Journal homepage www.jzs.univsul.edu.iq
Journal of Zankoy Sulaimani
Part-A- (Pure and Applied Sciences)

Environmental Friendly conversion of locally available low-cost materials to zeolite

Heman A.Smail[1], Kafia M.Shareef[1], & Zainab Ramli[2]

1 College of Science, Department of Chemistry -Salahaddin University, Kirkuk Road-Erbil-Iraq
2 Faculty of Science, Department of Chemistry-UniversitiTeknologi Malaysia of Johor bahru-Malaysia
Email:kafia.surchi@yahoo.com

Article info
Original:
4 November 2015
Revised:
25 February 2016
Accepted:
21 April 2016

***Key Words:**Zeolite*
Barley husk
chert rock
Shale clay
hydrothermal
crystallization

Abstract

Mordenite, NaY and NaX zeolites were hydrothermally synthesized from locally available low-cost materials such as, chert rock, barley husk, and shale clay without using organic templates, structure-directing agent, and additives. The as-synthesized zeolites were characterized by Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction (XRD), X-ray Fluorescence (XRF) and Field Emission scanning electron microscopy (FESEM). The results verified that mordenite, NaY and NaX zeolites obtained from hydrothermal condition, present a good zeolitic properties and then can be suitable for using in adsorption, ion exchange and catalysis experiments. The properties of zeolite materials formed are strongly depended upon the composition and the type of raw materials used.

Introduction

Recently, the increasing interest in zeolite synthesis from locally available low-cost materials has promoted the development of various research areas on their conversion to zeolite giving rise to an extensive literature. Several excellent review articles dedicated in the literature to different aspects of zeolite synthesis, recent developments, and applications appeared [1, 2].Few of them were, however, entirely dedicated to the area of zeolite nanocrystals. Considering the expanding interest in the subject, the growing number of zeolites prepared in a nanosized form and the emerging applications of zeolite nanocrystals or zeolite nanocrystal-built materials. Zeolite nanoparticles are believed to possess wide applications in catalysis and decontamination owing to their large surface and well-defined porosity. Moreover, the use of zeolites in nuclear waste decontamination is a common practice, it have also been used to decontaminate low and intermediate-level liquid nuclear wastes [3, 4]. The unique crystalline porous structure of zeolites yields valuable physicochemical properties for cation exchange, molecular sieving, catalysis and adsorption. Today, zeolites are widely employed in industrial, environmental, biomedical, and intensive agriculture applications [5]. Barley husk, which is often considered as a solid waste from barley milling contains more than 80%wt of silica (SiO_2) with high purity and amorphous phase. When the barley husk is leached with mineral acid and calcined in air, white powder of barley husk silica (BHS) is obtained. The BHS can be used as a new source of silica for the synthesis of porous materials such as zeolites [6]. Chert rock is the general term for very fine-grained and nonporous sedimentary rocks that consist mostly or entirely of silica, in the form of either amorphous silica or microcrystalline quartz presumably derived from recrystallization of amorphous silica [7]. The extraction of silica from clay by the use of alkali as leaching agent is dependent on calcination temperature, reaction time and may be the leaching agent [8].

The aim of this research was to study the structure and properties of zeolites synthesized from locally available low-cost materials which has dual benefit to the, environment and economy.

II. Materials and Methods

A. Materials

All the chemicals used in the present study were analytical grade and were used without pretreatments and further purification. The following raw materials were selected to extract silica for zeolite synthesis: Chert rock, shale clay, barley husk.

B. Methods

C. Extraction of Silica

Preliminary test was done on the selected raw materials for the presence of silica, it was found that chert rock, shale clay and barley husk are good sources for silica.

Barley Husk

Barley husk was washed thoroughly with distilled water, dried at 110°C overnight then refluxed in (3M) HCl solution for 6 h and filtered. The solid product was washed repeatedly with water until the filtrate was neutral and dried at 100°C overnight. Finally, the refluxed barley husk was pyrolyzed in a hot furnace muffle at 600°C for 4 h to remove the organic contents to obtain the white silica (BHS)[9].

Shale clay and chert rock

Shale clay and chert rock were collected from Shaqlawa, Hawler, Kurdistan, sites: 36° 24’ 54” N latitude and 44° 19’ 12” E longitude and 36° 24’ 12” N latitude 44° 15’ 15” E longitude respectively. The same procedure was followed to obtain silica from shale clay and chert rock. Both raw materials were thoroughly washed with distilled water, dried at 110 ºC for 12 h and calcined at 800 ºC for 4 h. A mixture of Shell clay or chert rock (10.03 g) and (5M) NaOH solution was stirred, at 600 rpm for (30 min), in open borosil beaker. The solution was filtered through Whatman No. 41 filter paper and the residue was washed with 20 ml boiled distilled water. The filtrate and washings were allowed to cool to room temperature and the solution pH was adjusted to pH 7.0 with (2.5M) H_2SO_4 at constant stirring at 600rpm. A soft white gel was formed and aged for 6 h, then washed by vacuum filtration and dried at 110ºC for 12 h[8].

Nanozeolite Preparation

Nanozeolitewas synthesized from silica obtained from the selected raw materials and their quantities were calculated based on their chemical composition according to their XRF analysis. Typically, (38. 90 g) of NaOH was dissolved in (249.3 mL) of water and then divided into two equal portions. In one portion, 5.56 g of silica was completely dissolved. To other portion (10.19 g) of $NaAlO_2$ was added to prepare a clear aluminate solution. Then the silicate solution was slowly poured into the aluminate solution with vigorous stirring, which resulted in a clear homogenous solution. The resultant mixture was stored in an oil bath at room temperature T = (25 ± 2)°C, in a sealed polypropylene bottle under steering at 250 rpm for 3 days at pH 14. Then the solid product was separated by centrifugation (14000 rpm, 30 min) then washed several times with distilled water, until the pH value dropped to 8.69 and dried at 110°C overnight***[10]***.

III. Characterization Tools

The following tools were used in the present study for characterization of different synthesized zeolotes: FTIR spectrophotometer, type Shimadzu IR Affinity-1, XRD Spectroscopy, type

PANalyticalExpyreanPixcel A Medipix2 Collaboration with Bragg-Brentano geometry and Ni filtered Cu Kα radiation (λ=0.1541 nm) at 40kv and current 30mA data were recorded in the range of 5–50°2θ with an angular step size of 0.05° and a counting time of 1 s per step, XRF Spectroscopy, type Oxford Instrument X-Supreme 8000, FSEM: Field Emission Scanning Electron Microscope. Type JEOL model JSM-6701F.Samples were coated with Pt powder at 5.0kV with 55.000 time magnification. Hot furnace muffle (Carbolite, CWF1200).

IV. Results and Discussion

The chemical composition of zeolites synthesized by utilization of silica extracted from the selected raw materials was summarized in table-1. Results in table-1 show that zeolite synthesized from silica extracted from chert rock has highest silica content. Data in table-2 represents the types of zeolites obtained from different sources of silica that identified according to their silicon to aluminum ratio [11]. The zeolites synthesized from chert rock (H_1), barley husk (H_2), and shale clay (H_3), were identified as mordenite and FUA type X and Y respectively. XRF based unit cell composition of synthesized zeolite were summarized in table-3.

Table-1: XRF based chemical composition of the synthesized zeolites.

Nanozeolites	*Oxides (weight %)*									
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	CaO	MnO	Fe_2O_3	H_2O
Chert rock	*0.039*	*0.442*	*9.873*	*68.566*	*0.102*	*0.449*	*2.221*	*0.032*	*0.569*	*17.70*
Barley husk	*0.708*	*0.136*	*41.908*	*47.011*	*0.118*	*0.461*	*1.334*	*0.029*	*0.150*	*8.140*
Shale Clay	*0.815*	*0.240*	*49.088*	*38.142*	*0.083*	*0.456*	*1.510*	*0.024*	*0.104*	*9.530*

Table-2: The silicon to aluminum ratio and the type of the synthesized zeolites.

Zeolite	*Sample specification*	*Si / Al Ratio*	*Type*	*Isotypes*
H_1	*Chert rock*	*12.266*	*MOR*	*Mordenite*
H_2	*Barley husk*	*1.981*	*FAU*	*Y*
H_3	*Shale Clay*	*1.372*	*FAU*	*X*

Table-3: The synthesized zeolite unit cell composition.

Nano zeolite	*Unit Cell composition*
H_1	$68.566\ SiO_2 : 9.873Al_2O_3 : 0.039Na_2O: 17.70H_2O$
H_2	$47.011\ SiO_2 : 41.908Al_2O_3 : 0.708Na_2O : 8.14H_2O$
H_3	$38.142\ SiO_2 : 49.088Al_2O_3 : 0.815Na_2O : 9.53H_2O$

FTIR analysis

FTIR in the range of 400–4000 cm^{-1} are shown in *(Figures: 1-3)*for H_1, H_2 and H_3respectively. The bands at 463,448-463 and 454 cm^{-1} are related to the T–O–T bending of vibration mode (T= Si or Al) [6].The bands around 515, 588 and 520-570 cm^{-1} are related to bending vibration of SiO_4 groups or in the vibration modes of the 4membered rings of silicate chains of the synthesized zeolites. The stretching vibration of SiO_4 are shifted towards lower frequency indicating that the presence of the internal Si-O···HO-Si bonds. The bands around 695 and 778,701 and 713 cm^{-1} Stretching modes involving motions primarily associated with the T-atoms, or alternatively described as symmetric modes ←O T O→ are assigned in the region of 820-650 cm^{-1} [12, 9].The bands at 802-875,857 and 860 cm^{-1} are assigned to symmetric T-O-T stretching vibration. The bands around 1086-1180,1013-1120 and 1013-1120 cm^{-1} are due to the Si-O-Si asymmetric stretching vibration and asymmetric stretching of SiO_4tetrahedra. While the bands around 1620, 1654 and 1654 cm^{-1} resulted due to bending vibration of H-OH. These bands were present even in sintered samples because water molecules were unable to escape from the silica matrix. The small peaks around 2510, 2364 and 2350 cm^{-1} are indicated that the carbonate which is absorbed in the sample from atmosphere during sample preparation. The band around 3440cm^{-1} for the three samples are due to the stretching vibration of the O-H bond from the silanol groups (Si-OH) and is due to the adsorbed water molecules on the silica surface. The bands at 3695, 3696&3683 cm^{-1} and 3850, 3741-3850 and 3820 cm^{-1} are related to the -OH stretching modes as well as Si-OH and occluded OH-groups in the zeolite surface. The vibrational frequencies especially which resulted from stretching and bending modes of the T-O unit indicate that SiO_4 or AlO_4 are linked for zeolite formation [13, 14].

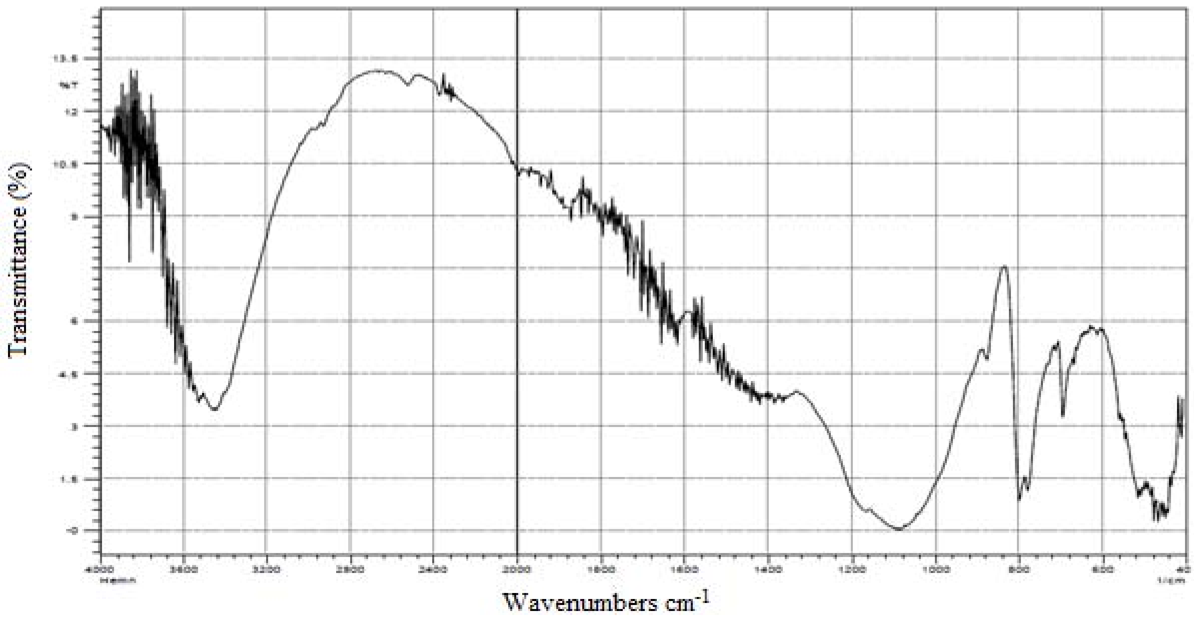

Figure-1: FTIR Spectrum for zeolite (H_1), synthesized from chert roc

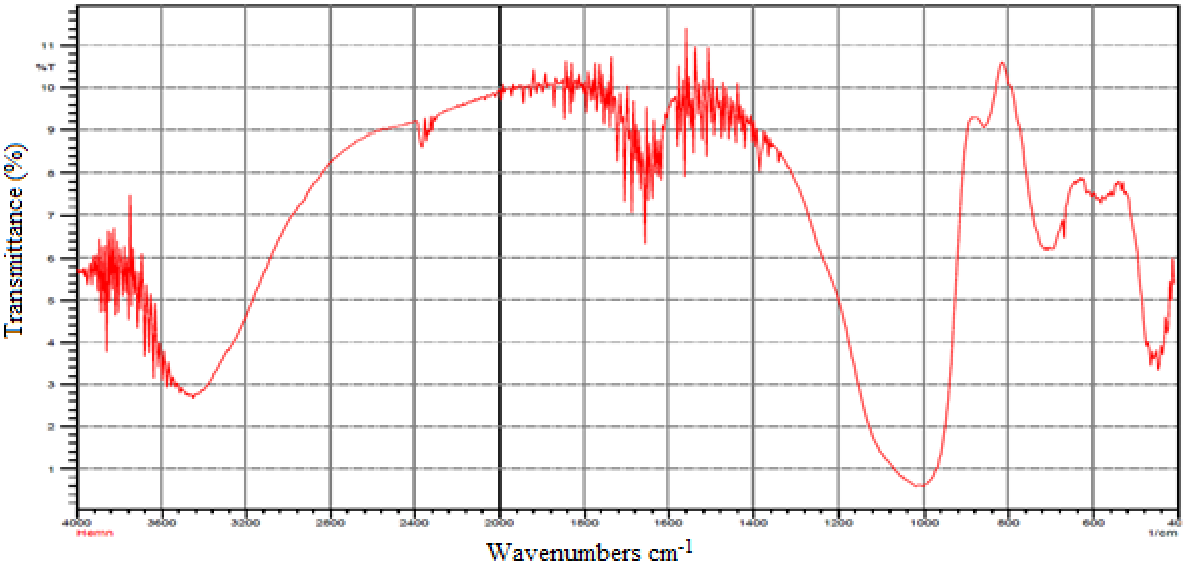

Figure-2: FTIR Spectrum for zeolite (H_2) synthesized from barley husk

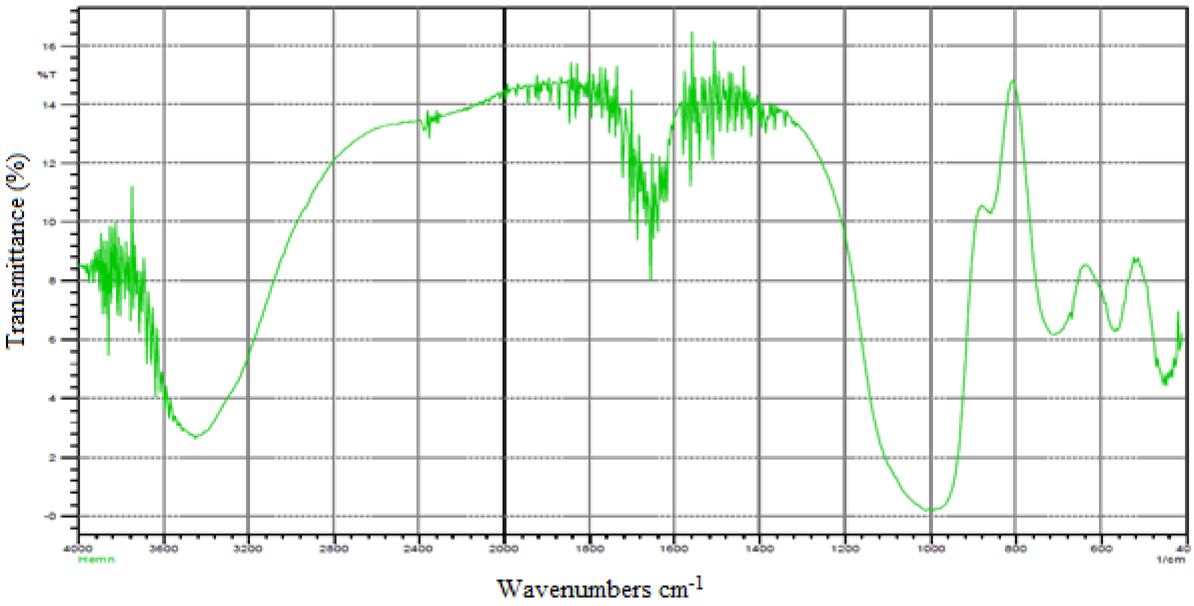

Figure-3: FTIR Spectrum for zeolite (H_3) synthesized from shale clay

XRD Analysis

The XRD spectra of zeolites (H_1), synthesized from chert rock in *(Figure: 4)*shows peaks at 2θ =6.514, 9.778, 18.073 20.34, 26.14, 28.89, 30.39, 36.00, 38.92, 39.75, 40.55, 41.9, 42.62, 44.68, 46.94, 47.98, 48.85 and 49.59. These peaks are characteristic for mordenite. XRD peaks in *(Figure: 5)*at 6.31, 10.31, 12.14, 26.07, 38.41, 42.09, 44.68 and 49.21 are characteristic of zeolite Faujasite type Y. Finally peaks at 21.29, 23.59, 26.77, 29.56, 33.81, 41.05 and 47.10 shown in *(Figure: 6)*are characteristic for zeolite Faujasite type X as compared with that recorded in literature [16-19].

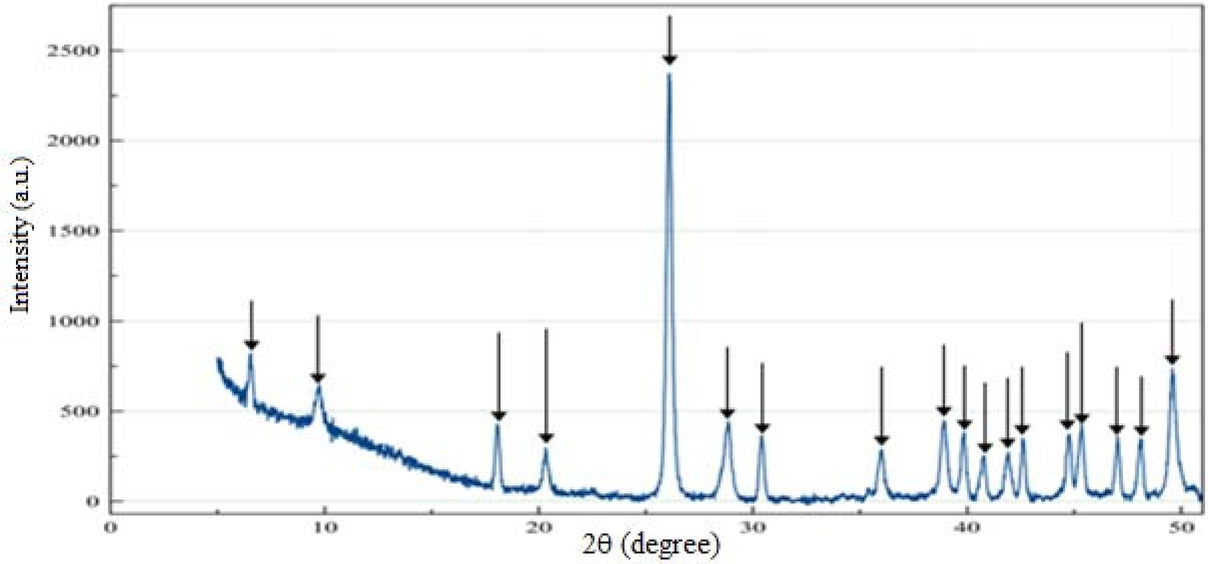

Figure-4: XRD Spectrum for zeolite (H_1) synthesized from chert rock

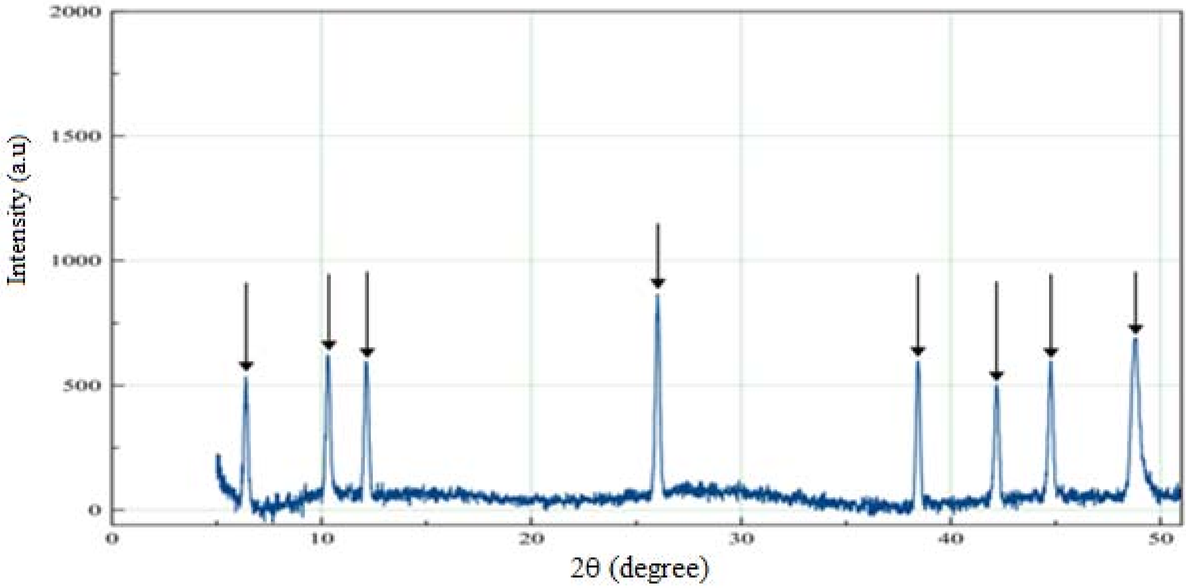

Figure-5: XRD Spectrum for zeolite (H_2) synthesized from barley husk

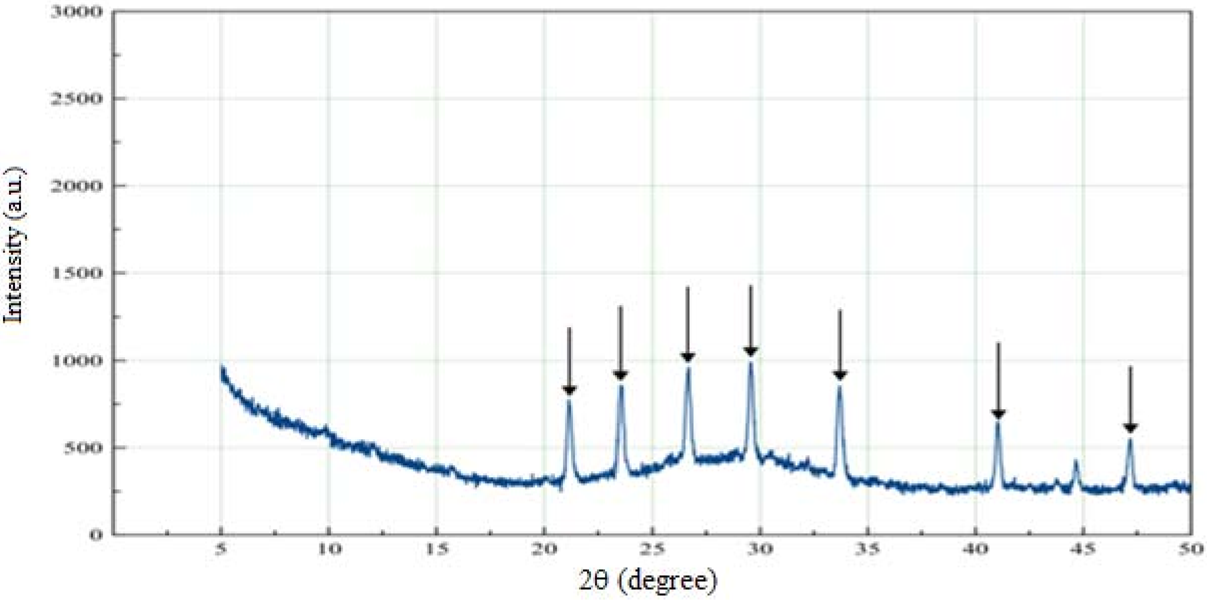

Figure-6: XRD Spectrum for zeolite (H_3) synthesized from shale clay

FESEM Analysis

FESEM images in *(Figure: 7)*for synthesized zeolite type mordenite shows that the most crystals formed as plates. Flat and prismatic crystals observed due to high concentration of silica, the solid product contained a mixture of multi-faced spherules crystal with an ice hockey shape with different particle diameter along with round amorphous particles [20]. *(Figure: 8)*shows the FESEM image characteristic to NaY type zeolite which has a plate-like morphology that is composed of Nano sheets. No physically isolated crystals or particles of the two phases were detected throughout the entire sample [15]. Since some particles apparently connected with other particles, the particle size distribution was expected to be large. In consequence of, they may be dissolved and oligomerized after crystal collapse time for hydrothermal zeolite NaY synthesis. This influence is caused by a long time of reaction with heating, as the mechanism of zeolitezation is closely related to this effect. Our results were in good agreement with that reported in literature [21, 22]. *(Figure: 9)* shows the FESEM image of prepared zeolite FUA X which exhibited random piling of nanoplate-like crystal morphologies [23]. FESEM image confirms the morphology of zeolite X were also found octahedron shapes remarkably the grain with smooth surface which suggests that the product has high crystalinity[24]. The FESEM analysis results for the three synthesized samples were confirmed by the results obtained from their FTIR, XRF andXRD . Data in table 2 together with FESEM images for the synthesized zeolites revealed that reducing the Si/Al ratio increases the crystalinity as well as the crystal size.

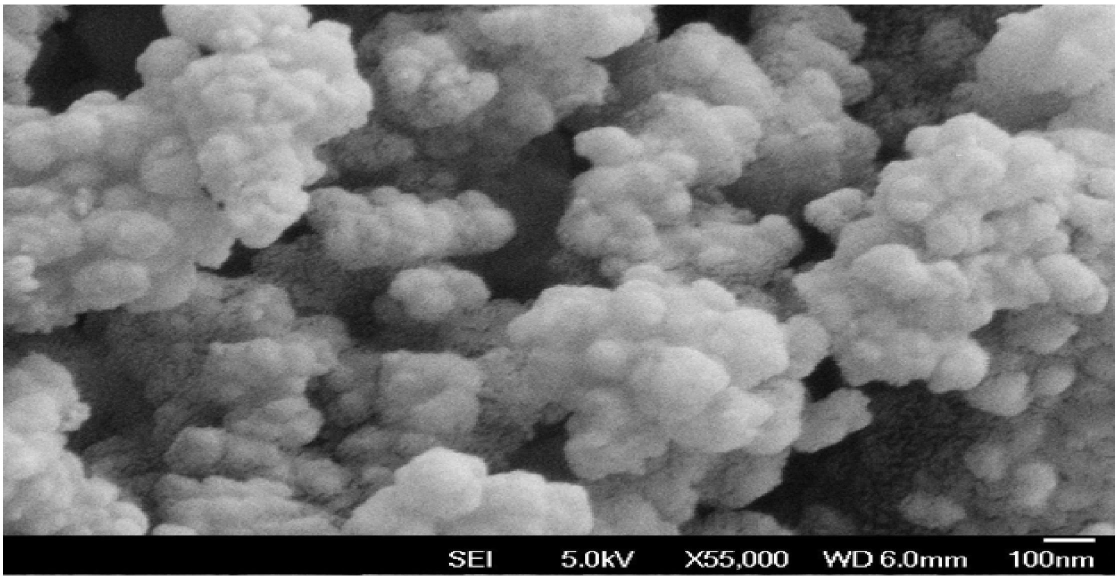

Figure-7: FESEM image for zeolite (H_1) synthesized from chert rock

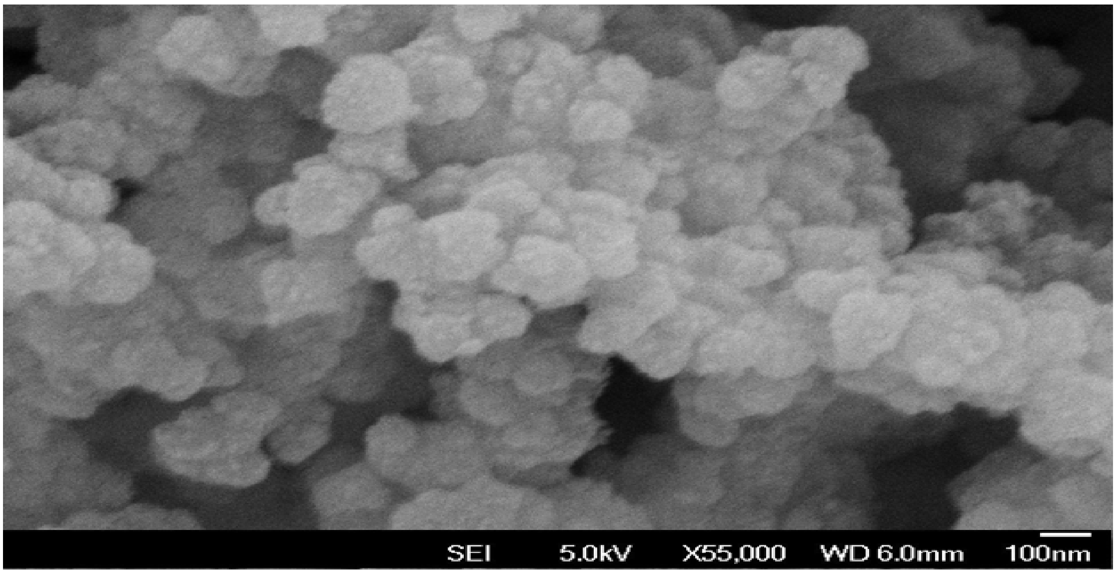

Figure-8: FESEM image for zeolite (H_2) synthesized from barley husk

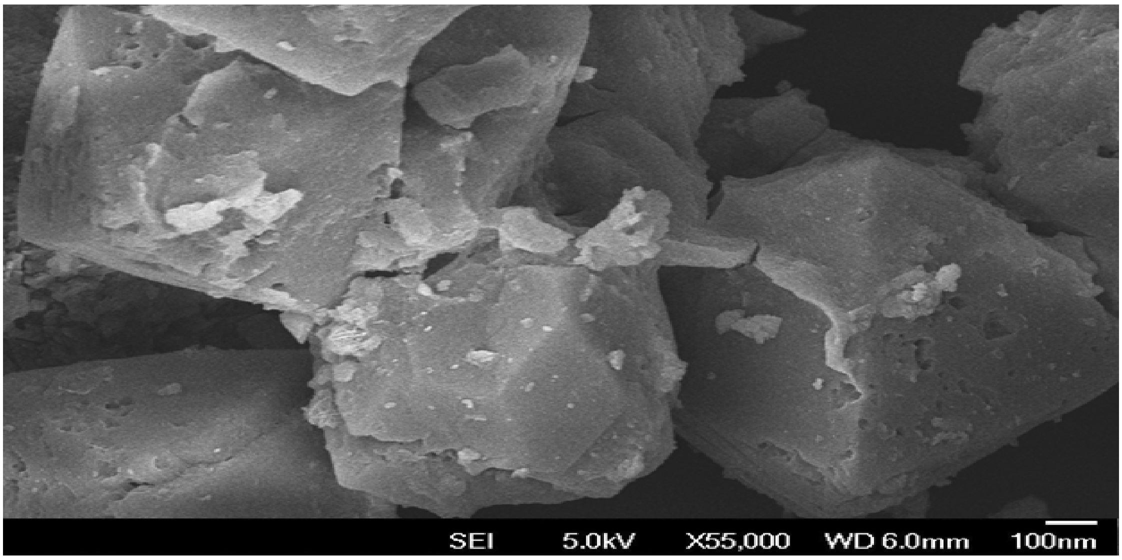

Figure-9: FESEM image for zeolite (H_3) synthesized from shale clay

V. Conclusion

In conclusion, the dual benefit to the environment and economy was achieved by reusing low cost materials to produce valuable products. Consequently barley husk, shale clay and chert rock are a new sources of silica and suitable for synthesis of different type of nanozeolite without addition any organic additives. Finally as the Si/Al ratio for the synthesized zeolite reduced, the crystalinity as well as the crystal size were increased.

Acknowledgment

Theauthorwouldliketothankdirectorate of construction Laboratories in Erbil for free XRF analysis of the synthesized samples.

References

[1] Lubomira, T. and Valentin, P.V. *"Nanozeolites: Synthesis, Crystallization Mechanism, and Applications"*, Chemistry of Materials, Vol. (17), No. 10, pp. 2494-2513. (2005).

[2] Hui, D. and Yan, G. *"Formation of NaP zeolite from fused fly ash for the removal of Cu (II) by an improved hydrothermal method"*, Royal Society of Chemistry Advances, Vol. (5), No. 12, pp. 9180-9188. (2015).

[3] Yuanyuan, H. Yahong, Z. and Yi, T. *"One-step hydrothermal synthesis of surface organosilanized nanozeolite under microwave irradiation"*, Chemical Communications, Vol. (46), No. 22, pp. 3875 – 3877, (2010).

[4] Jiafeng, Y. Chenchen, Q. Jixin, Z. Chun, B. and Hengyong, X. *"Synthesis of a zeolite membrane as a protective layer on a metallic Pd composite membrane for hydrogen purification"*, Journal of Materials Chemistry A, Vol. (3), No. 9, pp. 5000-5006. (2015).

[5] Eng-Poh, N. Gin, K. L. Guo-Lun, K. Kok-Hou, T. Boon, S.O. Farook, A. Tau, C. L. and Ka-Lun, W. *"Synthesis of colloidal stable Linde Type J (LTJ) zeolite nanocrystals from rice husk silica and their catalytic performance in Knoevenagel reaction"*, Materials Chemistry and Physics, Vol. (155), pp. 30-35. (2015).

[6] Seyed, N.A. Ahmad, R. D. and Amir, J. *"Synthesis and characterization of LTA nanozeolite using barley husk silica: Mercury removal from standard and real solutions"*, Materials Research Bulletin, Vol. (48), No. 5, pp. 1753-1759. (2013).

[7] Blatt, H. "*Sedimentary Petrology*", 2nd Edition: W.H. Freeman, 327 (1992).

[8] Abdullahi, Y. Ali, E.A. and Lawal, A.O. *"Roast-alkaline leaching of silica from kaolinitic clay"*, ARPN Journal of Engineering and Applied Sciences, Vol. (8), No. 10, pp. 864-870. (2013).

[9] Pongtanawat, K. Sanchai, P. and Jatuporn, W. *"Synthesis and characterization of zeolite LSX from rice husk silica"*, Suranaree Journal of Science and Technology, Vol. (14), No. 4, pp. 367-379. (2007).

[10] Zahra, G. and Habibollah, Y. *"Preparation and Characterization of NanozeoliteNaA from Rice Husk at Room Temperature without Organic Additives"*, Journal of Nanomaterials, Vol. (2011), pp. No. 50, 1-8. (2011).

[11] Haoyu, Z. Minqin, C. Zhan, S. Xianhui, B. Yaming, Z. Xin, X. and Dongyuan, Z.C. *"Hydrothermal Synthesis of New Pure Beryllophosphate Molecular Sieve Phases from Concentrated Amines"*, Chemistry of materials, Vol. (13), No. 6, pp. 2042-2048. (2001).

[12] Byrappa, K. and Suresh, K.B.V. *"Characterization of Zeolites by Infrared Spectroscopy"*, Asian Journal of Chemistry, Vol. (19), No. 6, pp. 4933-4935. (2007).

[13] Bhardwaj, D. Tomar, R. Khare, S.P. Goswami, Y. and Srivastva, P. *"Hydrothermal Synthesis and Characterization of Zeolite Effect of Crystallization Temperature"*, Research Journal of Chemical Sciences, Vol. (3), No. 9, pp.1-4. (2013).

[14] Atsuo, Y. Sayaka, Y. and Jun, S. *"Preparation of a Titania/X-Zeolite/Porous Glass Composite Photocatalyst Using Hydrothermal and Drop Coating Processes"*, Journal of Molecules, Vol. (20), No. 2, pp. 2349-2363. (2015).

[15] Jyoti, P.N. *"Preparation and Characterization of Bioactive Silica-based Ceramics derived from Rice Husk Ash"* Ph. D Thesis, Department of ceramic Engineering national Institute of Technology, Rourkela 2010.

[16] Treacy, M.M.J. and Higgins, J.B. *"In Collection of Simulated XRD Powder Patterns for Zeolites"*, 4th Ed, Elsevier, Amsterdam, 586 (2001).

[17] Agarwal, S.R. Sundarrajan, S. and Ramakrishna, S. *"Functionalized Cellulose, PET Polymer Fibers with Zeolites for Detoxification Against Nerve Agents"*, Journal of Inorganic Materials, Vol. (27), No. 3, pp. 332-336. (2012).

[18] Baoyu, L. Fei, C. Liming, Z. Jinghui, G. Hongxia, X. and Yu, Q. *"Synthesis and structural properties of hierarchically structured aluminosilicates with zeolite Y (FAU) frameworks"*, Royal Society of Chemistry Advances, Vol. (3), No. 35, pp. 15075-15084. (2013).

[19] Medina, A.R. Gamero, P.M. Almanza, J.M.R. Cortes, D.A.H. and Vargas, G.G. *"Study of the zeolitization process of fly ash using an orthogonal array of taguchi experimental design"*, Journal of the Chilean Chemical Society, Vol. (54), No. 3, pp. 244-251. (2009).

[20] Kim, G.J. and Ahn, W.S. *"Direct Synthesis and Characterization of High-SiO_2-Content Mordenites"*, Zeolites, Vol. (11), No. 7, pp. 745-750. (1991).

[21] Aveen, H.M. and Kafia, M.S. *"International, Comparison the Properties of Zeolite Nay Synthesized by Different Procedures"*, International Journal of Innovative Research in Science, Engineering and Technology, Vol. (3), No. 6, pp. 13334-13342. (2014).

[22] Rahmana, M.M. Hasnidab, N. and Wan, N.W.B. "*Preparation of Zeolite Y Using Local Raw Material Rice Husk as a Silica Source"*, Journal of scientific research, Vol. (1), No. 2, pp. 285-291. (2009).

[23] Jaeheon, K. Changbum, J. Seungjun, L. and Ryong, R. *"Bulk crystal seeding in the generation of mesopores by organosilane surfactants in zeolite synthesis"*, Journal of Materials Chemistry A, Vol. (2), No.30, pp.11905-11912. (2014).

[24] Htun, M.M.H. Htay, M.M. and Lwin, M.Z. *"Preparation of Zeolite (NaX, Faujasite) from Pure Silica and Alumina Sources"*, International Conference on Chemical Processes and Environmental (ICCEEI'2012)\ July 15-16, Singapore, pp. 212-216. 2012.