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The Potential of Saudi Arabian Natural Zeolites in Energy Recovery Technologies

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Abstract

Energy consumption in kingdom of Saudi Arabia (KSA) is growing rapidly due to economic development with raised levels of population, urbanization and living standards. Fossil fuels are currently solely used to meet the energy requirements. The KSA government have planned to double its energy generating capacity (upto 120 GW) by 2032. About half of the electricity capacity of this targeted energy will come from renewable resources such as nuclear, wind, solar, waste-to-energy (WTE) etc. Natural zeolites are found abundantly in KSA at Jabal Shamah occurrence near Jeddah city, whose characteristics have never been investigated in energy related applications. This research aims to study the physical and chemical characteristics of natural zeolite in KSA and to review its potential utilization in selected WTE technologies and solar energy. The standard zeolite group of alumina-silicate minerals were found with the presence of other elements such as Na, Mg and K etc. A highly crystalline structure and thermal stability of natural zeolites together with unique ion exchange, adsorption properties, high surface area and porosity make them suitable in energy applications such as WTE and solar energy as an additive or catalyst. A simple solid-gas absorption system for storing solar energy in natural zeolites will be a cheap alternative method for KSA. In anaerobic digestion (AD), the dual characteristics of natural zeolite like Mordenite will increase the CH_4 production of organic fraction of municipal solid waste (OFMSW). Further investigations are recommended to study the technical, economical, and environmental feasibility of natural zeolite utilization in WTE technologies in KSA.

Key Words: Natural Zeolites; Waste-to-Energy (WTE); Solar Energy; Anaerobic Digestion (AD); Pyrolysis

LIST OF ACRONYMS AND ABBREVATIONS

AD: Anaerobic Digestion
CH_4: Methane
EDS: Energy Dispersive Spectrometer
FFA: Free Fatty Acid
FAME: Fatty Acid Methyl Ester
GW: Gigawatts
GHG: Greenhouse Gases
KACARE: King Abdullah City of Atomic and Renewable Energy
KSA: Kingdom of Saudi Arabia
MSW: Municipal Solid Waste
NZ: Natural zeolite
OFMSW: Organic Fraction of Municipal Solid Waste
PVA: Poly Vinyl Alcohol
RDF: Refused Derived Fuel
SWM: Solid Waste Management
SEM: Scanning Electron Microscopy
WTE: Waste-to-Energy

1. Introduction

1.1 Energy Requirements of KSA

In 2013, the energy consumption in the Kingdom of Saudi Arabia (KSA) has increased up to 9 quadrillion British thermal units (Btu), due to a rapidly growing population, urbanization, and economic development. This placed the country to the world's 12 largest primary energy consumer [1]. Fossil fuels are currently solely used to meet the energy requirements. About 60% of the energy demand is fulfilled from petroleum and the remaining comes from natural gas. The government has planned to increase its electricity generating capacity of 55 gigawatts (GW) to 120 GW in 2032 to meet the ever-increasing electricity demand. For this, government has launched a special program; King Abdullah City of Atomic and Renewable Energy (KACARE) to establish the renewable-energy sources through science, research and industries [2]. The ambition is to generate about half of the electricity capacity from renewable sources such as solar, wind, nuclear and waste-to-energy (WTE) facilities by the year 2032 [1, 3].

1.2 Municipal Solid Waste (MSW) in KSA

In 2013, the total waste generation was 15.3 million tons with an average rate of 1.4 kg per capita per day [4, 5]. This waste rate is projected to double (30 million tons) in 2033 with the current population growth rate (3.4%) [6]. The MSW is consist of food waste (50.6%), plastic (17.4%), paper (12%), cardboard (6.6%), glass (2.9%), wood (2%), textile (1.9%), metals (1.9%), aluminium (0.8%), leather (0.1%) and others (3.7%) [4, 5]. Animal waste including rumen, blood, stomach, intestine and fats is another main source of waste generated from slaughter houses [7]. The municipalities regulate the solid waste management (SWM) activities in the KSA [4]. All the household and commercial places waste is collected and disposed at the landfills or dumpsites without value-added product or energy recovery [5]. The requirement for landfill is extremely high, about 28 million m^3 per year. The recycling of metals and card boards is the only waste recycling practice, which covers 10-15% of the total collected waste by informal sector [8].

1.3 Waste-to-Energy (WTE) Technologies in KSA

There are several WTE technologies in use worldwide: incineration, pyrolysis or gasification, plasma arc gasification, refused derived fuel (RDF), anaerobic digestion (AD), and transesterification to generate energy and value-added products in the form of electricity, transportation fuels, heat, fertilizers and chemicals [4, 9, 10]. Each of these technologies and their setup depends on the type of waste, capital and operational cost, technological complexity, labour skill requirements, geographical locations and the conversion efficiency of the technology [11, 12]. The possibilities of WTE have never been investigated in KSA until very recently. Ouda et al. [4, 5] showed the high environmental values of the two MSW management scenarios such as mass burn and mass burn with recycling over landfilling option with regards to energy demand, greenhouses gas (GHG) emission reductions, and landfill area saving.

1.4 The Role of Natural Zeolites in Energy Applications

Zeolites are micro-porous crystalline materials made up of mainly silicon, aluminium and oxygen atoms. There unique micro-porous framework structure gives them the capability to be used in a wide range of applications [13]. There are around 50 different types of naturally occurring and 150 synthetic zeolites identified all over the world [14, 15]. The zeolite applications include, but not limited to; petroleum industry, environmental sector, water purification, oil spill clean-up and radioactive substance adsorption etc. (Table 1). The use of natural zeolites in energy applications such as solar energy, pyrolysis, AD and transesterification have gained a significant interest due to their qualities of gas adsorption, moisture absorption and heat storage [14]. Rancon and Laurent [16] highlighted the availability of natural zeolites in KSA in the areas of Jabal and Harrat Shamah, near to Jeddah city. Different types of natural zeolites such as mordenite, heulandite/clinoptilolite, analcime, stilbite, thomsonite, natrolite, chabazite and wairakite were found in these areas [17].

1.5 Focus of the Paper

There is no WTE facility exist in KSA to convert waste into energy and value-added products. Similarly, the natural zeolites available abundantly in KSA are not characterized for their potential role in energy-related applications as a process catalyst and additive. Therefore, this research aims to study the physical and chemical characteristics of natural zeolite in KSA and review its potential utilization in selected WTE technologies and solar energy.

2. Materials and Methods

2.1 Study Area

Harrat Ash-Shamah is an area located in the North West of KSA. It is extended from North West KSA to Jordon and Syria. The word Harrat is meant to the lava fields in Arabian Peninsula [18]. These fields are made of fluid blastic lava. Small shield volcanoes, tuff ring, composite volcanoes and cinder cones are scattered across these fields. Minerals of olivine, pyroxene, plagioclase and zeolites are found in these fields [19]. Volcanic activity in the area start 10-14 million year ago, however the recent activity was about few hundred years ago. Lava field was established from these volcanic activities comprises of five episodes, which appeared during the different time periods. In the interval time between the volcanic eruption, wind had blown Arabian desert sands onto lava and hence layering of sediment and lava was found [18, 20].

The young volcanic Harrat fields is 600 km long on north southern chain (Makkah-Medina-Nafud volcanic line), having no direct link related to Red Sea Rift. The total area is broadly divided into two distinct areas i.e. between Makkah and Medina (20,000 km^2) and between Medina and Great Nafud (20,560 km^2). The area between Makkah and Medina have scoria cones (644 in number), shied volcanoes (36) and domes (24), while between Medina and Great Nafud there are also scoria cones (327 in number), basaltic shield volcanoes (46), domes (20), tuff cones (5), basaltic stratovolcano (1) and major lava flow (39). The areas lies in between Medina and Great Nafud are harrats Khaybar, Ithnayn and Kura. These are the biggest and longest basalt flow with most extensive lava-tubes in southern part of KSA [18-20].

Volcanic eruption and Red sea rifting are directly linked with the occurrence of zeolite in KSA mainly in the areas called Jabal Shamah and Harrat Shamah. Harrat tuffil was formed during the Plio-Pleistocene volcanic activity. It is mainly composed of thin blast flow. It has similar lithostratigraphic as the Jabal Shamah, however rhyolitic rocks are covered with recent basalt flow. Zeolite deposit found in this area has association with the pyroclastic green tuff of the field [21]. Exposure of Jabal Shamah is due to the early Miocene volcanic eruption and related to beginning of Red sea split in the Arabian-Nubian Shield. The whole area contains the deposits of hydrothermal and silicified pyroclastic pumiceous breccia and rhyolite lava [18, 20, 21].

2.2 Sample Collection

The areas in KSA with respect to zeolite occurrence are Jabal and Harrat Shamah. Harrat Shamah is located on coordinate E39°40’18” at the distance of 100 km south to south eastern Jeddah, while Jabal Shamah is located 1 km NW of Harrat tuffil. Various samples were collected from ~ 1.2 km^2 area at the Jabal and Harrat Shama occurrence based on spot sampling method. Among different collected samples, five samples were selected (NZ-1 to NZ-5) to represent zeolite-bearing rhyolite samples from different volcanic ash flows.

2.3 Analytical Methods

The selected natural zeolites samples (NZ-1, NZ-2, NZ-3, NZ-4, NZ-5) taken from different site locations were prepared by crushing and sieving before sending to the Institute of Particle Science & Engineering (IPSE), University of Leeds, UK for detailed chemical, thermal and physical analysis. The crystal structure and purity of natural zeolite samples was studied by Bruker D8 X-ray diffraction (XRD). The D8 was operated with Cu radiation at 30 kV and 45 mA. Each zeolite sample was scanned from 2θ angel range of 5° to 70° with step size 0.0495° at 35 sec per step. Fourier transform infrared spectroscopy (FT-IR) spectra of the zeolite samples were obtained using FT-IR Perkin Elmer's, UK. A minimum of 32 scans were performed at average signal of IR with a resolution 4 cm^{-1} in the ranges of 500 to 4000 cm^{-1}. BET surface area, pore size and volume measurements of natural zeolite samples were performed according to the multipoint nitrogen adsorption-desorption method at 77.3 K using Micromeritics TriStar 3000 (UK) surface analyser. The zeolite samples were degassed at 120 °C for 24 h under a vacuum of 10 mmHg in order to remove any moisture and gases from the samples prior to analysis. The Brunauer-Emmet-Teller (BET) method was used to calculate the average surface area. The thermal stability of natural zeolites was analysed by TGA (Mettler Toledo, UK) equipped with an intercooler system in order to help cooling of the system. 10±5 mg of sample was weighted in a 100 µl aluminium oxide crucible and placed in TGA sample chamber. The experiment was initiated by heating up the sample from 50 to 920°C at 10°C/minute under nitrogen purge gas at 50 ml/minute (constant flow rate). Mettler STARe software was used for programming the system and data processing. The particle size, morphology and elemental composition of natural zeolite samples was studied by Hitachi scanning electron microscopy (SEM). The energy dispersive spectrometer (EDS) was used to determine the percentage of the elements in the examined area of the zeolite samples and coloured elemental mapping. SEM samples were prepared by making a homogeneous suspension of zeolite powder samples in acetone using ultrasonic bath. Few drops of this suspension was then dropped onto the SEM sample stubs and later transferred to a zone SEM cleaner in order to remove any contaminants by using UV radiation at pressure 1 Pa for 10 minutes. After cleaning of samples, the sample holders were then transferred to the SEM instrument where the imaging of samples, EDS, and elemental mapping were taken and saved on the attached PC for further analysis.

3. Results and Discussion

3.1 Characterization of Natural Zeolite

3.1.1 Chemical and Structural Analysis of Natural Zeolite

The XRD analysis was performed to determine the crystal structure and chemical compositions of the five natural zeolite samples. The XRD patterns have been indexed using the reference data files from ICDD-PDF database. The XRD diffraction peaks of different samples matched with the different types of zeolites (Table 2). The XRD patterns (Figure 1 & Table 2) do confirm that all samples belong to zeolite group of alumina-silicate minerals with presence of other elements such as Na, Mg, Fe and K etc. However, the variation in the main peak positions and intensities indicate that the overall structures, chemical compositions, and the amount of impurities of all samples are slightly different. An attempt was made to analyse the percentage composition of different compounds that match with the XRD peaks of NZ-1 sample using Highscore Plus software. However, there were some peak overlapping and more than one possible matching combinations of different peaks and thus it is more of a qualitative than quantititive anaylsis. A detailed and accurate quantification of chemical compositions and identification and characterisation of natural zeolite structures can be achieved by Rietveld Refinment of XRD data. It is also observed that the nature of the peaks and minimum background of XRD patterns indicate that these natural zeolites are of high crystalline nature with little amorphous contents (Figure 1). This high crystallinity feature plays an important role in the zeolite applications as a catalyst in WTE technologies [13-15].

The FT-IR spectra of the natural zeolite samples were recorded for structural analysis. The vibrational bands were collected in the range 500 to 4000 cm^{-1} (Figure 2). The spectra for all samples showed very similar absorption bands position and intensities, indicating the overall structure of all samples contain same functional groups. The main bands in all samples with largest intensity are present in the range of 1000-1020 cm^{-1}, which are referred to Si-O-Si and Si-O-Al vibrations. While, the other three clear bands in the range of 547-549, 591-593 and 788-790 cm^{-1} can be attributed to different Al-O and Si-O vibrations [22, 23]. Moreover, the broad stretching between 3680-4000 cm^{-1} represent the vibrations of OH groups (Figure 2).

3.1.2 Thermal Stability Analysis

The thermal stability of all natural zeolite samples has been examined by TGA for temperature range of 50 – 920 °C, under nitrogen purge gas. It is very evident from the TGA curve (Figure 3) that there was no significant weight loss from any natural zeolite sample within the studied temperature range. This shows the excellent thermal stability of natural zeolites found in KSA as reported for other natural zeolites found throughout the world, which is higher than synthetic absorbents [24, 25]. The high thermal stability together with unique ion exchange, adsorption properties, high surface area and porosity make natural zeolites suitable in WTE technologies, especially in pyrolysis process of converting waste plastic into liquid fuel, where it's highly stable structure remains unchanged at high process temperature (300 – 600 °C).

3.1.3 Particle Size, Morphology and Elemental Composition of Natural Zeolites

The particle size, morphology and elemental composition of all natural zeolite samples have been analysed by SEM and EDS. The SEM images showed polydisperse nature of particle size and morphology distributions (Figure 4). These features are directly dependent on the milling process and thus can be optimized. The SEM images showed some smaller particles with spherical shapes in about 50-200 nm size range, and mostly large particles and agglomerates with irregular shapes. Some porous nature and layering surface features can be seen in the SEM images (Figure 4). However, higher resolution TEM analysis is required to have detailed observation and confirmation of the pores and crystal fringes of these natural zeolite materials (Box 1).

The quantitative analysis of natural zeolite samples was performed by SEM-EDS (Figure 5). Zeolites are generally a group of alumina-silicate minerals that can accommodate a wide variety of cations such as K^+, Na^+, and Ca^{2+} in their porous structures [26]. The EDS data confirms that the samples studied are different types of zeolites by showing the high concentrations of key elements such as Al, Si and O together with the presence of other elements such as Na, Mg, S, K, Ca, Ti, Fe, in smaller quantities. Different types of natural and synthetic zeolites have different Si/Al ratios depending on their chemical compositions, structures, and impurities [13, 26]. The EDS results showed some differences in the amount of each element present in all samples (Figure 5). The Si/Al ratios for NZ-1, NZ-2, NZ-3, NZ-4 and NZ-5 were found to be 4.6, 9.2, 6.3, 1.8 and 3.1 respectively (Table 3). There are many zeolite materials that have Si/Al ratios in between 1.4-6.1, such as Analcime, Chabasite, Clinoptilolite, Erionite, Heulandite, Laumontite, Mordenite, Phillipsite and Natrolite [26]. This finding also agree with FT-IR and XRD results, that there are some differences in the crystal structures and chemical compositions of all 5 natural zeolite samples collected from different sampling locations. It is evident that different types of zeolites have their own unique crystal structure, size and shape of cavities, porosity and other characteristics that lead to them having different physical properties and chemical composition [27].

SEM elemental mapping was also carried on a typical natural zeolite sample (NZ-1) as shown in Figure 6. The mapping images showed the location and rough amount of different elements, which are individually color coded. It is interesting to note that the main elements such as O, Al, Si are present in large quantities and spread almost throughout all the particles, as these elements are the main building blocks of zeolite structure. While, the other elements such as K and Fe can be seen in low quantities and less spread out (Figure 6).

3.1.4 BET Surface Area, Pore Size and Volume of Natural Zeolites

The surface area, pore size and volume are key characteristics of any material that has applications involving its surface and porosity such as zeolite catalysts. The surface areas of all 5 natural zeolite samples were found in the range of 3.214 - 8.947 m^2/g, with NZ-2 and NZ-4 having the lowest and highest surface area respectively (Table 4). Similarly, the lowest and highest pore volume was found to be 0.012 and 0.041 cc/g for the same samples. Interestingly, the pore sizes for all samples were almost same with value of 18.7 Å, except for sample NZ-2 having pore size of 8.3 Å, which is probably the reason for this sample having the lowest surface area and pore volume amongst all samples.

Overall the surface area, pore size and volumes of natural zeolite found in KSA are comparable to other reported natural and synthetic zeolites in different parts of the world. For example, ODA-hydrophobized Slovakian clinoptilolite-rich tuff, Silanized Slovakian clinoptilolite-rich tuff and Fe-alginate-clinoptilolite rich tuff pellet (1:2) were reported to have BET surface areas of 10.8, 0.48 and 21.2 m^2/g respectively. Similarly, synthetic clinoptilolite (University of Wolverhampton, GB) and Carbonized Slovakian clinoptilolite-rich tuff were reported to have pore size and volume of 14 and 8.39 Å and 0.015 and 0.0026 cm^3/g respectively [13].

The surface area and porosity of natural zeolites can be further enhanced by nano-milling of raw materials to achieve homogeneous particle morphology and sizes in a range of sub-micron to nano-meter (Box 1). Moreover, acid treatment can significantly increase the surface area of natural zeolites as reported in many studies [28-30]. This enhanced surface area and porosity of natural zeolites can improve its functioning in most of the WTE applications, hence optimizing the overall processes.

3.2 Use of Natural Zeolites in WTE Technologies and Solar Energy

The following WTE technologies were selected based on the main waste streams of KSA such as organic fraction of municipal solid waste (OFMSW), waste plastic and slaughterhouse waste and the available knowledge on the use of natural zeolites in energy-related applications. The selected WTE technologies and natural zeolite related glossary is given in Box 2.

3.2.1 Use of Natural Zeolites in Pyrolysis

The waste plastic is the second largest waste stream in KSA with total production of 2.7 million tons per year and 0.3 kg/capita/day [4, 5]. Most of the collected waste plastic ends up in landfill sites, where they cause operational and environmental problems due to slow degrading and clogging nature. Conventional mechanical recycling technologies such as sorting, grinding, washing and extrusion can recycle only 15-20% of all waste plastics. The catalytic conversion of waste plastics into liquid fuel through pyrolysis is one of the WTE methods for recycling plastic based wastes [36]. In pyrolysis, catalytic reforming is used to improve and enhance the liquid fuel using different catalysts [37]. The homogeneous and heterogeneous catalysts such as natural and synthetic zeolite, silica alumina, and fluid catalytic cracking catalysts have been used for studying the catalytic cracking of waste plastics [38].

In pyrolysis, natural zeolite affects the quantity and quality of produced liquid fuel. Use of catalyst decreases the liquid production of fuel and increase the gas production [39]. However liquid yield from natural zeolite is high in comparison to synthetic Y-Zeolite due to low BET surface area. The produced liquid fuel using natural zeolite has same density as using synthetic catalyst and even without any catalyst. However viscosity of produced liquid fuel using natural zeolite is higher than using synthetic catalyst such as Y-zeolite. In a study by Syamsiro et al. [40], the natural zeolite as a catalyst decreases the production of heavy oil fraction (>C20) and increases the light oil fraction (C5 - C12) by cracking long hydrocarbon chains into smaller chains. In another study by Sriningsih et al. [41], natural zeolite was pretreated by activating with hydrochloric acid (HCl). Acid leaching increased the pore size and acidity of natural zeolite, thus increased its catalyst efficiency. Natural zeolite composite was formed through wet impregnation with Ni, Ni-Mo, Co and Co-Mo. The results showed that composite of Co-Mo with NZ (Co-Mo/Z) produces more liquid yield with high concentration of gasoline at low temperature (350^{o}C) as compared to other catalyst. While characteristics of produced liquid fuel showed the hydrocarbon compounds such as paraffins, olefins and naphthenes from C6– C19.

3.2.2 Use of Natural Zeolites in Anaerobic Digestion (AD)

In KSA, the overall MSW is highly organic (upto 72%) in nature including OFMSW. AD is one of the promising WTE technologies used worldwide for treating OFMSW into biogas (energy) and digestate (organic fertilizer). It is observed that the addition of inorganic additives in organic waste at mesophilic temperature can increase the methane (CH_4) production from AD [42]. Different types of zeolites such as mordenite, clinoptilolite, zeolite 3A and zeolite 4A were studied as inorganic additives to examine the effect on methane production [43]. The results showed that all zeolite types increased the removal of NH_4^+ from the sludge, as being a toxic element for anaerobes [44]. However, the natural zeolite type such as mordenite resulted in maximum CH_4 production (3 times) with highest NH_4^+ removal by adsorbing the NH_4^+ through addition of Ca^{2+} in sludge in comparison to other synthetic zeolites. The synthetic zeolite 3A although is a good adsorbent of NH_4^+, but also have ability to adsorb Ca^{2+} ions in excessive quantities. Therefore, it decreased the CH_4 production from sludge. The dual characteristics i.e. adding Ca^{2+} and removing NH_4^+ of natural zeolite like mordenite, which is available in KSA, will increase the CH_4 production of OFMSW at recommended quantities of 5% and 10% as an inorganic additive [45].

3.2.3 Use of Natural Zeolites in Transesterification

Zeolite can also be used as a catalyst in transesterification process for converting animal fats or used/ waste oil into biodiesel. In a study by Endalew et al. [46], a zeolite-based catalyst was prepared by pelletization method using zeolite powder, kaolinite and poly vinyl alcohol (PVA). The catalyst was used to enhance the conversion of free fatty acid (FFA) from used-oil into fatty acid methyl ester (FAME) known as biodiesel. Filtration, centrifugation and mixing with n-hexane were performed to remove zeolites impurities. The transesterification process was carried out in round-bottom flask equipped with a reflux condenser, temperature controller and mechanical stirrer. The result showed 46% conversion of FFA into FAME at 70^{o}C temperature, 5.1 molar ratio of methanol/used-oil and 6 hours reaction time. Temperature more than 70^{o}C lead to methanol vaporization, which negatively affected the process. Moreover, the reaction time exceeding than 6 hours resulted in the accumulation of impurities on the active site of catalyst [47]. The use of natural zeolite as a catalyst in the transesterification is limited due to narrow pore size of zeolite. Moreover, it limits the diffusion of triglyceride adsorption. As FFA has low molecular size than triglyceride, so natural zeolite is better for esterification process in comparison to transesterification process. However, the surface modification in natural zeolites by increasing its mesopores can enhance catalytic performance in transesterification [47].

3.3 Use of Natural Zeolites in Solar Energy

Natural zeolite has the ability to store heat energy for a longer period of time due to natural adsorption and desorption characteristics without affecting or damaging the internal structure. Alfed et al. [48] and Kato et al. [49] studied the use of zeolite in seasonal storage of energy and found that zeolites alone in storing solar energy will be expensive. On the other hand, the use of single material like magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) showed great potential in energy storage by endothermic dehydration of the salt via obtained heat from solar collector. The stored heat is then released by salt rehydration through exothermic process using humid air. However, the drawback of this material is the use of $MgSO_4$; a crusts of $MgSO_4.7H_2O$ is formed over the material surface during hydration. Therefore, making a composite of magnesium sulphate with natural zeolite through wet impregnation can improve the adsorption capacity of material by increasing the surface area and internal structure [50]. Such composites not only solve the economic problems of zeolites alone, but also increase the overall efficiency of solar energy storage. KSA has excellent solar conditions for producing solar energy. A simple solid-gas absorption system for storing solar energy in natural zeolites will be a cheap alternative method [51] for KSA. However, for the assessment and optimization of such system, factors such as zeolite types, moisture, and temperature range are needed to study in detail.

4. Conclusion

- All of the collected and analysed natural zeolite samples showed the standard zeolite group of alumina-silicate minerals with the presence of other elements such as Na, Mg and K etc. A highly crystalline structure is found in natural zeolites, which is critical when using in the energy-related applications.
- KSA has excellent solar conditions for producing solar energy. A simple solid-gas absorption system for storing solar energy in natural zeolites will be a cheap alternative method for KSA.
- In pyrolysis, the high thermal stability together with unique ion exchange, adsorption properties, high surface area and porosity make natural zeolites suitable as a catalyst. The composites of natural zeolites will produce more liquid fuel high concentration of gasoline at low temperature (350^{o}C) as compared to other synthetic catalysts.
- In AD, the dual characteristics of natural zeolite like Mordenite, which is available in KSA, will increase the CH_4 production of OFMSW as an inorganic additive.
- In transesterification, the surface modification in natural zeolites by increasing its mesopores can enhance catalytic performance.

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References

[1] US Energy Information Administration (US-EIA). Country Analysis Brief: Saudi Arabia. 2014. Available from : http://www.eia.gov/countries/cab.cfm?fips=sa

[2] Royal Decree establishing King Abdullah City for Atomic and Renewable, No. A 35, 17 April 2010. http://www.energy.gov.sa/_pdf/KACARE%20Royal%20Decree%20english.pdf

[3] Gipe P. 2012. Saudi Arabia Launches Massive Renewable Program with Hybrid FITs. News article published at Renewable Energy website. 2012.. Available from: http://www.renewableenergyworld.com/

[4] Ouda O. K. M., Cekirge H. M., Raza S.A. 2013. An assessment of the potential contribution from waste-to-energy facilities to electricity demand in Saudi Arabia. Energy Conversion and Management, 75: 402-406.

[5] Ouda OKM, Raza SA, Al-Waked R, Al-Asad JF, Nizami AS . 2015. Waste-to-Energy Potential in the Western Province of Saudi Arabia, Journal of King Saud University: Engineering Sciences, 2015. doi:10.1016/j.jksues.2015.02.002

[6] CDSI: Population & Housing Census for 1431 A.H (2010 A.D) Findings. Central Department of Statistics & Information. Available from: http://www.cdsi.gov.sa.

[7] Amtul S. 2014. Kingdom: 2.5m animals sold in Saudi Arabia during hajj. Saudi Gazette. Available from: http://www.saudigazette.com.sa

[8] Khan MSM, Kaneesamkandi Z. 2013. Biodegradable waste to biogas: renewable energy option for the Kingdom of Saudi Arabia. International Journal of Innovation and Applied Studies, 4 (1): 101-113.

[9] AS Nizami. Anaerobic digestion: processes, products, and applications. 2012. Chapter in 'Potential of Activated Sludge Utilization'. ISBN: 978-1-61324-420-3. Nova Science, Commack, New York.

[10] NE Korres, AS Nizami. 2013. Variability in anaerobic digestion: The need for process monitoring. Chapter in 'Bioenergy Production by Anaerobic Digestion Using Agricultural Biomass and Organic Waste'. Publisher: Routledge, Taylor and Francis, US. Pp 194-231, ISBN 13: 978-0-415-69840-5 (hbk).

[11] Szarka N, Scholwin F, Trommler M, Jacobi Fabian H, Eichhorn M, Ortwein A. A novel role for bioenergy: a flexible, demand-oriented power supply. Energy 2013;61:18e26.

[12] AS Nizami, A Singh, JD Murphy. 2011. Design, commissioning, and start-up of a sequentially fed leach bed reactor complete with an upflow anaerobic sludge blanket digesting grass silage. Energy and Fuels, 25 (2), 823–834.

[13] Inglezakis VJ, Zorpas AA. 2012. Handbook of Natural Zeolites. Bentham Science Publishers,ISBN: 978-1-60805-446-6.

[14] Baerlocher Ch. and L.B. McCusker. 1996. Database of Zeolite Structures. Website. Accessed November 2007. http://www.iza-structure.org/databases/.

[15] MassNanoTech. 2007. University of Massachusetts Nanoscale Science and Engineering. Website. Accessed October 2007. http://www.umass.edu/massnanotech/faculty_auerbach.htm.

[16] Rancon, S.P. and Laurent, D. 1988. Exploration for zeolite in the Jabal and Harrat Shama areas. Saudi Arabian Deputy Ministry for Mineral Resources. Open File Report BRGM-OF-08-7, 24 p.

[17] Saudi Geological survey, Section; Natural Hazards, Geological Studies of mineral wealth. 2015. http://www.sgs.org.sa/English/NaturalHazards/PublishingImages/27.jpg excess date 28th of Feb, 2015

[18] Volcanology- GHRU. 2013 –. Faculty of Earth Sciences, King AbdulAziz University, Jeddah, Saudi Arabia. http://earthscience.kau.edu.sa/Content.aspx?Site_ID=145&lng=EN&cid=230383

[19] Hay, R.L. (1986): Geologic occurrence of zeolites and some associated minerals. Pure and Applied Chemistry, Vol.52, pp. 2II5-2130.

[20] Salf, S.I. and Shah, S.M.A. 1988. Field and petrographic characteristics of Cenozoic basaltic rocks, northwestern Saudi Arabia. Journal of African Earth Sciences, Vol. 7, No. 5, pp. 805-809.

[21] Collenette, P. and Grainger, D.J. (1994): Mineral Resources of Saudi Arabia, Ministry of Petroleum and Mineral Resources Directorate General of Mineral Resources Jeddah, Kingdom of Saudi Arabia. 322 p.

[22] Rondón W., Freire D., Benzo Z., Sifontes A. B., González Y., Valero M., Brito J. L. 2013. Application of 3A Zeolite Prepared from Venezuelan Kaolin for Removal of Pb (II) from Wastewater and Its Determination by Flame Atomic Absorption Spectrometry. American Journal of Analytical Chemistry, 4: 584-593.

[23] Peter A., Cozmuta L. M., Cozmuta A. M., Nicula C., Indrea E., Tutu H. 2012. Calcium- and ammonium ion-modification of zeolite amendments affects the metal-uptake of Hieracium piloselloides in a dose-dependent way. J. Environ. Monit., 14: 2807-2814.

[24] Zarchy AS, Correia R, Chao CC. Process for the adsorption of hydrogen sulfide with clinoptilolite molecular sieves. US Patent 5164076, 1992.

[25] Ogawa H, Ito Y, Nakano M, et al. Method for adsorbing and removing ethylene and method for purifying an exhaust gas. US Patent 6309616, 2001.

[26] Breck DW (1974) Zeolite molekular sieves, John.Wiley&Sons, New York

[27] Pond NG, Lee JT. Physiological effects of clinoptiloliteand synthetic zeoliteA in animals. In Zeo Agricultural: Use of Natural Zeolites in Agriculturaland Aquaculture, eds. Pond WG, Mumpton FA. Pp 129. Westview Press Boulder, Colorado.

[28] Hotta M, Asaka M, Torii K. Changes in physico-chemical properties of clinoptilolite tuff by chemical treatment. 2. Effect of acid solution treatment on Chromatographic separation properties. J Japan Assoc Min Petri Econ Geol 1980; (75): 77-85.

[29] Grejták F, Horváth I, Kubranová M, et al. The acidity of dealuminated clinoptilolite investigated by DSC, DTA and TG metods. Therm Acta 1992; 207(C), 209-217.

[30] Kurama H, Zimmer A, Reschetilowski W. Chemical modification effect on the sorption capacities of natural clinoptilolite. Chem Eng Techn 2002; 25(3): 301-305.

[31] Tippayawong N, Thanompongchart P. Biogas quality upgrade by simultaneous removalofCO2 andH2S ina packedcolumnreactor.Energy2010;35(12):4531e5.

[32] Rafique R, Poulsen TG, Nizami A, Asam ZZ, Murphy JD, Kiely G. Effect of thermal, chemical and thermo-chemical pre-treatments to enhance methane production. Energy 2010;35(12):4556e61.

[33] Tedesco S, Marrero Barroso T, Olabi AG. Optimization of mechanical pretreatment of Laminariaceae spp. biomass-derived biogas. Renew Energy 2014;62:527e34.

[34] Tedesco S, Mac Lochlainn D, Olabi AG. Particle size reduction optimization of Laminaria spp. biomass for enhanced methane production. Energy 2014;76:857e62.

[35] Tedesco S, Benyounis KY, Olabi AG. Mechanical pretreatment effects on macroalgae-derived biogas production in co-digestion with sludge in Ireland.Energy 2013;61:27e33.

[36] Yuan, X., Converting Waste Plastics into Liquid Fuel by Pyrolysis : Developments in China, in Feedstock Recycling and Pyrolysis of Waste Plastics, J. Scheirs and W. Kaminsky, Editors.2006, John Wiley & Sons, Ltd: Changsha, P.R. China. p. 729-755.

[37] Serrano DP, Aguado J,Escola JM. Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. ACS Catal. 2012;2:1924-1941.

[38] Aguado, J., D.P. Serrano, and J.M. Escola, Catalytic Upgrading of Plastic Wastes, in Feedstock Recycling and Pyrolysis of Waste Plastics, J. Scheirs and W. Kaminsky, Editors. 2006, John Wiley & Sons, Ltd: Mostoles, Spain. p. 73-110.

[39] Lee KH. Thermal and catalytic degradation of pyrolytic oil from pyrolysis of municipal plastic wastes. Journal of Analytical and Applied Pyrolysis 2009; 85:372-379.

[40] Syamsiro M, Saptoadi H, Norsujianto T, Noviasri, Cheng S, Alimuddin Z, Yoshikawa K. 2014. Fuel oil production from Municipal plastic wastes in sequential pyrolysis and catalytic reforming reactors. Energy Procedia 47. 180-188.

[41] Sriningsih W, Saerodji M G, Trisunaryanti, Armunanto R, Falah I I. 2014. Fuel production from LDPE plastic waste over Natural Zeolite supported Ni, Ni-Mo, Co and Co-Mo metals. Procedia Environmental Sciences 20: 215-224.

[42] Hansen, K.H., Angelidaki, I., Ahring, B.K., 1999. Improving thermophilic anaerobic digestion of swine manure. Water Res. 33 (8),1805–1810.

[43] Milan, Z., Sanchez, E., Weiland, P., Borja, R., Martin, A., Ilangovan, K., 2001. Influence of different natural zeolite concentrations on the anaerobic digestion of piggery waste. Biores. Technol. 80, 37–43.

[44] Hendrinksen, H.V., Ahring, B.K., 1991. Effects of ammonia on growth and morphology of thermophilic hydrogen-oxidizing methanogenic bacteria. FEMS Microbiol. Ecol. 85, 241–246.

[45] Tada C, Yang Y, Hanaoka T, Sonoda A, Ooi K, Sawayama S. 2005. Effect of natural zeolite on methane production for anaerobic digestion of ammonium rich organic sludge.Bioresource Technology 96: 459-464.

[46] Endalew AK, Kiros Y and Zanzi R. 2011. Inorganic heterogeneous catalyst for biodiesel production from vegetable oils, Biomass Bioenergy. 35: 3787-3809.

[47] Hassani M, Najafpour D G, Mohammadi M and Rabiee M. 2014. Preparation, characterization and application of zeolite-based catalyst for production of biodiesel from waste cooking oil.Journal of Scientific and Industrial Research vol. 73: 129-133.

[48] Alefeld G., P. Maier-Laxhuber, and M. Rothmeyer, “Thermochemical heat storage and heat transformation with zeolites as adsorbents” in: “Proceedings of IEA conference on new energy conversion technologies and their commercialization”, Berlin; 1981. pp. 796–819.

[49] Kato Y., “Chemical energy conversion technologies for efficient energy use” in: “Thermal energy storage for sustainable energy consumption”, Springer, 2007. pp. 377–91.

[50] Whiting G., D. Grondin, S. Bennici, and A. Auroux., SOLMAT, 2013.

[51] McCusker, L.B. and C. Baerlocher, Zeolite Structures. 3rd Revised Edition ed. Introduction to Zeolite Science and Practice, ed. G. Centi. Vol. 2. 2007, Zurich, Switzerland: Elsevier B.V. 13-38.

Box 1. Future Work

- Improving the surface area, pore size and its volume by nano-milling system to optimize catalyst performance.
- Analysis of crystalline structure and chemical compositions of different zeolite families by Rietveld Refinement of XRD data and XRF analysis.
- Understanding the surface chemistry of natural zeolites using X-ray photoelectron spectroscopy (XPS) and other relevant surface analysis techniques.
- Study the application of natural zeolite catalyst in a two stage pyrolysis reactor and its effect on parameters such as product quality, yield, process retention time and temperature.
- Study the potential of local KSA natural zeolites in solar energy and other waste-to-energy applications.
- Evaluating the surface modification via chemical, thermal or physical routes to optimize the catalytic performance of natural zeolites in WTE technologies.
- Study the technical, economical, and environmental feasibility of natural zeolite utilization in WTE technologies in KSA.

Box 2. Glossary [31-35]

Waste-to-Energy (WTE): Energy from waste is the processing of waste into heat, electricity or fuel through energy recovery technologies such as incineration, pyrolysis, gasification, anaerobic digestion (AD), refuse derived fuel (RDF) etc.
Anaerobic digestion (AD): It is a biological degradation of organic matter in the absence of oxygen into biogas as a source of energy and nutrient rich digestate.
Pyrolysis: It is a thermochemically decomposition of organic material in the absence of oxygen at elevated temperatures into liquid fuel as a source of energy and charcoal.
Transesterification: It is a reversible chemical reaction through interchange of ester groups (one ester is converted into another) with an alcohol in the presence of a catalyst. The vegetable/used oil or animal fats is chemically breakdown into constituent molecules to produce biodiesel through transesterification.
Solar Energy: The solar energy is the processing of sun energy into heat and electricity using technologies such as solar heating, photovoltaics, solar building and photosynthesis.
Natural Zeolite: It is a crystalline mineral with tetrahedral structure, consisting four O atoms surrounding a silicon or aluminium atom.

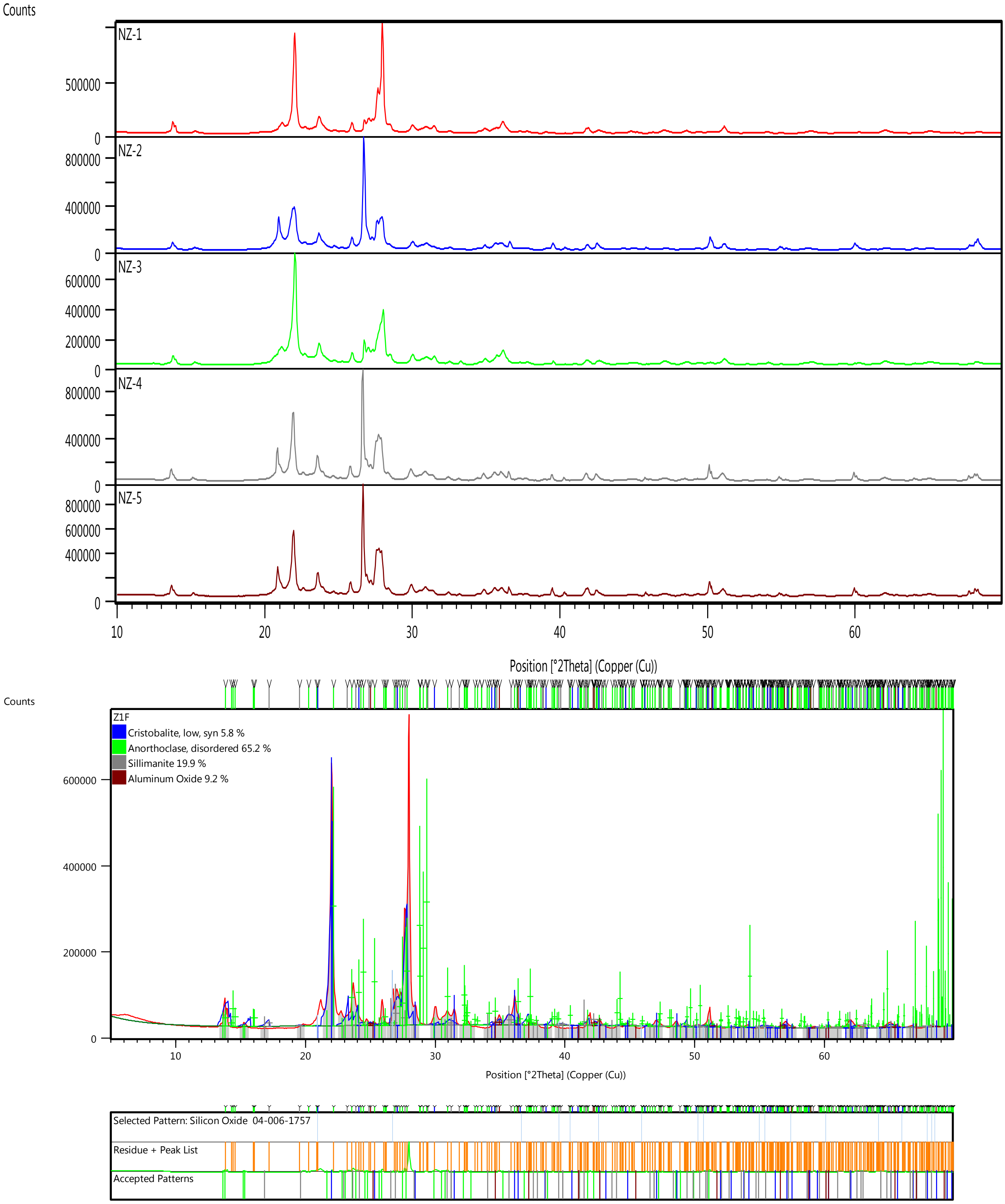


Figure 1: XRD patterns of the natural zeolites samples NZ-1, NZ-2, NZ-3, NZ-4 and NZ-5 (top) and peak matching and percentage composition mixture using Highscore Plus Software (bottom).

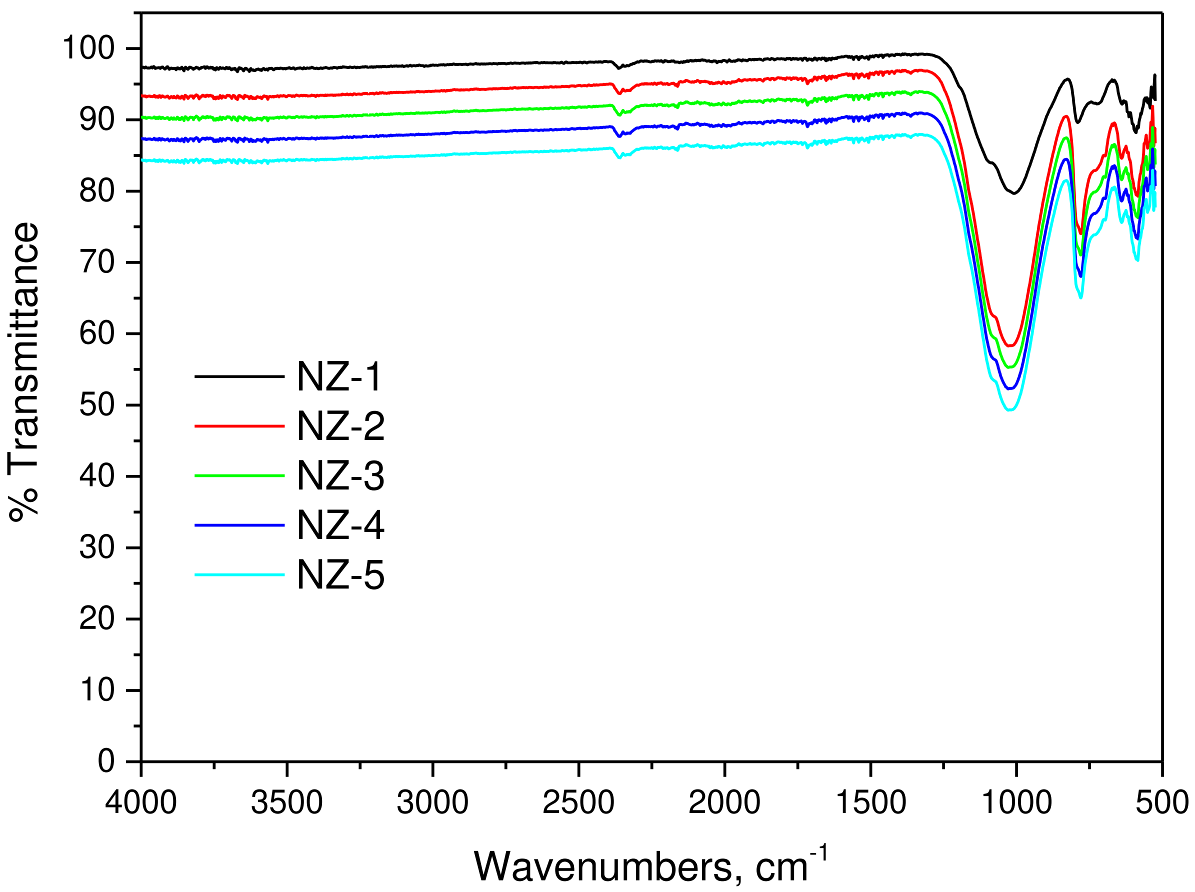


Figure 2: FT-IR spectra of the all 5 natural zeolite samples.

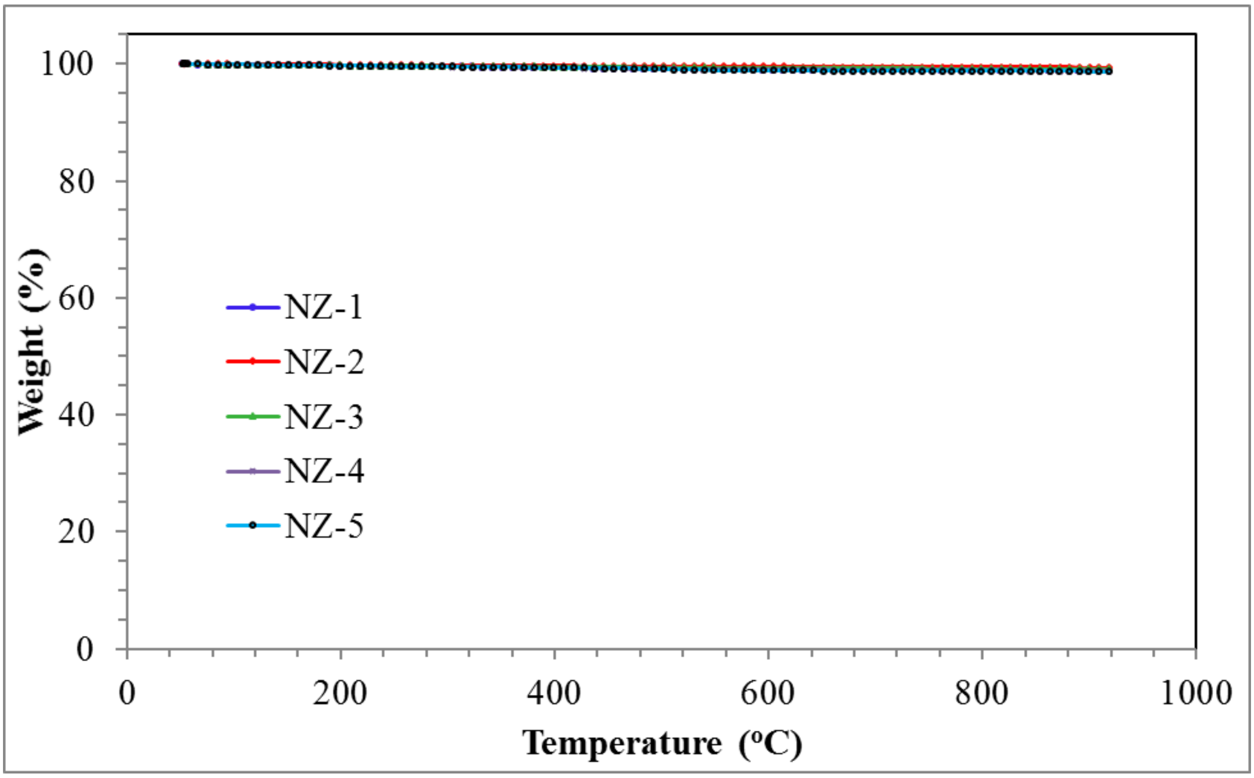


Figure 3: TGA curve showing the thermal stability of all 5 natural zeolite samples.

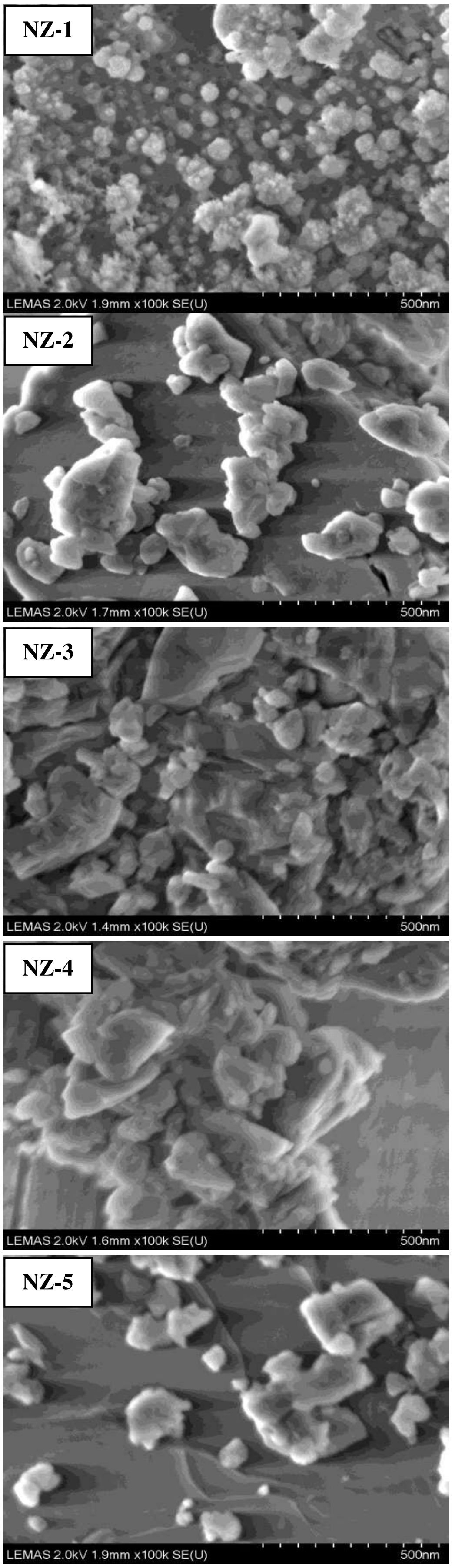
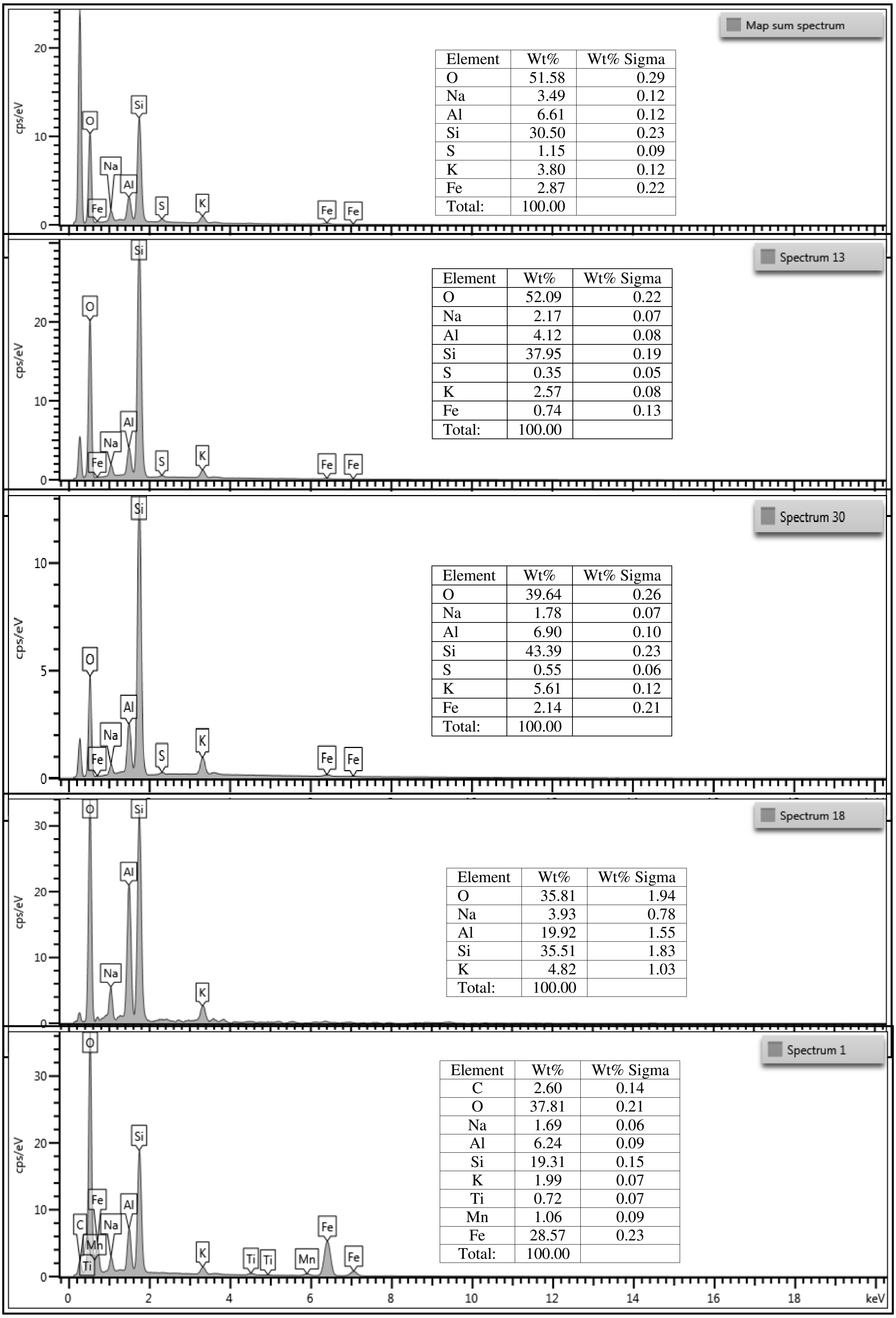


Figure 4: SEM images of the anatural zeolite samples.



Element	Wt%	Wt% Sigma
O	51.58	0.29
Na	3.49	0.12
Al	6.61	0.12
Si	30.50	0.23
S	1.15	0.09
K	3.80	0.12
Fe	2.87	0.22
Total:	100.00	

Element	Wt%	Wt% Sigma
O	52.09	0.22
Na	2.17	0.07
Al	4.12	0.08
Si	37.95	0.19
S	0.35	0.05
K	2.57	0.08
Fe	0.74	0.13
Total:	100.00	

Element	Wt%	Wt% Sigma
O	39.64	0.26
Na	1.78	0.07
Al	6.90	0.10
Si	43.39	0.23
S	0.55	0.06
K	5.61	0.12
Fe	2.14	0.21
Total:	100.00	

Element	Wt%	Wt% Sigma
O	35.81	1.94
Na	3.93	0.78
Al	19.92	1.55
Si	35.51	1.83
K	4.82	1.03
Total:	100.00	

Element	Wt%	Wt% Sigma
C	2.60	0.14
O	37.81	0.21
Na	1.69	0.06
Al	6.24	0.09
Si	19.31	0.15
K	1.99	0.07
Ti	0.72	0.07
Mn	1.06	0.09
Fe	28.57	0.23
Total:	100.00	

Fgure 5: EDXS of natural zeolites samples showing elemental compositions and quantities (wt%) of each sample.

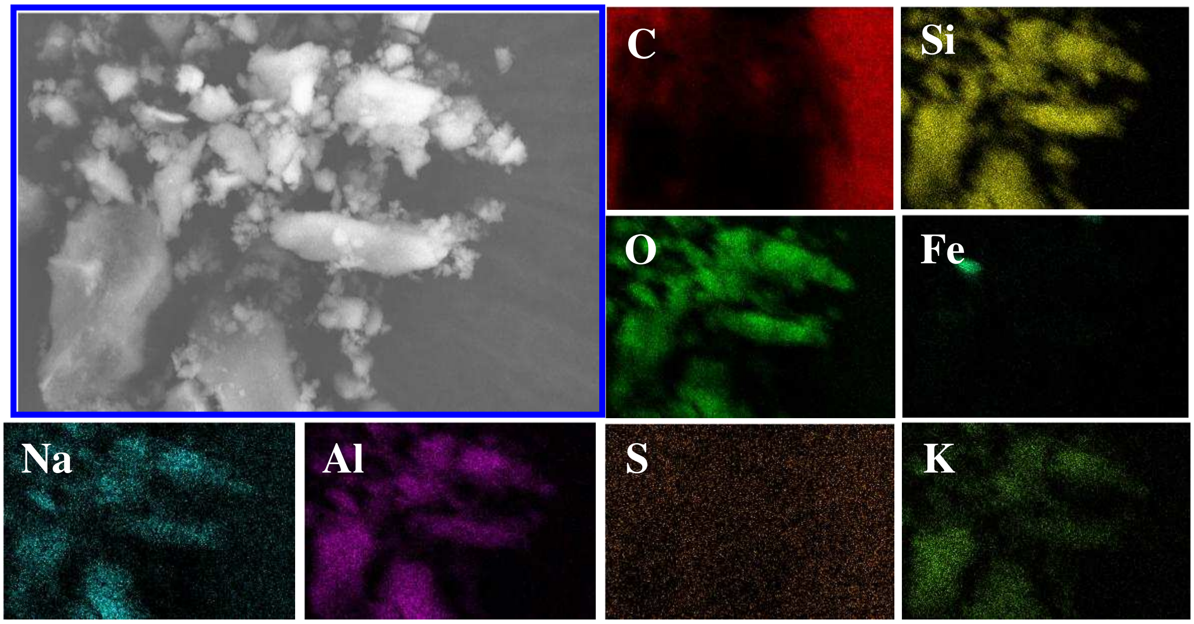


Figure 6: SEM elemental mapping for a typical natural zeolite sample shoiwng the location and quantities of individual elements (NZ-1).

Table 1. Application of natural zeolite in various fields [13-15]

Area	Used as	Function
Ecology	Cleaner/Filter	Wastewater cleaning Air cleaning
Agriculture	Adsorbent/ Fertilizer	Keep the seed dry A good source of nutrients Keep the soil fertile for long period of time
Livestock and poultry feeder	Dietary additive Deodorant	Dietary additives in food of animals Deodorant for cattle breeding and bird farm
Mining	Adsorbent	Remediation of mines via adsorption and retention of dangerous heavy metals and other metallurgical waste
Aquaculture	Adsorbent Filter	Decrease ammonia level in ponds Clean water through filtration
Petrochemical Industries	Catalyst	Increase cracking reaction in petro-chemical industries.
Waste to energy	Catalyst	Improve the quality of produce fuel-oil from pyrolysis of plastic waste Increase the conversion of Free Fatty Acid into biodiesel through esterification process Increase the production of methane gas in anaerobic digestion process.
Alcohol, Methyl chloride and Ethyl ethane formation	Dehydrator	Dehydration
Cosmetic Industry	Dehydrator	Dehydration
Pollution Control	Catalyst/adsorbent/ filter	Increase biological activity, reduce nutrients, BOD, Ammonia and sludge quantity. Can be regenerated and use as fertilizer with ammonia. Increase the sewerage plant capacity and life cycle.

Table 2: XRD diffrcation results showing the various specis of natural zeolites

Sample	Mineral Name	Chemical Name	Chemical Formula	Reference Code
NZ-1	Anorthoclase	Potassium sodium aluminium silicate	Na,K $(Si_3Al)O_8$	00-009-0478
	Sillimanite	Aluminum oxide silicate	$Al_2(SiO_4)O$	04-013-1827
	Cristobalite	Silicon oxide	SiO_2	04-008-7742
		Aluminium oxide	(Al_2O_3)	04-004-5290
NZ-2	Orthoclase	Potassium aluminium silicon oxide	$KAlSi_3O_8$	04-009-3610
	Albite	Sodium aluminium silicate	$Na(Si_3Al)O_8$	00-010-0393
	Quartz	Silicon oxide	SiO_2	01-085-0865
NZ-3		Aluminium oxide,	$Al_2O_{2.67}$	04-016-0539
		Potassium aluminium	$KAlSi_3O_8$	04-009-3610
NZ-4	Anorthite	Calcium Aluminum	$CaAl_2Si_2O_8$	00-041-1486
	Quartz	Silicon Oxide	SiO_2	04-003-6495
	Cristobalite	Silicate	SiO_2	04-008-7637

Table 3: Si/Al ratios for the different natural zeolite samples

Samples	NZ-1	NZ-2	NZ-3	NZ-4	NZ-5
Si/Al	4.6	9.2	6.3	1.8	3.1

Table 4: Physical properties of natural zeolite samples

Physical properties of natural zeolites	NZ-1	NZ-2	NZ-3	NZ-4	NZ-5
BET surface area (m^2/g)	4.266	3.214	5.657	8.947	6.003
Pore volume (cc/g)	0.018	0.012	0.022	0.041	0.024
Pore radius (Å)	18.669	8.341	18.660	18.758	18.699