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RESEARCH PAPER

Synthesis and Characterization of Zeolite A from Alkaleri Kaolin using Conventional Hydro Thermal Synthesis Technique

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ABSTRACT

Zeolite A was synthesized via a two-step hydrothermal transformation of kaolin. The kaolin was first transformed to meta kaolin by calcination at 600^{o}C, then treated with 3M NaOH solution (1:5 ration) in a stainless-steel autoclave with a teflon liner. The mixture was heated to 121°C for 2h to insert the sodium ions into the metakaolin structure. The treated kaolin clay was washed three times with deionized water to remove the excess unreacted NaOH, filtered and dried in an oven at 100°C overnight. Different analytical techniques were used to characterize the synthesized Zeolite A and the individual zeolie/metal oxide nanocomposites including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray (EDX), X-ray fluorescence (XRF), Furrier transform infrared (FTIR), and Brunnuer Emmett teller (BET) analysis. FTIR confirmed the presence of Si-O, Si-Al, Al-O, and metal oxygen bonds. SEM/EDX revealed a cubic morphology with some bigger particles that are mono dispersed and partially spherical, along with different compositions of the elements present. XRD showed a face-centered cubic (FCC) structure with 25.73 nm lattice, while XRF confirmed the presence of SiO_2, Al_2O_3 as well as with different major and trace metal oxides. The BET analysis showed 3.9457 and 4.3044 (m^2/g), 0.6032 and 0.5598 (cm^3/g), 603.087 and 617.503(Å) for both the kaolin clay and the synthesized zeolite A, respectively. The results of this synthesis route demonstrate that Zeolite A was successfully synthesized.

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INTRODUCTION

Zeolites are micro-porous allumino-silicate three-dimensional crystalline solid minerals that are commonly used as commercial adsorbents and catalysts. They occur naturally and are also produced industrially on a large scale. Zeolites are the major mineral components of altered volcanic elastic rocks, varying in age and composition. They are mainly formed by the alteration of volcanic glass in various geological environments under varying geochemical and temperature conditions [1]. Zeolites have small openings fixed in them which allow small molecules to pass through them easily, while large molecules cannot. They consist of aluminum, silicon, and oxygen in their regular frameworks; cation and water are located in the pores. The silicon and aluminum are tetrahedraly coordinated with each other [2]. Zeolites have many advantages over sand and can be used directly to replace sand in a normal sand filter. They can also be used in industry, catalysis, gas separation, ion exchange (resin), and other applications etc. Zeolites can be produced industrially (synthetically), as the main raw materials used to manufacture them, silica and alumina, are among the most abundant minerals on the earth. This means that the potential to supply zeolites is virtually unlimited [1-2]. Natural zeolites are found in mafic volcanic rocks,

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as cavity fillings, probably due to deposition by fluids or vapor in sedimentary rocks. Zeolites are a type of alteration product of volcanic glass and serve as cementing materials in detrital rocks. They are also found in chemical sedimentary rock of marine origin [1-3]. Zeolites are highly stable solid under different environmental conditions, with a very high melting point of nearly 1000^{O}C and insolubility in water and many inorganic solvents. They do not undergo oxidation in the presence of air and have a boiling point of 80.20^{0}C [2-3]. Zeolites are used in a variety of industrial applications, such as softening water, catalyzing chemical reactions, and absorption of environmental decontamination. They are also central to green chemistry due to their ability to minimize the need for organic solvents [4]. The preliminary interpretation of the infrared spectra for zeolite suggests the specificity for zeolite structure type, group, and for secondary building units like double rings and large pores opening [5]. The major structural group present in zeolites can be detected from their infrared patterns and other analysis such as X-ray flourescence [6]. Zeolites, which belong to a large family of allumino-silicate composed of corner-like TO_4 tetrahedral units (T = Si or Al) that can form a remarkable variety of crystalline structures containing channels and/or cavities with different dimensions, have been synthesized [7-8].

MATERIAL AND METHODS

Chemical/Reagents

NaOH, Distilled Water**.**

Instrument and Apparatus

A variety of laboratory equipment was used in this study, including a pH meter, beakers, weighing balance, heating mantle, autoclave, filter paper, desiccator, magnetic stirrer, muffle furnace, oven, X-ray diffractometer RIGAKU Miniflex 600 JPeg, UV-Visible spectrophotometer, Furrier transform infrared machine (SHIMADZU 8400S), scanning electron microscopy machine coupled with EDX, XRF (X-ray fluorescence) XRF, THERMOSCIENTIFIC ARL OP-TIMIX 166 analysis machine, Barrrnuer Emmett Teller Machine(Micrometric ASAP 2020 3 flexVersion 1;02) and funnels.

Sample Collection

The kaolin powder was collected from Farin Ruwa of Gwaram ta Bauchi Alkaleri Local Government Bauchi State, North Eastern Nigeria, and it was identified by the University Geology and Mining Department in Gombe State University, Gombe Nigeria.

Sample Preparation

The kaolin samples were crushed and milled into powder using a porcelain mortar before being sieved using laboratory soil sieves. The mesh sizes selected for the collection of the kaolin particles was 90 µm.

Synthesis of Zeolite and Metal Oxides Nanocomposites
Synthetic Zeolite Procedure

The kaolin samples were crushed and milled into a powder using a porcelain mortar and then sieved using laboratory soil sieves. The mesh sizes selected for the collection of the kaolin particles was 90µm. Synthesizing zeolite A from kaolin involved the following two basic steps: the first step was meta kaolinization, which is the thermal treatment of the raw kaolin at a high temperature of 600°C for 3 hours, and the second step was the chemical treatment of the prepared meta kaolin with 3 M sodium hydroxide (NaOH) [9,3].

Calcination (Metakaolinization) and Synthesis of Zeolite

Using the conventional hydrothermal synthesis technique, 50 grams of kaolin clay powder (with particle sizes of 90 µm) was calcined at 600°C for 3 hours to convert it to meta-kaolin. This process caused a change in the structure of the kaolin, resulting in the evolution of volatile matter and the formation of the meta-kaolin. The produced meta-kaolin was then treated with 3M NaOH solution in a ratio of 1:5, heated in stainless steel autoclaves with a teflon liner to 121°C for 2 hours to insert the sodium ions into the meta-kaolin structure. The treated kaolin clay was then washed three times with deionized water to remove the excess unreacted NaOH, filtered and dried in an oven at 100°C overnight. Various samples with different NaOH concentrations were prepared in order to study the optimum concentration required for the synthesis of zeolite A [9].

CHARACTERIZATION

Scanning electron microscopy (SEM) coupled with EDX (Energy Dispersion X-Ray) Analysis. (XEMATRIX EDXRF LTD ISRAEL))

The SEM coupled with EDX analysis was carried out to determine the morphology and elemental composition of the elements present

in the synthesized zeolite A. It was done using (XEMATRIX EDXRF LTD ISRAEL) model microscopy under electrical high tension (EHT) 10.00kV and 20.00kV. Signal A = secondary electron (SE) and variable pressure secondary electron (VPSE). WD = 6.0-8.5mm at different magnifications while EDX spectrophotometer was coupled for the identification of different metals and their percentage compositions.

Furrier Transform Infrared (FTIR) Analysis (SHIMADZU 8400S)

FTIR analysis was conducted to determine the functional group present on both the kaolin powder and synthesized zeolite A. It was recorded in the ranges between 400 – 4000 cm^{-1}

X-Ray Diffraction (XRD) Analysis (RIGAKU Miniflex 600 Jpeg)

XRD analysis was performed to find out the average crystalline size. Debye Scherer equation was applied to calculate the average crystalline size of the synthesized zeolite A. The Debye Scherer equation is as follows:

$$D = K\lambda/\beta COS\theta$$

Where D = Particles size = 0.94
K = Constant volume
λ = X-ray wavelength (0.154nm)
P = Line broadening at half the maximum intensity
Θ = Braggs angle (in degree).

The XRD analytical technique used for the phase identification of the samples was set with a copper k-alpha radiation of 50mA and 50kV. The secondary machromation was used and the data was obtained at 2-theta ranging from 60-680.The results were compared with the standard line pattern data base for international center for diffraction data (ICDD) and indexed based on the joint committee on powdered diffraction standard (JCPDS).

X-Ray Flourescence (XRF) Analysis (XRF, THERMOSCIENTIFIC ARL OP-TIMIX 166)

XRF analysis was conducted in order to identify the different metal oxides present in the synthesized Zeolite A. The samples was prepared by pressing the powdered samples into cellulose and then analyzed on a PW2400 Philip XRF spectrometer with the aid of calibration software prepared from standard referencing materials.

BET Analysis (Brunnauer Emmett Teller) Analysis (Micrometric ASAP 2020 3 flexVersion 1;02).

The BET analysis was conducted to determine the surface area, pore volume, and pore size of the ordinary kaolin powder and synthesized zeolite A. The automated gas sorption system (quantuchrome autosorp) model Micrometric ASAP 2020 3 flex Version 1;02 of window 1.50 operating with nitrogen as analysis gas and adsorbate cross-sectional area of 16.20 Å /mole with non-ideality of 6.58e-05 was employed to record the surface area, pore volume, and pore size of the ordinary kaolin powder and the synthesized zeolite A. The operating conditions include bath temperature of 77.40^{0}C, out gassing temperature of 300^{0}C and out gassing time of 23 hours with a zero P/tolerance, a three-hours equilibrium time, and 1500-minutes analysis time.

RESULT AND DISCUSSION

This investigation entitled "Zeolite/Metal oxides nanocomposites: Synthesis, Characterization and its Catalytic Degradation of Some Dyes" was conducted and the results were presented in the form of tables, figures and charts. These results were also discussed in this chapter. Kaolin can be transformed to metakaolin at temperature between 450^{0}C - 650^{0}C. The dehydration of kaolin begins at temperatures between 550 and 6000^{0}C during which the metakaolin is produced [9]. Kaolin dehydration occurs between 400 and 650^{0}C, which is the stage of transformation of kaolin to metakaolin. In this study, kaolin transformed to metakaolin at the temperature of 600^{0}C.

The FTIR (Furrier Transform Infrared) Spectrophotometric Analysis Results

The following table and different infrared spectrums summarize and describe the Furrier transform infrared (FTIR) results as conducted using the FTIR spectrometric analysis machine model SHIMADZU 8400S at the national research institute technology, Zaria, Kaduna state, Nigeria.

The FTIR analysis of the raw and synthesized materials (Kaolin powder and the synthesized Zeolite A), as shown in Figs. 1 and 2, was conducted at the National Research Institute for Chemical Technology, Zaria, Kaduna State, Nigeria, using machine model FTIR-SHIMADZU 8400S in the range of 400-4000cm^{-1}. The FTIR spectra of the raw kaolin powder (Fig. 1) displayed several peaks at 3694cm^{-1} and 3400 cm^{-1}, which are

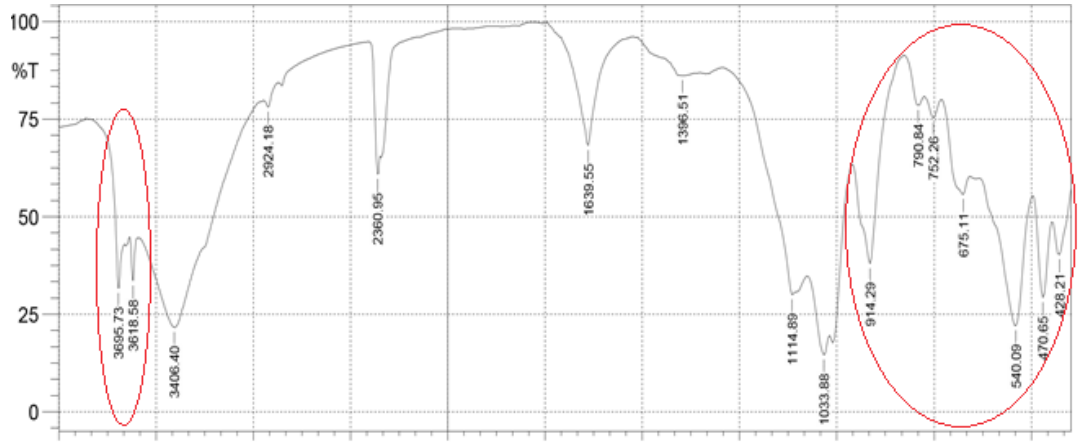


Fig.1 Showing the FTIR results of the raw kaolin powder (K)

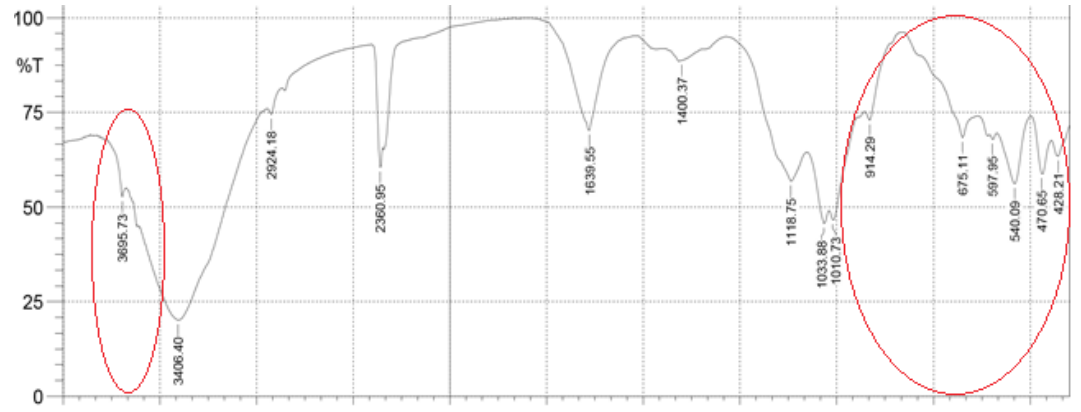


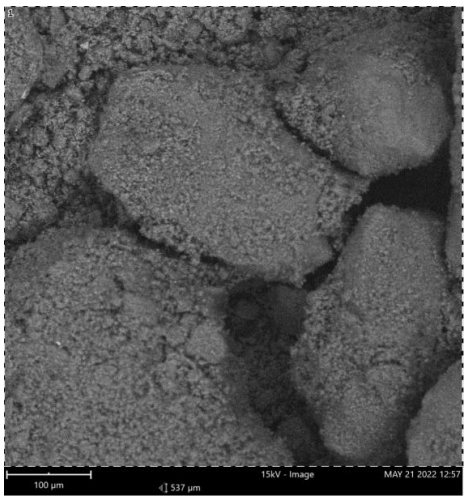
Fig. 2 Showing the FTIR results of the synthesized Zeolite A (Z)

attributed to the stretching vibration mode of inner hydroxyl group O-H located in the octahedral and tetrahedral sheets of kaolin and that of zeolite water, respectively [9]. The peaks at 2924 cm^{-1} and 2360 cm^{-1} are stretching vibration attributed to O-H-O within the kaolin pores and extra framework in the zeolite opening [10]. Other peaks at 1639 cm^{-1}, 1400 cm^{-1}, 1396 cm^{-1}, 1118cm^{-1} cm^{-1} and 1114 cm^{-1} are responsible for Si-O and Al-O bonds in the kaolin and zeolite structures. In addition, peaks at 1033 cm^{-1}, 1010cm^{-1} and 914 cm^{-1} were also responsible for the Si-O-Si, Si-O-Al and Al-O, respectively, attributed to AlO_4, SiO_4 and Al_2O_3 [9]. Other peaks at 790 cm^{-1}, 675 cm^{-1}, 671 cm^{-1}, and 428 cm^{-1} are also assigned to stretching vibrations due to Si-O-Si, TO_4 tetrahedra, N-H wag and Si-O within the kaolin and zeolite structure [9,10]. Finally, the peak at 597 cm^{-1} confirmed the formation of zeolite A [9,6], while that of 470 cm^{-1} and 540 cm^{-1} were responsible for Si-O and TO_4 in the primary building unit of zeolite and the interaction between alumina tetrahedral structures of the zeolite pores.

SEM (Scanning Electron Microscope) coupled with EDX (Energy Dispersion X-Ray).

Fig. 3 shows the results obtained from the SEM coupled with EDX analysis. The surface morphology and percentage elemental composition of major and trace elements present in the synthesized zeolite A was determined using the machine model (XEMATRIX EDXRF LTD ISRAEL) at the National Research Institute for Chemical Technology, Zaria, Kaduna State, Nigeria. Under the electron high tension (EHT) was set at 15Kv, with a signal of A = secondary electron (SE) and variable pressure secondary electron (VPSE) and a width of 6.5 at different magnifications. The results of the analysis are summarized and discussed as follows.

Fig. 3 demonstrates the results of the SEM/EDX analysis for the synthesized zeolite nanocomposites



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
35	Br	Bromine	11.12	31.69
8	O	Oxygen	48.25	27.53
14	Si	Silicon	17.46	17.49
38	Sr	Strontium	3.67	11.47
13	Al	Aluminum	13.02	5.58
11	Na	Sodium	5.18	4.24
29	Cu	Copper	0.77	1.74
7	N	Nitrogen	0.53	0.26

FOV: 537 µm, Mode: 15kV Image, Detector: BSD Full, Time: MAY 21 20 22 12:57

Fig. 3 The results obtained from the SEM/EDX analysis of the synthesized zeolite A nanocomposites. (Z),

(Z). Based on the results, the zeolite has a cubic morphology with the presence of some bigger particles that are mono dispersed and partially spherical, attributed to the aggregation and overlapping of some smaller particles during the zeolite preparation. The elemental composition is 17.46% silicon and 13.02% aluminum, together with other elements such as 48.25% oxygen, bromine 11.12%, 3.67% strontium, 5.18% sodium, 0.77% copper, and 0.53% nitrogen. The results obtained are in agreement with the literature reported by [11], who synthesized manganese dioxide nanoparticles-Y zeolite as a nanocomposite catalyst for the decontamination reactions of S-diethyl phosphonothiolate which shows cubic morphology with the presence of some bigger particles attributed to the aggregation and overlapping of some smaller particles during the zeolite preparation.

XRD (X-Ray Diffraction) Analysis

The XRD analytical technique used for the phase identification of the samples was set with a copper k-alpha radiation of 50mA and 50kV. The secondary machromation was employed and the data was obtained at 2-theta ranging from 60-680. The results were compared with the standard line pattern data base for international center for diffraction data (ICDD) and indexed based on the joint committee on powdered diffraction standard (JCPDS) Fi.

The results obtained from the XRD analysis of the synthesized zeolite A (Z) with the Bragg angle of 12.54-67.91° was observed along with the weak peaks, as shown in Fig. 4. Six prominent peaks were observed at 2θ=12.54°, 14.09°, 24.41°, 36.10, 45.64 and 67.91° with respect to the plane of (101), (110), (210), (211), (222) and (310). The results revealed a face-centered cubic (FCC) structure and the average crystalline size of 25.73 nm; the diffraction peaks are indexed based on JCPDS file number 83 - 1533 and it corresponds to the literature reported by [12], indicating a FCC structure for the synthesis and characterization of zeolite A by hydrothermal transformation of Jordanian kaolin [13], which prepared and characterized Nay Zeolite for biodiesel production and [9] in their work entitled "Synthesis of zeolite A from Iraqi natural kaolin using a conventional hydrothermal synthesis technique."

The X-Ray Fluorescence (XRF) Analysis

The X-ray fluorescence (XRF) analysis was conducted using the machine modeled XRF, THERMOSCIENTIFIC ARL OP-TIMIX 166. It showed the elemental compositions and different metal oxides present in the synthesized zeolite A, including manganese oxide, copper oxide, nickel oxide, iron oxide, zeolite/manganese oxides, zeolite/copper oxides, zeolite/nickel oxides and zeolite/iron oxide nanocomposites as determined based on cross road scientific XRS reports File C / users / xenemetrix / new folder (45), type: bulk, units mg/cm^2, density: 0.00F and a total of 100% compositions.

Table:1 Summary of determination of chemical composition of Zeolite A using XRF analysis

Composition	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	ZrO_2	V_2O_5	SO_3	K_2O
% Weight	54.74	1.61	36.17	4.90	0.59	0.21	0.27	0.021

Table 2 Brunnuer emmett teller (BET) analysis results obtained from kaolin powder and synthesized Zeolites A.

Samples	Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Kaolin (K)	3.9457	0.6032	603.087
Zeolite A (Z)	4.3044	0.5598	617.503

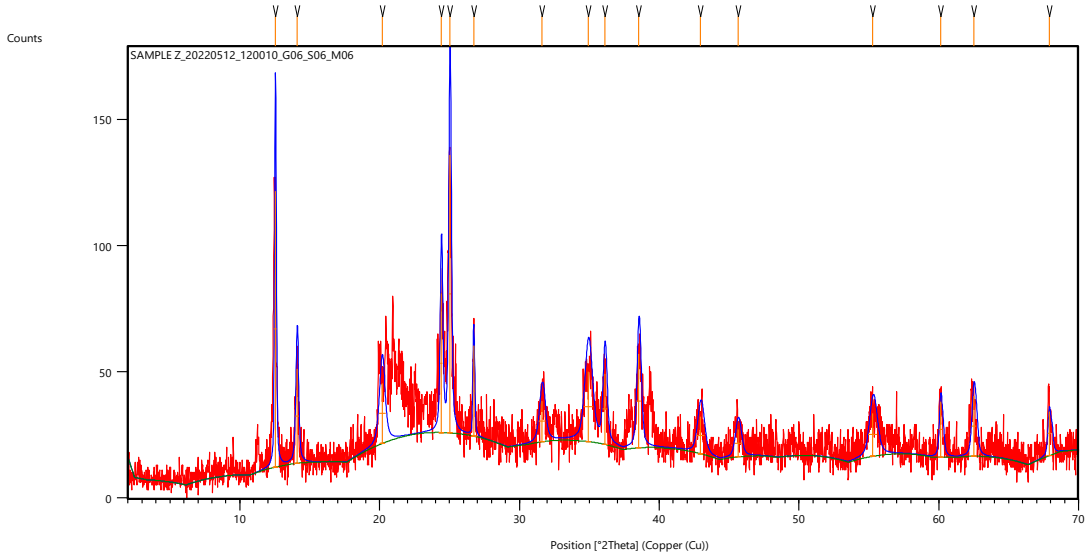


Fig. 4 XRD Spectral result for the synthesizes zeolite A

Table 1 shows different metal oxides based on elemental composition percentages in the synthesized zeolite A. It shows 54.74% SiO_2, 36.17% Al_2O_3, 4.90% TiO_2, 1.61% Fe_2O_3, 0.27% SO_3, 0.59% ZrO_2, 0.21 V_2O_5%, and 0.21 K_2O % which clearly indicates that the synthesized zeolite A possessed the required amount of silicon and aluminum needed for the synthesis of zeolite as an allumminosillicate material together with different minor and trace elements. The table of the XRF results shows 49.15% O,19.15% Al, 25.59% Si, 2.92% Ti, 1.13% Fe and 0.439 Zr together with different minor and trace elements which is nearly in agreement to that obtained by EDX analysis, showing 48.25% O, 17.46% Si, 13.02% Al, 11.12% Br, 5.18% Na, 3.67% Strontium, 0.77% Cu, and 0.53% N.

The Brunnueremmett Teller (BET) Analysis results on (Kolin Powder and the Synthesized Zeolite A)

The results of BET surface area (m^2/g), pore volume (cm^3/g), and pore size (Å) characterizations for the kaolin powder and the synthesized zeolite A are presented in Table 2. It was measured at low nitrogen adsorption temperature and calculated using the BET (Brunauer Emmett teller) equation. It shows 3.9457 m^2/g for the kaolin powder and 4.3044 m^2/g for synthesized Zeolite A which is higher than that of the kaolin powder. This increase in surface area is attributed to the micro porosity of the synthesized zeolite A which is expected to increase the adsorption efficiency [14]. The ordinary kaolin powder before the synthesis of the zeolite A had a lower surface area than the synthesized zeolite A. This increase in surface area was due to the opening

of the synthesized zeolite pores, which were covered by impurities in the ordinary kaolin powder. This opening occurred during the hydrothermally activation process, which evaporated some of the water molecules and other impurities that covers the kaolin pores, causing an increase in the surface area. The pore volume and pore size are inversely related to the surface area. The pore volume, which is the measure of the void space, as measured by nitrogen adsorption temperature, [15] was 0.6032 cm^3/g for the kaolin powder which later reduced to 0.5598 cm^3/g for the synthesized Zeolite A. Likewise the pore size for the kaolin powder was found to be 603.087 Å and reduced to 617.503 Å after the synthesis of the zeolite A. Note that the increase in the surface area and little reduction in the pore volume has an impact on the degradation process since the surface area and pore volume can increase the adsorption capacity [16].

The BET surface area of the ordinary kaolin powder increases from 3.9 to $4.3m^2/g$ for the synthesized Zeolite A since the porous layer is increasingly formed on the surface and also in the channel of the kaolin powder during the synthesis procedure.

CONCLUSION

Zeolite A was successfully synthesized hydrothermally from kaolinite clay, and characterized using FTIR, UV-Vis, SEM/EDX, XRD, XRF and BET analysis. FTIR confirmed the presence of Si-O, Si-Al, Al-O and metal oxygen bonds. SEM/EDX showed cubic morphology with the presence of some bigger particles that are mono dispersed and partially spherical, together with different compositions of the elements present. XRD revealed FCC with 25.73nm, and XRF confirmed the presence of SiO_2, Al_2O_3 together with different major and trace metal oxides. Moreover, the BET showed 3.9457 and 4.3044 (m^2/g), 0.6032 and 0.5598 (cm^3/g), 603.087 and 617.503(Å) for both the kaolin clay and the synthesized zeolite A, respectively. The results from this synthesis route indicate that Zeolite A was successfully synthesized as confirmed by the characterization results.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

REFERENCES

1. Rhodes C. The Properties and Applications of Zeolites. Science progress. 2010;93:223-84. 10.3184/003685010X12800828155007
2. Yahaya N, Danbature W. Preparation, Characterization and Antimicrobial Activity of Bentonite Clay Obtained from Sabon Kaura Deposit in Pindiga, Gombe State, Nigeria. 2022:62-6. 10.36686/Ariviyal.CSER.2022.04.10.059
3. Singh NJ, Wareppam B, Kumar A, Singh KP, Garg VK, Oliveira AC, et al. Zeolite incorporated iron oxide nanoparticle composites for enhanced congo red dye removal. Journal of Materials Research. 2023;38(4):1149-61. 10.1557/s43578-022-00859-w
4. Shaban M, Abukhadra MR, Shahien MG, Ibrahim SS. Novel bentonite/zeolite-NaP composite efficiently removes methylene blue and Congo red dyes. Environmental Chemistry Letters. 2018;16(1):275-80. 10.1007/s10311-017-0658-7
5. Abdullah FO, Omar KA. Iris barnumiae extract-coated Fe3O4 nanoparticles for the removal of Congo red dye in aqueous solution. Journal of the Iranian Chemical Society. 2022;19(8):3317-25. 10.1007/s13738-022-02525-8
6. Byrappa K, Kumar BVS. Characterization of zeolites by infrared spectroscopy. Asian Journal of Chemistry. 2007;19:4933-5.
7. K B, W S, KGS G, V V. Characterizations of Zeolites by Different Spectroscopy. Journal of Material Science Letters. 1986:203.
8. Stout SC, Larsen SC, Grassian VH. Adsorption, desorption and thermal oxidation of 2-CEES on nanocrystalline zeolites. Microporous and Mesoporous Materials. 2007;100(1):77-86. https://doi.org/10.1016/j.micromeso.2006.10.010
9. Dastafkan K, Sadeghi M, Obeydavi A. Manganese dioxide nanoparticles-silver-Y zeolite as a nanocomposite catalyst for the decontamination reactions of O, S-diethyl methyl phosphonothiolate. International Journal of Environmental Science and Technology. 2015;12(3):905-18. 10.1007/s13762-014-0701-1
10. Salih AM, Khanaqa P, Williams C. Synthesis of Zeolite A from Iraqi Natural Kaolin Using a Conventional Hydrothermal Synthesis Technique. UKH Journal of Science and Engineering. 2020;4. 10.25079/ukhjse.v4n2y2020.pp11-23
11. Srilai S, Tanwongwan W, Onpecth K, Wongkitikun T, Panpiemrasda K, Panomsuwan G, et al. Synthesis of zeolite A from bentonite via hydrothermal method: The case of different base solution. AIP Conference Proceedings. 2020;2279(1):060006. 10.1063/5.0025043
12. Gougazeh M, Buhl JC. Synthesis and characterization of zeolite A by hydrothermal transformation of natural Jordanian kaolin. Journal of the Association of Arab Universities for Basic and Applied Sciences. 2014;15:35-42. https://doi.org/10.1016/j.jaubas.2013.03.007
13. Abbas A, Abbas R. Preparation and Characterization of Nay Zeolite for Biodiesel Production. Iraqi Journal of Chemical and Petroleum Engineering. 2015;16:19-29.
14. Auerbach SM, Carrado KA, Dutta PK. Handbook of zeolite science and technology: CRC press; 2003.
15. Zubir M, Chin S. Kinetics of modified zirconia-catalyzed heterogeneous esterification reaction for biodiesel production. Journal of Applied Sciences. 2010;10(21):2584-9.
16. Gayatri R, Agustina TE, Moeksin R, Bahrin D, Gustini G. Preparation and Characterization of ZnO-Zeolite Nanocomposite for Photocatalytic Degradation by Ultraviolet Light. Journal of Ecological Engineering. 2021;22:178-86. 10.12911/22998993/131031