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Short Communication

SYNTHESIS OF ZEOLITE-A FROM LOCALLY AVAILABLE FULLER'S EARTH IN KARNATAKA, INDIA

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ABSTRACT

In this investigation, Zeolite-A, has been synthesized using Fuller's earth, a naturally occurring clay in the Gulbarga region of Karnataka, India. Silica and alumina are the chief source minerals for the formation of zeolites. Fuller's earth used in this work, containing about 48.523 % silica and 9.682 % of alumina has been used to synthesize a zeolitic material by conventional alkali fusion-hydrothermal method. NaOH was used as an activator and mineralizer at an optimum temperature, to form soluble sodium silicate and sodium aluminate that converted to zeolite during hydrothermal treatment. Hydrothermal treatment was carried out at a specific temperature and time period to convert the aged material, into a porous crystalline zeolitic material. XRD and FTIR analysis carried out on the final products confirmed the type of zeolite formed. Highly valuable zeolites that can be used as catalyst, adsorbent and as ion exchange material can be synthesized from the naturally available inexpensive, local clay.

Keywords: *Zeolite, Catalyst, Adsorbent, Molecular sieves, Alkali fusion, Hydrothermal treatment*

1. INTRODUCTION

Zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline or alkaline earth metals, which produces a system of pores and cavities showing molecular dimensions [1]. The structure of zeolite is composed of $[SiO_4]^{-4}$ and $[AlO_4]^{5}$ tetrahydra, which 'corner share' to form different open structures [2]. $M_{x/n}[(Al_2)x(SiO_2)_y].zH_2O$ is the general formula used to indicate zeolite, where n represents the charge of cation M, the values of x, y and z depend according to the type of zeolite [3, 4].

Clay minerals have been used for the synthesis of zeolite as early as 1961 and the first reported synthesis of zeolite from kaoline was about 54 years back. Kaolin on heating gives a highly reactive material called metakaolin which will help in the effective synthesis of zeolite. Zeolites are hydrated aluminosilicate minerals of group I and group II and till day more than 191 synthetic zeolites [5] and about 40 are naturally existing [6].

Zeolites are very useful in environmental applications. Chemically synthesized zeolites were first utilized commercially as a molecular sieve adsorbent and also they find more use in extracting trace heavy metals from waste water [7, 8]. Due to high cation exchange capacity, specific pore size, large surface area and structural characteristics, zeolites facilitate pollutant adsorption and encapsulation, as a catalyst [9]. The properties/characteristics of zeolites can be improved by varying the parameters in synthesis procedures using several source materials such as Fuller's earth, fly ash, rice husk ash, kolinite etc.

Fuller's earth is a mineral extracted from earth crust; it is a calcium based off-white material, with high adsorbing power. It has the capability to decolorize and purify oil and other liquids. The use of fuller's earth as raw material in the synthesis of zeolite initially requires calcination at 700-900^{0}C for its dehydration and volatilization. The local industries in Gulbarga are using fuller's earth for oil purification process after treating it with HCl. However, further treatments like alkali fusion and hydrothermal treatment may increase its adsorption power since alkali fused and hydrothermal treated Fuller's earth converts to a porous crystallinity.

In this work, the locally available Fuller's earth has been alkali fused and hydrothermally treated to produce a zeolite and characterized.

1.1. Related work

Various investigators used clays such as bentonite, kaolin, rectorite, etc as a source material for the synthesis of different types of zeolites, as given in Table 1.

In our present research, an effort has been made to utilize Fuller's earth from the Gulbarga region of Karnataka, India, to produce an industrially useful and competitive zeolite, which can used as an adsorbent.

Table 1: Literature on zeolite synthesis

Authors	Raw material	Synthesis route	Type of zeolite obtained	Application of the zeolite	References
M. Mezni, A. Hamzaoui, N. Hamdi, E. Srasra	Illite clay	Alkali fusion-hydrothermal	Na (chabazite type zeolite)	For Cation exchange capcity	10
Ian D.R. Mackinnon, Graeme J. Millar, Wanda Stolz	Kaolinite and Montmorillo-nite	Alkali fusion-hydrothermal	N (anedingtonite EDI frame work zeolite)	For Cation exchange capcity	11
Mansoor Kazemimoghadam, Toraj Mohammadi	Kaolin	Alkali fusion-hydrothermal	HS (hydroxy sodalite type zeolite)	For separation of mixtures	12
Ian D.R. Mackinnon, Graeme J. Millar, Wanda Stolz	Kaolin	Alkali fusion-hydrothermal	K-F (a structural code for EDI type zeolite)	For Cation exchange capcity	13
Yunan Ma, Chunjie Yan, Aref Alshameri, Xiumei Qiu, Chunyu Zhou, Dan li	Low grade Kaolin	Alkali fusion-hydrothermal	13X (faujasite type zeolite)	----	14
Haiyan Liu, Tong Shen, Tiesen Li, Pei Yuan, Gang Shi, Xiaojun Bao	Rectorite	In-situ	P (a zeolite of alumina to silica molar ratio 1.66)	----	15
Chao Chen, Dong-Wha Park, Wha-Seung Ahn	Bentonite	Alkali fusion-hydrothermal	13X	For CO_2 capture	16
Mousa Gougazeh, J.-Ch. Buhl	Jordian Kaolin	Alkali fusion-hydrothermal	A (silicate group zeolite linde A type) and HS	-------	17
E.B.G. Johnson, Sazmal E. Arshad and Jahimin Asik	Kaolin	Hydrothermal route	A	-------	18
Dr. Phyu Phyu Win	Clay	Hydrothermal route	X (a zeolite of silica to alumina molar ratio 1,25)	Ion-exchanger	19
M. A. Moneium and Ezzat A. Ahmed	Clay	Alkali fusion-hydrothermal	Na-X (a zeolite of silica to alumina ratio 3)	For removing heavy metals from aqueous solution	20

2. Equipment, materials, reagents and methods

2.1. Equipment:

The following major equipments were used in the synthesis: A high temperature muffle furnace for alkali fusion of the raw material, magnetic stirrer to carry ageing of the fused product, a temperature controlled water bath for hydrothermal treatment of the aged product, hot air over to dry the samples, X-ray fluorescence (ARL/XRF- 8600) to analyze chemical composition of raw material, powder X-ray diffractometer to carry out diffraction studies (Bruker AXS D8 Advance), Fourier Transform Infrared spectrometer (PerkinElmer UATR) to study the structural features of raw material used as well the end product, and surface area analysis (SMART SORB-93) for raw material and product.

2.2. Raw material and reagents

The raw material for the synthesis of zeolites was Fuller's earth obtained from Khooba Fuller's Earth Works, Gulbarga district, Karnataka, India. Reagents used were Hydrochloric acid for the removal of iron from fuller's earth and Sodium Hydroxide solution for alkali fusion of the raw clay.

3. EXPERIMENTAL METHODS

3.1.1. Zeolite synthesis

Calcination: Fuller's earth obtained from Fuller's Earth Works was powdered and screened through a 110 mesh screen. It was then calcined in a muffle furnace at 870 °C for 2 h to remove volatile and organic matter.

Acid treatment and alkali fusion: Calcined Fuller's earth was then treated with 5M HCl to remove iron and the digested material thoroughly washed with distilled water and dried. A few grams of acid digested material was taken in a nickel crucible and mixed with 5M NaOH, in a predetermined ratio and kept in a muffle furnace and heated to 850 °C for 5h. The resulting material after fusion was cooled down to room temperature.

Ageing: Ageing of fused sample was carried by mixing a few grams of fused sample with optimum amount of distilled water in a Teflon container, and the mixture was stirred for 32 h at room temperature to aid the formation of gel like precursor for hydrothermal treatment.

Hydrothermal treatment: The aged material was mixed with distilled water taken in a Teflon bottle and kept in a constant temperature water bath maintained at 85 °C for 6 h. The

product zeolite formed was then washed thoroughly with distilled water in order to remove excess / un reacted alkali, filtered and dried at 110 °C in an air oven.
The processing flow chart for the synthesis of zeolite is shown in Fig. 1

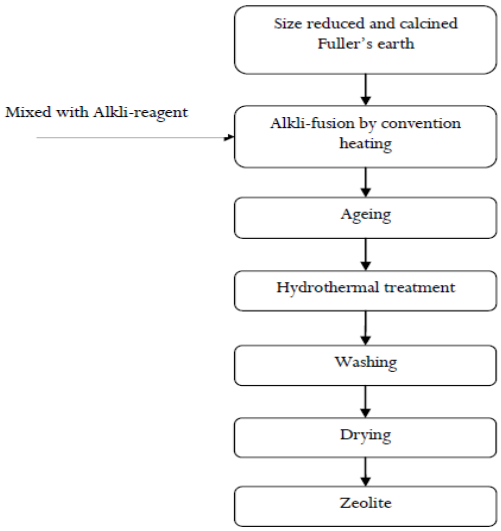

Fig. 1: A General flow diagram for the Synthesis of Zeolite by conventional method

3.1.2. Property determination

The properties / specifications of the raw material Fuller's earth like Silica/Alumina ratio, loss on ignition, specific gravity, and pH are given in Table 2.

Table 2: Specifications of Fuller's earth

Specifications of Fuller's earth	
SiO_2/Al_2O_3	5.011
Particle size range	212µ to106µ
Average particle size	~160µ
Specific gravity	2.4
pH	8
Langmuir surface area	101 m^2/g
Loss on ignition	11.1%

Silica/Alumina ratio is the molar ratio of silica to alumina present in the Fuller's earth, determined from XRF analysis.

Loss on ignition (LOI): The raw material Fuller's earth was first heated to 900 °C for 2 hr to remove the volatile matter present in it. The percentage loss on ignition of the raw material was determined by:

$$\% LOI = \frac{W_2}{W_1} \times 100$$

Where,
W_1 = Weight of raw sample before firing
W_2 = Weight of sample after firing at 900 °C for 2 h

Specific gravity (G_s): The specific gravity of the raw material was determined by pycnometric method using the formula:

$$\text{Specific gravity } G_S = \frac{W_0}{W_0 + (W_A - W_B)}$$

Where,
W_0 = weight of dry sample
W_A = weight of pycnometer filled with water
W_B = weight of pycnometer filled with water and sample

pH of raw sample (FE): About 10 g of dried clay sample is taken in a 1000 mL beaker. 300 mL of freshly boiled and cooled water (adjusted to pH 7) is added to the clay sample in the beaker and heated to boiling. Digestion is carried out for 10 minutes and the solution filtered while hot, rejecting the first 20 mL of the filtrate. The filtrate is cooled to room temperature and its pH determined using glass electrode (BIS) [21, 22].

Chemical composition: The chemical analysis of oxides present in the Fuller's earth was determined by X-ray Fluorescence. The composition is given in Table 3.

Table 3: Oxide composition of Fuller's earth

Chemical compound	Weight %
SiO_2	48.523
Al_2O_3	9.682
Fe_2O_3	18.809
CaO	17.042
MgO	3.971
K_2O	1.768
Na_2O	0.139
SO_3	0.065

Characterization of Fuller's earth: The phase composition of Fuller's earth was determined by XRD and it is given in Table 4. FTIR analysis for the raw material, calcined product and the product zeolite was also carried out and the patterns are shown in Fg.4. The surface area of Fuller's earth and final product zeolite was also determined by dynamic BET method.

4. RESULTS AND DISCUSSION

Zeolite synthesis: In the synthesis of zeolite, the raw material Fuller's earth was first treated with 5M HCl to remove unwanted minerals and iron, as much as possible, that may significantly affect the formation and crystallinity of zeolite and act as a poison during catalytic application of the final product [23- 27]. The purpose of calcination of the thoroughly washed acid treated material at 850 °C is to remove the volatile matter and to destroy its structure and convert it to more reactive metakaolin. This metakaolin is fused with the alkali reagent 5M NaOH in order to decompose the aluminosilicate in the raw material into soluble sodium aluminosilicate [28] and to aid in zeolite formation during hydrothermal process, in the

alkali reagent Na^+ cation play a significant role in zeolitization and more over sodium ions are known to stabilize the sub-building units of zeolite frameworks. The fused material is then aged in a Teflon container under continuous stirring for about 32 h, to develop tiny nuclei in the material during ageing period [29]. An effective ageing process will reduce the duration of the hydrothermal treatment step [30]. The aged material was then treated hydrothermally in a constant temperature water batch at 85 °C, during which tiny nuclei of aluminosilicates crystallizes into zeolites.

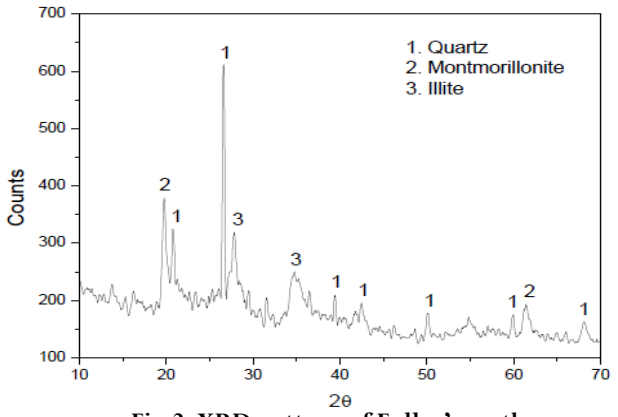

Fig.2: XRD pattern of Fuller's earth

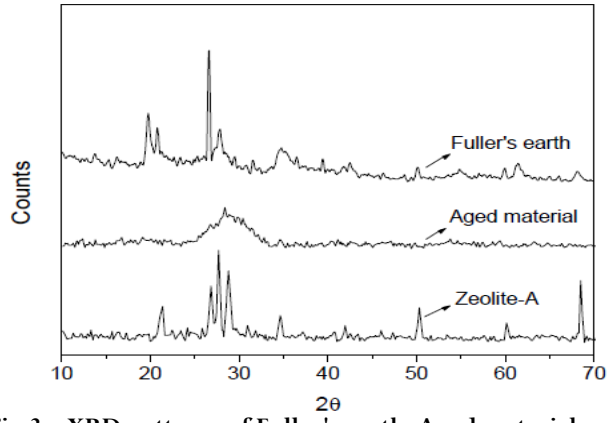

Fig.3: XRD patterns of Fuller's earth, Aged material and Zeolite-A

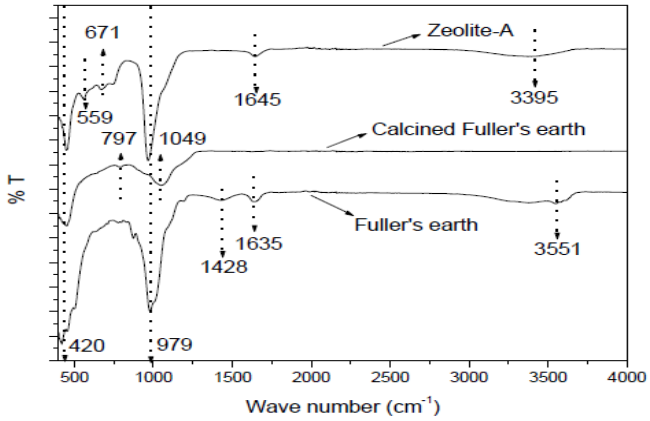

Fig. 4 FTIR pattern of Fuller's earth, Calcined Fuller's earth and Zeolite

Phase analysis of raw material, aged and final product zeolite: The phase analysis of Fuller's earth was carried by XRD and Fig.2 shows the major peaks for quartz, montmorillonite and illite and their phase compositions are given in Table 4. Fig. 3 shows a combined XRD pattern for the raw material, aged material and the final product zeolite. In this figure, the aged sample clearly shows amorphosity of the soluble sodium aluminosilicate in the gel material formed after ageing. The XRD pattern of the zeolite formed from this amorphous material, indicates conversion to crystalline state. The zeolite-A formed was confirmed by JCPDS Card No. 860188, ICSD: 080883, System: Cubic, Lattice: Primitive, Chemical composition: $Al_2Si_{12}O_{48}$ and chemical name: Sodium Aluminum Silicate. Table 5. shows the peak matching (2θ) of the JCPDS values with the values of the product zeolite.

Table 4: XRD phase analysis of Fuller's earth

Material	Compounds	Chemical formula
Fuller's earth	Quartz	SiO_2
	Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2.Si_4O_{10}(OH)_2.xH_2O$
	Illite	$KAl_2(Si_3Al)O_{10}(OH)_2$

Table 5: Peak matching for the synthesized zeolite-A

Peak Number (Decreasing intensity)	2θ	
	JCPDS values	Actual value
Peak 1	27.20	27.695
Peak 2	67.9	68.477
Peak 3	21.73	21.389
Peak 4	49.86	50.296

FTIR analysis: FTIR pattern of FE, calcined FE and zeolite-A is shown in Fig. 4.

In the FTIR pattern of Fuller's earth the characteristic bands of aluminosilicate phases and quartz are identified from 420 cm^{-1} to 550 cm^{-1} and 900 cm^{-1} to 1200 cm^{-1} regions. The OH bending vibrations, Si-O vibrations and Al-O vibrations are found between 1200 cm^{-1} to 400 cm^{-1}. The bands in the raw clay near 420 cm^{-1} and at 496 cm^{-1} indicates the bending mode of Si-O-Si vibrations and were of T-O bending mode (where T is of Si or Al) [31]. Similarly the band near 973 cm^{-1} in the raw clay refers to asymmetric stretching mode of Si-O-Si vibrations and assigned to T-O stretching mode and the band near 873 cm^{-1} refers to OH- bending vibrations [32]. The band at 777 cm^{-1} refers to quartz of Si-O-Si vibrations.

In the FTIR pattern of calcined FE, the band near 452 cm^{-1} is assigned to tetrahedral T-O vibrations (T is of Si or Al).

In the FTIR pattern of zeolite-A, its structural information can be observed between the vibration frequencies from 200 cm^{-1} to 1500 cm^{-1} [33, 34]. The bands from 450 cm^{-1} to 678 cm^{-1} are designated to the internal shrinkage-linkage vibrations of TO_4-Tetrahedral and owing to symmetrical stretching. The broad peak at 3395 cm^{-1} and at 1645 cm^{-1} is of O-H stretching and bending. The bands at 967 cm^{-1} is assigned to asymmetric stretching vibrations of Si-O-Si bond with Si_4 [35,36]. The broad band at 3362 cm^{-1} and at 1647 cm^{-1} refers to zeolite water, i.e. the water molecules present in the zeolitic (porous) channels [37]. At the band 558 cm^{-1}, crystallization of zeolite begins and at this band of weak intensity, the presence of zeolite is indicated [38].

Surface area of zeolite: The surface area of the synthesized zeolite was determined by N_2 adsorption-desorption using SMART SORB-93 surface area analyzer. The surface area of raw fuller's earth was 101 m^2/g and that of synthesized zeolite is 173 m^2/g. An increase in surface area of about 73 m^2/g was observed.

5. CONCLUSION

In this work, zeolite-A was successfully synthesized from a locally available clay at the Sulepeth village, in the Gulbarga district of Karnataka, India. Addition of alkali activator (NaOH) for fusing the raw material, completely dissolved the crystalline phases of silica, illite and montmorillonite present in it into sodium alumnosilicate, that was converted to amorphous form after ageing, which produced the zeolite after hydrothermal treatment. The XRD studies confirmed the presence of zeolitic phases in the end product. FTIR studies indicate characteristic vibrations of zeolitic material and zeolite water. Surface area studies indicate an increase in surface area of about 73 m^2/g for the synthesized zeolite-A, when compared to the raw FE.

Hence, the local clay used in this study, is suitable for the synthesis of different types of zeolites by varying the experimental conditions, and such zeolite can be utilized for many industrial applications; especially as an adsorbent. Further work is being carried out to evaluate the effectiveness the synthesized zeolite as ion exchangers, adsorbents and catalysts.

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