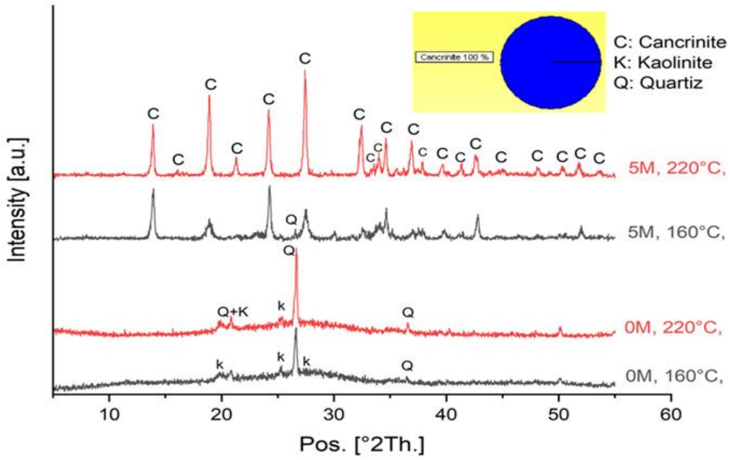

Figure 7. XRD patterns of zeolites synthesized at different hydrothermal temperatures.

when alkaline solution is used, the structure is composed of very fine particles when the hydrothermal treatment is achieved at 160°C as shown in Fig.8A. When the hydrothermal treatment's temperature reaches 220°C, the structure turned to needle like shape crystals, as per the XRD results and the findings of the previous studies [62], [63], [64], [65], these crystals are belonged to the CAN zeolite as shown in Fig.8B-D.

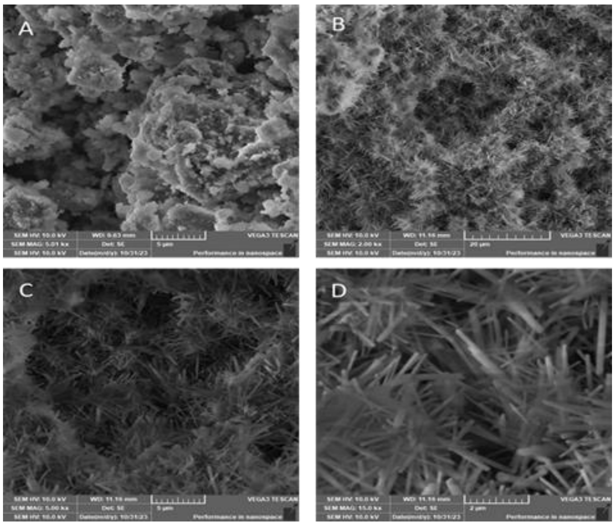

Figure 8. SEM micrographs of geopolymer sample hydrothermally treated in 5 M NaOH solution for 6 hours at (A) 160°C and (B-D) at 220°C at different magnifications.

For the Analcime spectra, the band that located at the lowest wavenumbers 401cm−1 is corresponding to the characteristic bending vibrations carried out in the 4-membered rings [66], the bands at 447 cm−1 is related to the T–O–T bending of vibration mode (T = Al, Si) [67], [68], the double rings, D4R and D6R, in the Analcime framework structures are connected to the band at 617 cm−1[69], the symmetric stretching vibration of four-membered rings is linked to the band 740 cm−1 [70], the zeolitic water in the zeolite channels is identified by the band 1643 cm−1 [71], and the asymmetric stretching mode of molecular water coupled to the zeolite channel margins is responsible for the bands at 3425 and 3749 cm−1 [72], [73].

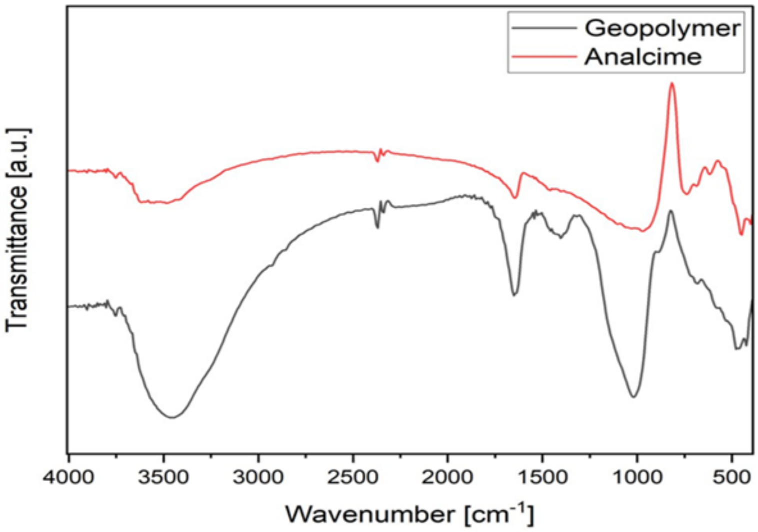

Figure 9. FTIR of geopolymer and Analcime zeolite synthesized at 240°C for 6 hours.

Whereas the FTIR spectra of the geopolymer and Cancrinite zeolite are shown in Fig.10. For the geopolymer spectra, the most characteristic band is located at 1018 cm-1, which is attributed to the asymmetric stretching of Si-O or Al-O present in the aluminosilicates, the amorphous structure of the material and the short-range ordering of the Si and Al tetrahedron are the primary causes of this band's size, the small bands located at 612, 686, and 740 cm-1 are attributed to the bonds present in the metakaolin source, and two more bands were located at 1643 cm-1 and 3425 cm-1 are correspond to geopolymer hydration, i.e., corresponding to the water molecules present in the material [74].

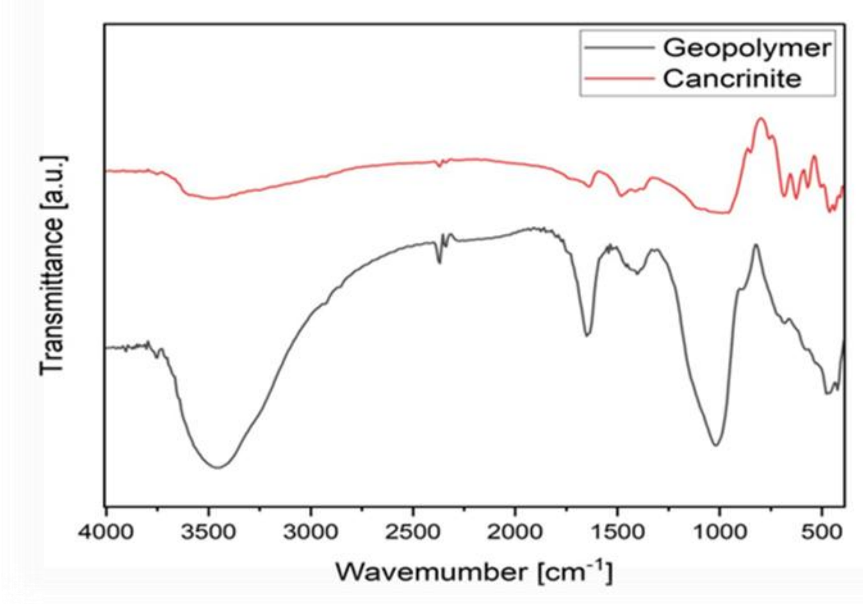

Figure 9. FTIR of geopolymer and Cancrinite zeolite synthesized at 220°C for 6 hours.

The FTIR spectra of CAN revealed a noticeable change at 220°C of the hydrothermal reaction. The OH group 3749 cm-1 frequency and intensity have been reduced. Additionally, new weak bands around 686 cm-1 and a strong band about 624 cm-1 were also brought about by the hydrothermal treatment; these bands can all be attributed to the bending mode of the Si-O-Si group of the newly created cancrinite [75].

The results showed that the compressive strength of the Analcime is 62 MPa whereas the compressive strength of the Cancrinite is 56 MPa, this confirms that the Analcime and Cancrinite zeolites prepared in the current study are a self-supporting material. This high strength is a result of the robust structure of the Analcime and Cancrinite zeolites, this structure is related to the structurally robust geopolymer which has a strength of 123 MPa. The reduction in strength of the geopolymer after the hydrothermal treatment can be attributed to the intrinsic properties of the two phases as well as the changes in the physical properties, shown in Table 2, during the hydrothermal treatment.

Table 2. The physical properties of geopolymer and hydrothermally treated samples.

Sample	True Density (g/cm3)	Bulk Density (g/ cm3)	Apparent Porosity (%)	Water Absorption (%)
Geopolymer	2.21	1.57	28.75	18.22
ANA-160°C	2.42	1.19	50.62	42.27
ANA-220°C	2.09	1.14	45.61	39.97
ANA-240°C	2.17	1.48	31.63	21.26
CAN-160°C	1.79	1.24	30.68	24.72
CAN-220°C	1.92	1.02	46.42	45.12

5. CONCLUSION

In this study, metakaolin-based geopolymer was utilized to synthesize Analcime and Cancrinite zeolites via a simple hydrothermal treatment, the results reveal that using alkaline solution in the hydrothermal treatment is important to facilitate the phase transformation of amorphous geopolymer to crystalline zeolite. It was highlighted that alterations in synthesis conditions, such as temperature, alkaline solution, and processing time, significantly influence the phase purity of the resulting zeolite. Also, obtaining phase-pure Analcime and Cancrinite zeolites is attainable at a temperature of 240°C and 220 respectively, concentrations of NaOH alkaline solution of 1-5M, and a processing time of 6 hours only. Such simple treatment was sufficient to produce self-supporting Analcime and Cancrinite zeolites with high compressive strengths of 62 MPa and 56 MPa sequentially. Building upon this foundation, the utilization of geopolymer as a precursor for the preparation of Analcime and Cancrinite zeolites presents a promising and innovative approach in materials science and sustainable chemistry. This method offers several advantages, such as utilizing abundant and locally available raw materials, minimizing environmental impact, and providing a sustainable alternative to traditional zeolite synthesis routes.

Declarations

Conflicts of interest: The authors declare no conflicts of interest or competing interests related to this paper.

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