

Zeolite Synthesis from Waste and its Applications: A Retrospective

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Abstract:- The zeolites have enormous applications in the removal of various toxic materials like pesticide, ammonium ions and heavy metals from wastewater, protection of the environment from radioactive waste, emission control from gasoline used vehicle and so on. This short review focuses on the zeolites as molecular sieves and explains its effectiveness in agriculture, aquaculture industry, biomedical engineering, and petroleum refining process. A debate of types of natural and synthetic zeolites and their comparison has been also cited. The process involved for the synthesis of various zeolites from waste like fly ash, blast furnace slag, municipal solid waste ash, rice husk ash, paper sludge, lithium slag and from kaolin is described. Finally, the chemical compositions of the above-mentioned wastes are shown after reviewing various articles.



❖ Pictorial Representation of Abstract

Keywords:- Zeolites; Molecular Sieve; Waste; Environment.

I. INTRODUCTION

Zeolites (clinoptilolite) are volcanic tuff minerals, which are formed when ash and lava from a volcano have a chemical reaction with cool sea water, are naturally negatively charged with a cage-like structure. The most prominent features of Zeolites include the exchange of cations and absorption of inorganic and organic molecules of specific dimensions. Their high mechanical strength, chemical stability, and abrasion values make Zeolites a special material for water purifications and many more applications. The negative charges act as a magnet to attract positively charged toxins and heavy metals to the Zeolites. It

is a micro-porous mineral i.e. the crystal structure shows relatively large cavities interlinked by channels with diameter 0.2 to 0.7 nm, whose application covers as a catalyst in many industrial purposes like water purification and air purification. The tetrahedron structure [Fig.-1] of Zeolites is hydrated Sodium aluminosilicates and general formula is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x=2-10$ and $y=2-6$.

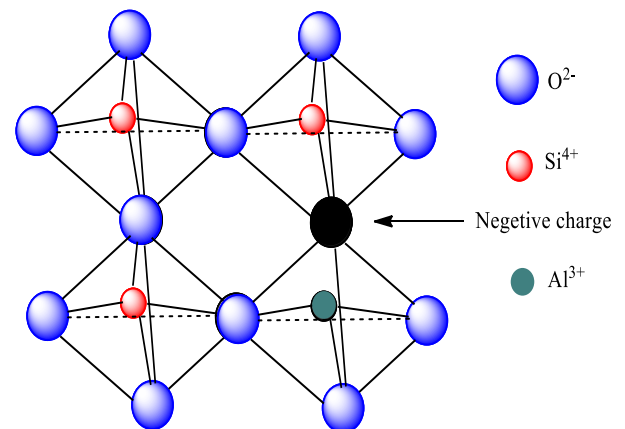


Fig 1:- The ideal configuration of Zeolite assembly of tetrahedral with Si/Al exchange yielding negative charge [6]

The natural occurred Zeolites are the glauconites or greensand, are used for water softening. Permutites are the synthetic Zeolites, which are mostly used in water softening. They have the capacity of ion exchanging and odor removal in a water softener. Due to more porous, glassy, and have the higher softening capacity, the Permutites are better than greensands. Zeolites are typically soft to relatively hard, light in density, insoluble in water but can be active as base exchangers in contact with water containing cations. Hence, these are capable of taking out Ca^{2+} and Mg^{2+} ions from water when hard water passes through it. This is due to the volume of cavities that is 20 to 50 % of the total volume of the Zeolite. In these cavities, the univalent and bivalent cations of alkali metals and alkali earth metal (Na, K, Ca) are found surrounded by water molecules. The elements can be replaced by other elements present in the surrounding of zeolites. Compared to polymeric ion exchangers (sulfonated and aminated copolymer of styrene and some percentage of divinylbenzene) Zeolites have higher stability and easy rejuvenation capacity [1].

A. Structure and Properties

Zeolite, a three-dimensional porous structure having molecular sieve type A and molecular sieve type X, is the readily available commercial adsorbents. Due to the occurrence of alumina, Zeolite exhibits a negatively charged scaffold in which cations can be exchanged in the pore with aperture dimensions 2-10 Å. The sodium type of Zeolite A has a pore size of about 4 Angstrom called 4A molecular sieve. When sodium ion is exchanged with the larger potassium ion, the pore size reduces to around 3 Angstrom called 3A molecular sieves. When one calcium ion replaces two sodium ions, then pore size increases to 5 Angstrom called 5A molecular sieve. The sodium form of Zeolite X has pore size approximately 8 Angstrom (Fig. 2) [42]. There are 4 types of Zeolite based on pore diameter. These are (i) Small

pore Zeolite with diameter 0.3-0.45nm having 8 rings. (ii) Medium pore diameter 0.45-0.6 nm having 10 rings. (iii) Large pore Zeolite with diameter 0.6 -0.8 nm having 12 rings. (iv) Extra-large pore Zeolite with 0.8-1.0 nm having 14 rings [29].

Zeolite (especially Chabazite) as a molecular sieve, has the ability to absorb small size gas molecules, was found out in 1930. The adsorption on the molecular sieve is reliant on two substantial molecular properties. (a) Bulk size and shape i.e. molecules having a larger size than pore cavity of molecular sieve can't be adsorbed while smaller molecules can. (b) Molecular polarity i.e. molecules exhibiting larger polarity can be adsorbed under certain conditions [2, 4].

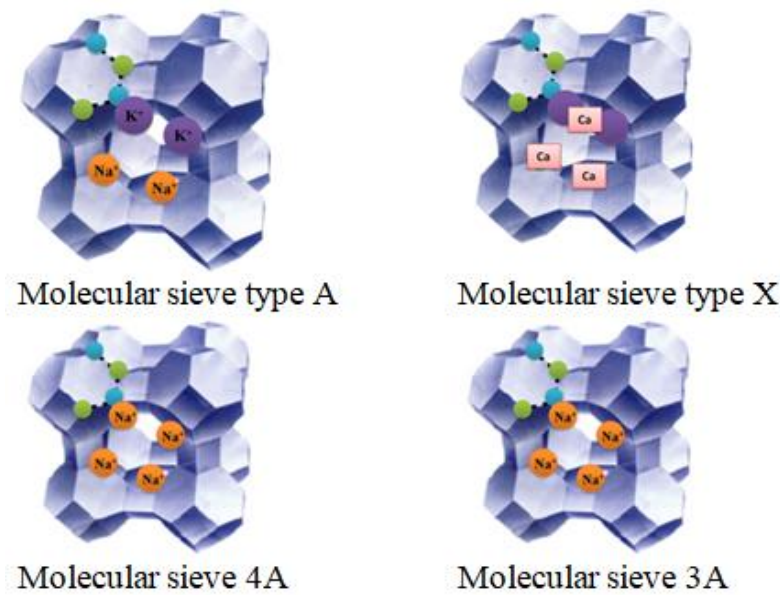


Fig 2:-Different type zeolites as molecular sieve [42]

B. Natural Zeolite and Synthetic Zeolite

There are numerous types of natural Zeolites (Table1) with different chemical compositions and crystal structures, mined from different parts of the world. The other factors like particle density, molecular pore size, strength, and cation selectivity may differ from Zeolite to Zeolite. Some of the viable Zeolites are A, Beta, Mordenite, Y, ZSM-5 etc.

The basic differences among natural and synthetic (man-made) Zeolites are

- Synthetics are developed from energy consuming chemicals Whereas naturals are processed from natural ore bodies.
- Synthetic Zeolites have a silica to alumina ratio of 1:1, while clinoptilolite (clino) Zeolites have ratio 5:1.

- Clino natural Zeolites do not rupture in a slightly acidic environment, whereas synthetic Zeolites do. The natural Zeolite constitution has more acid opposing silica to hold its structure mutually. The clino is mostly used for the agricultural industry as a soil amendment and as an aquafeed preservative.

Between natural and synthetic Zeolite (say Zeolite 5A and 13X) the ammonium ion (NH₄⁺) removal efficiency from a water source like surface water, groundwater, industrial or household wastewater is similar at low ammonium concentration. But Synthetic Zeolite ZSM-5 has much higher NH₄⁺ removal capacity [3].

Types of Zeolite	Elemental blueprint	Structure Type	Symmetry, Space Group
Clinoptilolite	$(K_2, Na_2, Ca)_3Al_6Si_{30}O_{72} \cdot 21H_2O$	HEU	Monoclinic, C2/m
Mordenite	$(Na_2, Ca)_4Al_8Si_{40}O_{96} \cdot 28H_2O$	MOR	Orthorhombic, Cmcm
Chabazite	$(Ca, Na_2, K_2)_2Al_4Si_8O_{24} \cdot 12H_2O$	CHA	Rhombohedral or triclinic P1
Phillipsite	$K_2(Ca, Na_2)_2Al_8Si_{10}O_{32} \cdot 12H_2O$	PHI	Monoclinic, P21/m
Scolecite	$Ca_4Al_8Si_{12}O_{40} \cdot 12H_2O$	NAT	Monoclinic, Cc
Stilbite	$Na_2Ca_4Al_{10}Si_{26}O_{72} \cdot 30H_2O$	STI	Monoclinic, C2/m
Analcime	$Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$	ANA	Cubic Ia3d
Laumontite	$Ca_4Al_8Si_{16}O_{48} \cdot 16H_2O$	LAU	Monoclinic, C2/m
Erionite	$(Na_2K_2MgCa_{1.5})_4Al_8Si_{28}O_{72} \cdot 28H_2O$	ERI	Hexagonal P63/mmc
Ferrierite	$(Na_2, K_2, Ca, Mg)_3Al_6Si_{30}O_{72} \cdot 20H_2O$	FER	Orthorhombic, Immm Monoclinic, P21/n

Table 1:- Types of Natural Zeolites with different chemical Compositions and structures [3]

Out of 63 natural Zeolite, only six Zeolites named as analcime (ANA), chabazite (CHA), clinoptilolite (HEU), erionite (ERI), mordenite (MOR) and phillipsite (PHI), are available in huge quantity. Mordenite and ferrierite are prepared in large quantities because synthetic mordenite has large pores compared to natural mordenite [4].

Apart from synthetic mordenite and ferrierite, the other synthetic aluminosilicate Zeolites are Linda Type –A (LTA), Linda Type-B (GIS), Linda Type X and Y, silicate-1 and ZSM-5(MFI). Other synthetic Zeolites or pure silica analogs (aluminosilicates) are Beta (BEA), Linda Type-F(EDI), Linda Type-L (LTL), Linda Type-W(MER), and SSZ-32(MTT). Linda Type-A is the first synthetic Zeolite to be used as an adsorbent to eradicate oxygen from argon [4].

II. SYNTHESIS OF ZEOLITES

More than 180 synthetic Zeolites are accessible now. Due to spotlessness of crystalline product and uniform particle sizes, the synthetic Zeolites are used commercially. Between 1930 and 1945, R. M Barrer[43] worked on Zeolite adsorption and synthesis. He classified Zeolite mineral depending on the size of the molecule absorbable capacity into 3 types i.e. quickly, gradually and not significantly at room temperature or above. Between 1949 and 1954, Milton and D.W. Breck discovered various types of commercially required Zeolites like type A, X, and Y(see figure-3)[44, 45]. Union Carbide was the first to proclaim synthetic Zeolite as an industrial material for separation and purification [4, 5].

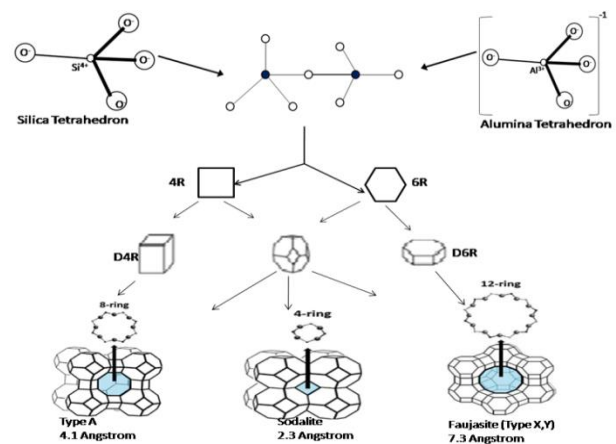


Fig 3:- Three different Zeolites [6]

Synthetic Zeolite with higher SiO₂ performs better hydrothermal constancy, stronger acid catalytic exercise, and superior hydrophobicity as an adsorbent. When SiO₂ content is lowered, it gives better cation exchange capacity (CEC) and superior adsorbent for polar molecules. Depending on end-use, the synthesis process follows the percentage of materials. At higher silica deposition, the crystallinity of Zeolite A remains unaffected but oxygen, nitrogen, and argon adsorption capacity decrease. 3A and 5A molecular sieve are prepared by the cation exchange of synthetic Zeolite type NaA with potassium and calcium. Faujasite-type Zeolite i.e. Zeolite X having large microporous can be used for decontamination and separation of gases and organic components. It can also be used as adsorption of heavy cations and radionuclides [2, 5, 6, 49].

To amalgamate Zeolite (through hydrothermal crystallization of aluminosilicates) from raw material like commercial silica sources like silica gel silica fumes or amorphous solid and different aluminum like alumina, sodium aluminate, (NaAlO_2) is quite expensive. So it is better to use cheaper raw materials like clay, natural Zeolite, pulverized fuel ash (fly ash), municipal solid waste fly ash, GGBS (ground granulated blast furnace slag), lithium slag and paper sludge ash. These raw materials are the wastes, which destroy the equilibrium of the environment and ecosystem [5].

A. Flyash-based Zeolites Synthesis

Fly ash is the byproducts of the pulverized coal from various thermal power plants. In India, approximately 112 million tones are produced annually and it will reach 225 million ton by the end of 2017. If these fly ashes are not managed properly, it will go to the sea/river and will cause damage to the aquatic ecosystem. It also contaminates groundwater because fly ash contains heavy metals as well as toxic particles. Depending on the source, the fly ash mainly contains silicon dioxide (SiO_2) (both amorphous and crystalline), Aluminium oxide (Al_2O_3) and calcium oxide (CaO). The chemical compositions of fly ashes are given in the following table (table-2)[7].

Molecules present	Chemical composition (wt %)
SiO_2	51.5
Al_2O_3	23.63
Fe_2O_3	15.3
CaO	1.74
TiO_2	1.32
P_2O_5	1.31
MgO	1.2
K_2O	0.84
Na_2O	0.38
SO_3	0.28
MnO	0.13
Loss of Ignition	1.78

Table 2:- Average chemical composition of fly ash determined by XRF [7]

As fly ash is rich in aluminosilicate component, it can change to Zeolite crystal by alkali hydrothermal reaction. The alkali sources are NaOH , Na_2CO_3 , and KOH which can be used to prepare the fly ash slurry having a solid-liquid ratio $100\text{g}/400\text{cm}^3$. Then this slurry will agitate in the 800cm^3 autoclave at the temperature of 250°C to 120°C for 24 hours. Actually, Zeolite synthesis from coal-based fly ash involves three processes (a) dissolution of Si^{4+} and Al^{3+} in fly ash. (b) Formation of aluminosilicate gel through condensation of silicate and aluminate ion in alkali solutions. (c) Crystallization of aluminosilicate gel to make Zeolite crystals. Generally, Zeolite P and Chabazite are synthesized from fly ash [8]. G.G Hollman et al (1999) synthesized pure Zeolite (Na-P1, Na-X, Na-A) of 85 gram from 1 kg of fly ash by incubated fly ash at 90°C with an

alkali solution. They synthesized the pure form of zeolite in two-step synthesis method after adjusting the Si/Al molar ratio to 0.8-2 by adding aluminate solution. They demonstrated that pure Zeolite has CEC ranged from 3.6 to 4.3 meq/g and Zeolite with residual of fly ash had CEC 2.0 to 2.5 meq/g. They had also shown that pure Zeolites are efficient for the removal of ammonium ions and heavy metal ions from wastewater. To obtain different types of Zeolite (table-3), the conversion of fly ash into Zeolite is depends on different activation solution to fly ash ratios, temperature, pressure and reaction time. The alkaline solution with different molarity, temperature range from 80 - 200°C and reaction time with 3 to 48 hours have been preferred in order to get 13 different types of Zeolite from fly ash [9, 10, 50].

Name of Zeolite	Chemical Formula	JCPDS
Na-P1 Zeolite	$\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 12\text{H}_2\text{O}$	39-0219
Phillipsite	$\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot \text{H}_2\text{O}$	30-0902
K-Chabazite	$\text{K}_2\text{Al}_2\text{SiO}_6\cdot \text{H}_2\text{O}$	12-0194
Zeolite Flinde	$\text{KAlSiO}_4\cdot 1.5\text{H}_2\text{O}$	25-0619
Herschelite	$\text{Na}_{1.08}\text{Al}_2\text{Si}_{1.68}\text{O}_{7.44}\cdot 1.8\text{H}_2\text{O}$	31-1271
Faujasite	$\text{Na}_2\text{Al}_2\text{Si}_{13}\text{O}_{38.8}\cdot 6.7\text{H}_2\text{O}$	12-0228
Zeolite A	$\text{NaAlSi}_{1.1}\text{O}_{4.2}\cdot 2.25\text{H}_2\text{O}$	43-0142
Zeolite X	$\text{NaAlSi}_{1.23}\text{O}_{4.46}\cdot 3.07\text{H}_2\text{O}$	39-0218
Zeolite Y	$\text{NaAlSiO}_{2.43}\text{O}_{6.86}\cdot 4.46\text{H}_2\text{O}$	38-0239
Perialite	$\text{K}_0\text{NaCaAl}_{12}\text{Si}_{24}\text{O}_{72}\cdot 15\text{H}_2\text{O}$	38-0395
Analcime	$\text{NaAlSi}_2\text{O}_6\cdot \text{H}_2\text{O}$	19-1180
Hydroxyl-sodalite	$\text{Na}_{1.08}\text{Al}_2\text{Si}_{1.68}\text{O}_{7.44}\cdot 1.8\text{H}_2\text{O}$	31-1271
Hydroxyl-cancrinite	$\text{Na}_{14}\text{Al}_{12}\text{Si}_{13}\text{O}_{31}\cdot 6\text{H}_2\text{O}$	28-1076
Kalsilite	KAlSiO_4	33-0988
Tobermorite	$\text{Ca}_3(\text{OH})_2\text{Si}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$	19-1364

Table 3:- Zeolite and other neomorphic phases synthesized from fly ash and a joint committee of powder diffraction standard (JCPDS) codes for XRD detection [10].

B. Synthesis of Zeolites from Blast Furnace Slag

Blast furnace slag (BFS) is a nonmetallic co-product, produced when pig iron is manufactured. In the manufacture of iron, iron ore, or pellets, flux like limestones or dolomites are fed to blast furnace with coke as a burning agent. At the temperature of 1500°C-1600°C, the molten slag floats above the molten iron and then molten iron is taken out. Then molten slag is water quenched, dried and then crushed to required sizes. It looks like glassy granulates; yellow/green colored having a sulfurous odor with mildly alkaline and having specific gravity 2.9. BFS is primarily composed of silicates, aluminosilicates, and calcium-alumina –silicates. Depending on cooling criteria, the slag is of various types such as air-cooled blast furnace slag, expanded or foamed blast furnace slag, pelletized blast furnace slag, and granulated blast furnace slag. The chemical compositions of BFS in Indian condition are as given in the table -4.

Chemical composition	Range (%)
Calcium oxide (CaO)	31%-40%
Silicon dioxide (SiO₂)	29%-38%
Aluminum Oxide (Al₂O₃)	14%-22%
Magnesium Oxide (MgO)	7%-11%
Ferrous Oxide (FeO)	0.1%-1.9%
Manganese Oxide (MnO)	0.01%-1.2%
Sulfur	1%-1.9%
Basicity (CaO/SiO₂)	0.9%-1.3%

Table 4:- Chemical composition of BF Slag (ispatguru.com)

Yoshiyuki SUGUNA et. al (2005) investigated the alkali hydrothermal synthesis of Zeolite A. They suggested that the most favorable slag composition of synthesis of Zeolite A, are a molar ratio of Si to Al should be 1 and CaO percentage should come down to 15. When they used BF slag having Si/Al molar ratio 1.95 and CaO+MgO=49.15 mass percentage through direct hydrothermal treatment, the product was tobermorite (a calcium silicate hydrated mineral) and hydrogarnet (calcium aluminate hydrated mineral). Then they synthesized Zeolite-A (82%) with tobermorite and hydrogarnet using melted BF slag maintaining the composition of CaO+MgO to 15% with Si/Al molar ratio to 1. In the same way, they synthesized Zeolite Na-P1 from direct BF Slag after maintaining the composition of CaO+MgO to 15%. The resulted Na-P1 Zeolites were 50% and tobermorite plus hydrogarnet were 50%. Furthermore, they synthesized taking the same composition and molar ratio with the raw materials BF slag, SiO₂, and NaAlO₂. The result was 75% of Zeolite A and rest were tobermorite and hydrogarnet. So, they synthesized the Zeolite-A using BF slag and alkali solution using a rotating ball type reaction vessel containing SiC balls taking the above conditions. He found that at 873K temperature synthesis of Zeolite A, is stable [11].

Yasutaka Kuwahara et al (2007) synthesized FAU Zeolite i.e. Y-Zeolite, X-zeolite from steel slag (BF slag) through hydrothermal thermal treatment. First, they treated the slag with acid for removal of CaO species. Then, to enhance a hydrophobic surface property of Zeolite and photocatalytic degradation of organic pollutant present in the liquid, they added nano-sized TiO₂. Due to the presence of TiO₂, the adsorption properties of Zeolite increases [12].

From the iron smelting progression, cupola slag is the byproduct containing lime and amorphous silica with another oxide. Cupola furnace (CF slag) slag and Blast furnace slag are quite similar by their properties, (see the table-5) chemical composition, and nature. Basicity, i.e. when a base replaces hydrogen atom, is one of the most significant chemical properties of slag. Basicity of BF slags in the region of acid slag whereas the CF slag has basicity between acid to base slag [13].

In India, there is a huge amount of unused slag creating a barrier to waste management. So there are various innovation approaches, to minimize the waste, for converting the waste into various value-added products. Rewadee Anuwattana et al (2008) synthesized high silica Zeolite after treating the Cupola slag in acid to remove other oxide impurities. Generally, the high silica Zeolite is ZSM-5, has been used as a catalytic converter of ethanol to hydrocarbons, polymerizations, dehydrogenations, isomerization, and reduction of NO. In fluidized catalytic cracking (FCC) and fine chemical production, ZSM-5 type catalysts are largely used. They synthesized ZSM-5 zeolite using both hydrothermal heating and microwave heating at temperature 130-200°C. Both acids treated and untreated cupola slags along with NaOH are used as precursors. In conventional hydrothermal heating, the particle size of ZSM-5 was 3 µm wherein microwave heating the size was 0.3 µm. They suggested that the optimum condition of ZSM-5 Zeolite is 150°C for 24h by conventional heating and the configuration of Zeolite crystals increased by 4 times at 150°C in microwave heating than conventional heating [14].

	CaO	SiO ₂	Al ₂ O ₃	MgO	MnO	FeO
BF Slag	36-50	25-55	5-20	0.5-30	1-4	1-15
CF slag	20-25	30-42	7-18	2-12	0.4-1.1	0.4-1.1

Table 5:- Comparison of Chemical composition of BF slag and CF slag [13].

C. Zeolites from Municipal Solid Waste (MSW) Fly Ash

Due to urbanization and population growth, the solid waste is increasing day by day. Presently, India produces 42-45 million tons of municipal solid waste annually and it is increasing 5% annually. Solid waste management is a major concern in various municipal bodies as it affects the healthy environment of the city. If we characterize the MSW we find 30-55% matters are biodegradable or compostable which can be used as fertilizer. 40-45% inert material goes for landfill and 5-10% is recyclable materials.

In developed countries like the USA, Japan, Municipal solid waste is incinerating to minimize the waste amount and to get energy from it. Due to the burning of MSW, the huge amount of Fly ash (called MSW incineration fly ash) is produced containing hazardous organics like dioxin, heavy metal etc.

The chemical composition and heavy metal in MSWI fly ash are given in the TABLE 6 [14].

Elements	Al	O	Na	Mg	Si	P	S	Ca	K	Ti	Fe	Cl
Content	1.76	28.09	3.87	1.28	4.24	0.50	3.51	28.87	6.71	0.54	2.48	18.15

Table 6:- Elements present In MSW fly ash by EDS (%) [14].

Mantong Jin et al (2011) experimented that heavy metal like Zn is highest and Hg is lowest (TABLE 7). They also evaluated the leaching extent of various heavy metals using the formula:

$$\text{Leaching rate} = \frac{\text{Leachate quality of heavy metals in the fly ash} \left(\frac{\text{mg}}{\text{kg}}\right)}{\text{Total mass of heavy metal in the fly ash} \left(\frac{\text{mg}}{\text{kg}}\right)} \times 100\%$$

In the fly ash, the leaching rate of heavy metal are in the order as follows

$$\text{Pd} > \text{Cr} > \text{Hg} > \text{Cu} > \text{Zn} > \text{Cd}$$

Heavy metal	Pb	Zn	Cu	Cr	Cd	Hg
Heavy metal content	3084	4745.6	587.6	160.8	125.04	5.84
Leachate concentration	577.6	30.68	6.34	8.39	0.02	0.2
Leaching rate	18.7	0.65	1.08	5.22	0.016	3.42

Table 7:- Basic properties of MSWI fly ash [14].

We have discussed the synthesis and process involved of making Zeolite from pulverized coal ash (fly ash) as both (fly ash and Zeolite) has similar chemical composition i.e. rich in aluminosilicates and high specific surface. Similarly, MSWI fly ash contains minerals like SiO₂ and Al₂O₃ and has a high surface area. But as compare to Coal fly ash, the quantity of SiO₂ and Al₂O₃ is less. G.C.C Yang et al (1998) have synthesized Zeolite from MSWI fly ash, following the same procedure in case of coal fly ash. They reported that the quality of Zeolite from MSWI fly ash is lower than another adsorbent like natural Zeolite and activated carbon. As our major concern is the environment, it is essential to use Zeolite that is synthesized from waste. They also reported that, after synthesis of Zeolite from MSWI fly ash, the residual liquid contains a high amount of heavy metal like Pd and Zn, which need to be treated properly. Yao et al (1999) synthesized tobermorite (Ca₅(OH)₂Si₆O₁₆·4H₂O) Zeolites from MSWI fly ash substituting Al. This tobermorite is used as removal of Cs⁺ and NH₄⁺ from wastewater [15, 16].

D. Synthesis of Zeolites from Rice Huskash (RHA)

Rice husk is a residue obtained through milling of rice grain and rice husk ash is produced after combustion of rice husk which has super pozzolanic properties. As India is the largest producer of rice in the world (approx 110 million tons), there are million tons of rice husk and rice husk ash. There is estimated that 200 kg of rice husk is removed from 1000 kg of rice grains. Generally, rice husk is used for power generation in the power plant (which uses the waste) as rice husk has the ability to burn 72 hours and give the temperature of 400-600°C. At high temperature, the amorphous silica of husk converted to crystalline silica. It has been found that the temperature regulation is the reason for the production of amorphous as well as crystalline silica. Crystalline silica comes under Group-1 hazardous materials as announced by

the International Agency for Research on Cancer (IARC) in 1997. This crystalline silica causes a respiratory problem such as asthma and damage of the tissue which gradually leads to cancer. As RHA contains abundant quantity (Table-8) of silica, hence needs the proper storage and utilization of it to a suitable application [17].

Chemical composition	Weight %
SiO ₂	99.64
Al ₂ O ₃	0.08
K ₂ O	0.04
Na ₂ O	0.00
P ₂ O ₅	0.10
CaO	0.04
SO ₃	0.03
Fe ₂ O ₃	0.04
CuO	0.01
MoO ₃	0.01
Other	0.03

Table 8:- Chemical analysis of RHA (XRF) [17]

W. Pampaet.al[17] reported that as RHA has a huge amount of silica it can be converted to silicate riched Zeolite i.e. ZSM-5. They synthesized ZSM-5 Zeolite through hydrothermal hydrolysis from RHA silica at 150°C under autogenous pressure in a reaction time 4-14 hours SiO₂/Al₂O₃ with molar ratios from 30 to 2075 were used. The finding was at 80 molar ratio (SiO₂/Al₂O₃), the result is optimum i.e. Zeolite obtained is 84% (w/w). Ajay K. Dalai et al [18] synthesized Sodium X Zeolite

($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2 \cdot 6\text{H}_2\text{O}$) from rice husk ash considering temperature range from 95 to 120°C and duration was from 1 to 24 hours. The molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ were 2 to 7, 2.4 to 10 and 96 to 890 respectively. The increment of temperature the formation products as follows Z-21 Zeolite \rightarrow NaX Zeolite \rightarrow High silica Zeolite \rightarrow analcime was also reported. NaOH plays an important rule for conversion from NaX Zeolite to High Silica Zeolite. Also, time affects the NaX crystallization [17, 18]. Wang-cheng Tan et al [19] reported that the synthesis of Zeolite A (NaA) and Faujasite(NaY) from RHA which is used as catalysts and adsorbents. NaA and NaY are similar structure except for the no of member ring. These Zeolites are used in petroleum and petrochemical industry, removal of Zink ion as heavy metal and ammonium ions from wastewater and removal of sulfonamide antibiotic from aquatic species. They synthesized Zeolite as a following flowchart(figure-4)[19].

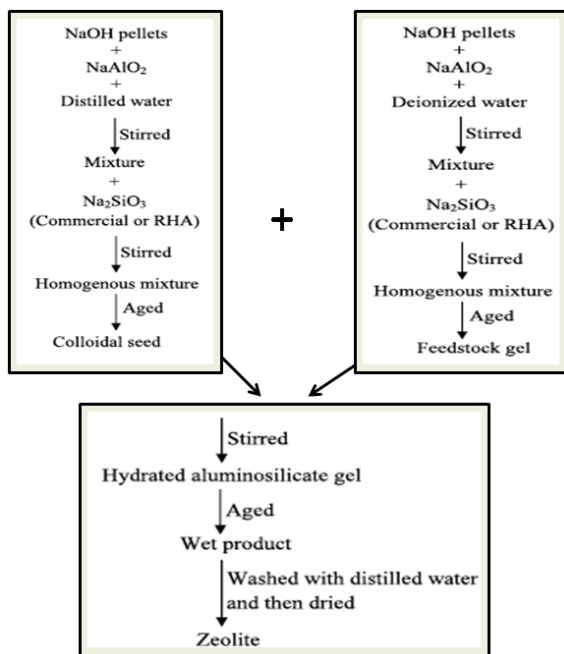


Fig 4:- Flow diagram of Zeolite synthesis [19]

E. Zeolites from Kaolin

Kaolin or clay is the mineral of kaolinite, is a two-layered aluminosilicate material having chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ appeared as white. The crystal system is triclinic in which tetrahedral plane of SiO_4 is connected through an oxygen atom to the octahedral plane of AlO_6 . It has the lowcation-exchange capacity as well as low shrink-swell-capacity [20]. The chemical characterization of low-grade natural kaolin is given in the table-9.

Component	Content (%)
SiO ₂	56.30
Al ₂ O ₃	29.52
Fe ₂ O ₃	1.32
MgO	0.35
CaO	0.056
Na ₂ O	0.056
K ₂ O	2.99
TiO ₂	0.28
P ₂ O ₅	0.32
MnO	0.012
H ₂ O	0.28
LOI	9.8

Table 9:- Chemical composition of low grade natural kaolin (weight %) [20].

Yanam Ma et al(2014) synthesized 13X Zeolite from low-grade natural kaolin after fusing it in NaOH followed by hydrothermal handling without adding extra Silicon material or dealumination. They reported that the optimum result i.e.a pure form of 13X Zeolite came when the fusion of kaolin follows NaOH/Kaolin weight fraction is 2 at 200°Cfor 4 hours. After fusion the paste was stirred at 50°Cfor 2 hours then crystallization carried out at 90°Cfor 8 hours [20]. MousaGaugazeh et al (2014) investigated to synthesize Zeolite A considering various concentrations of NaOH with natural kaolin from Jordan at 100°Cfor 20 hours. They obtained a mixture of Zeolite A, hydro silicate sodalite, and quartz. They reported that When NaOH concentration lies between 1.5-3.5 M the Zeolite is the main product with small traces of Quartz and hydro silicate sodalite [21].Jing-Quanwang et al (2014) synthesized Zeolite A without high-temperature calcination.They synthesized Zeolite A using a new method i.e. they added NaOH solution of various concentration. in raw kaolin then heated in a stainless steel autoclave at 10°C/min rise of temperature up to 190°Cfor some time then 240°Cfor some time. Then treated kaolin is leached by diluted HCl to remove unreacted solid residue followed by filtration. Then a gel of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is formed followed by hydration leads to Zeolite A. Comparing with Zeolite formed through calculations, Zeolite formed through above method shown a controlled size, high brightness and high cation exchange capacity [22]. Carolina ResminiMelo et al (2012) developed 5A zeolites via ionic exchange from 4A zeolite which was synthesized from kaolin. The 5A zeolite was performing satisfactory as an adsorbent for arsenic ions [23].

F. Zeolites from Lithium Slag

Lithium slag is an industrial waste, produced when lithium carbonate (Li_2CO_3) is manufactured by the sulfuric acid method when the ore named as spodumene ($\text{LiAlSi}_2\text{O}_6$) is calcined about 1200°C. There is a statistic, to produce 1-ton

lithium carbonate, 9 tons of lithium slag is discharged and a few tons are used as raw material for constructions. Lithium slag is yellowish in color generally amorphous silica and alumina (Si/Al is 2-3) having a large inner surface area as well as high porosity. Due to the presence of cheap Si and Al source(table-10), the lithium slag can be utilized for the synthesis of Zeolite through the hydrothermal process [24, 25].

Materials	Weight %
SO ₃	7.15
SiO ₂	53.22
Fe ₂ O ₃	1.48
Al ₂ O ₃	17.11
CaO	10.11
MgO	0.41
K ₂ O	0.53
Na ₂ O	0.33
LOI	8.25

Table 10:- Chemical composition of lithium slag (weight %) [24]

Dan Chen et al (2012) synthesized Zeolite NaX-1 by hydrothermal reaction with alkali fusion. They attained a high degree of conversion i.e.94.31% from lithium slag and high thermal stability. Comparing with commercial Zeolite NaX (0.3303 kg/kg), the NaX-1 Zeolite had shown similar water adsorption capacity (0.3208kg/kg) [25].Gua Lin et al (2015) synthesized co-crystalline Zeolite FAU/LTA (NaX or 13X) by a hydrothermal method from lithium slag.The Zeolite 13X has higher magnesium ion exchanging capacity than Zeolite 4A but lower calcium ion exchanging capacity. Then they utilized mother liquid which is generated at the process of synthesis of Zeolite contain a large amount of Silicon for the synthesis of FAU/LTA-1a and then adding NaAlO₂ added to prepare FAU/LTA-1b.The author's group analyzed both FAU/LTA-0(without mother liquid) and FAU/LTA-1b (with mother liquid) and found both have similar diffraction peak. From these, it is cleared that mother liquid can be recycled as it is derived from FTA/LAU-0having the same basic component. They had also shown the cation exchange capacity (CEC) for both Ca and Mg at different doses of mother liquid comparing with 4A Zeolite in Table 11. [26].

Zeolites	Mother liquid(ml)	CEC for Ca (meq/100g)	CEC for Mg meq/100 g)
FAU/LTA-1b	200	312	175
FAU/LTA-1b	150	343	180
FAU/LTA-1b	100	333	172
4A		336	164

Table11:- CECs of Zeolite for Ca and Mg [26]

G. Zeolites from Paper Sludge Ash

Paper sludge is an industrial waste contains organic fiber, inorganic clay materials and 60% of water (see table-12). It is produced when the paper is recycled. To reduce the volume of waste, paper sludge is burned and paper sludge ash (PSA) is formed. Paper consumption in India approximately 10millions tones per annum. It indicates that PSA is generated a huge amount .from which small portion is used in construction, but maximum PSA is going for landfill which is causing a severe environmental effect. One of the best

approaches to use this PSA is converting into Zeolite which can use as adsorbents for water purification, catalysts in the petrochemical industry and soil conditioner [27].TakaakiWajima et al (2006) prepared Zeolite-P from PSA at 90°C.As PSA is low Si content, they added a silica-rich sedimentary deposited material called diatomite. They reported that Na-P1 Zeolite has high CEC for NH₄⁺ ions with the removal of PO₄³⁻ by precipitation and it is increasing as the addition of diatomite increased from 0 to 64 grams at 3M NaOH solution [27].

Components (Wt %)	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	Fe ₂ O ₃	TiO ₂
Paper sludge Ash	35.9	22.8	33.2	0.6	-	4.5	0.9	2.2
Diatomite	92.8	3.4	0.3	0.5	0.5	0.5	2.0	-

Table 12:- Chemical composition of paper sludge ash and Diatomite [27]

Again TakaakiWajima (2004) reported that calcination of paper sludge contains an abundant amount of Ca in the form of gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) because of calcite a limestone used as filler in the paper. They applied HCl acid for leaching to reduce the Ca amount from PSA. Then the leached ash was treated with 2.5M NaOH solution at 800°C for 24 hours. From this, they synthesized Linda type A (LTA) and hydroxyl sodalites when pH is greater than 5. When the pH is 1-5 then LTA and Na-P1 are produced. They also reported the CEC of hydroxyl sodalite is lower than LTA and Na-P1. When the PSA solution of pH is 3, the Zeolite has high Cation exchange capacity [28].

III. APPLICATIONS

A. Zeolites for Agriculture

Food is the most basic need for mankind. Food security is one of the most challenging obstacles for the survival of the 70 billion people in the world. Fertile land is limited but food demand is high. Day by day quality of the soil is decreasing and climate change is the most vital factor for a high production rate of crops. So researchers are continuously on the way for new alternatives in cultivation [29].

As we know, Zeolites have multiple physical and chemical properties like high porosity, cation exchange capacity especially for ammonium and potassium ion and sorption properties; it can be used in agriculture. Without changing the crystal structure, the Zeolites lose and gain the water or vice versa. They can be used as fertilizer, stabilizers, and chelators as it binds tightly the metal ions. The focused usages of Zeolites are capture, storage and slow release of nitrogen without losses to the environment. Due to a large area of porosity, Zeolite increases the soil water holding capacity for plants. In the 1960s, the Japanese farmers were using the Zeolite rocks to control the moisture and to increase the pH value of acidic volcanic soil. Out of different Zeolites, Clinoptilolite is extensively used to modify physical, chemical and biological properties of soils. Zeolite also increases the solubility capacity of phosphate materials as well as acts as a nutrient carrier and a medium to release nutrients [29, 30].

Zeolites are capable of controlling the odor coming from organic manure, as they can absorb volatile substances like acetic acid, butanoic acid etc. Adding Zeolite with organic manure gives the good agronomic properties by reducing losses of nitrogen to the environment. When 25% of Zeolite is added with fertilizer, it performs the same result as 100% fertilizer performs [29].

ZSM-5 Zeolites are most hydrophobic in nature which absorb atrazine an herbicide ($\text{C}_8\text{H}_{14}\text{ClN}_5$) inside the voids of Zeolite where organics are present. This herbicide will release slowly to perform. Also, Clinoptilolite is considered as the suitable Zeolite for the removal of atrazine from soil and water [29, 30].

We noticed that Zeolites are used for organic manure handling, nitrogen management, phosphorus management, carrier and slow release of nutrients, improvement of physical properties of soil and slow release of herbicide. Apart from these, it has been reported that certain sodium Zeolite affects the plant growth and yield. Erionite ($\text{Na}_2\text{K}_2\text{MgCa}_{1.5})_4\text{Al}_8\text{Si}_{28}\text{O}_{72}\cdot 28\text{H}_2\text{O}$) Zeolite can be dangerous for health when inhaled by animal and human. So, it required a suitable selection of Zeolites for agriculture [29, 30].

B. Zeolites for Aquaculture

Aquaculture is an important sector to fulfill the fish requirement of people. It occupies more than 50% of human food. As the population of earth is growing, it required appropriate technology for high production rates of fish and also to counter the pernicious effect of high production rate on the environment. So aquaculture industry (sea water and fresh water) is focusing to reduce harmful contaminants from waters and wastewater in the recycling system of aquaculture pond. So Zeolites (natural, synthetic or modified) are more prominent inorganic adsorbent for treating the water as they are microporous in structure. The negatively charged Zeolite is neutralized by cations of alkali and alkali earth metal and having molecular sieve characteristics which enable effective trapping of different heavy metal cation like Cadmium, Lead, Nickel, Manganese, Zinc, Chrome, Iron and copper from water [30, 31].

Natural Zeolite such as Clinoptilolite traps toxic heavy metal ion and ammonia ion from freshwater fishery making healthy water condition for fish growth. The ion exchange capacity (CEC) of Zeolite depends on factors like types of Zeolite, pore dimension, particle size, composition and salinity of wastewater [30].

In the closed aqua system, densities of fishes are very high. In aquaculture feed, de-amination of protein causes ammonia nitrogen which is toxic to fish. This metabolic ammonia pollutant will adversely affect the fish growth and health. When the concentration of ammonia reaches more than 0.02ppm, the fishes will become languid and gradually they die. Total ammonia nitrogen is constituted of ionized ammonium (NH_4^+) and unionized ammonia (NH_3). After digestion of feed by the fish, the nitride enters the aqua system and excess nitrogen will convert to ammonia which will act as a severe waste in water [30,31].

It has been reported that Clinoptilolite and Chabazite are most usable for the removal of ammonia. In tilapia fish, recirculated aquaculture system (RAS) sodium natural Chabazite is highly beneficial for ammonia removal. Application of 15 g/L and 12 g/L of Zeolite in the noxious concentration of ammonia water will save beluga and Persian sturgeon respectively. 10g/L of Zeolites is used for the renovation of water quality in angel culture. Zeolite is also used as a feed stabilizer to improve fish health and growth [30, 31].

There are lots of researches going on. Application of synthetic Zeolite has limited application comparing to natural Zeolites. It is reported that Zeolite is not beneficial to remove ammonia from saline water and shrimp plant or saline prawn plant due to limited cation exchange capacity of it. The use of natural and their modified form has numerous applications for cleaning of the aquatic ecosystem and these are affordable and economic [30, 31].

C. Zeolites in Healthcare Applications

Since the medical application is analogous to ion exchange, adsorption, catalysis, and molecular sieve, the natural Zeolite plays an extensive role in this sector. Both synthetic and natural Zeolites are having potential applications in the biomedical and pharmaceutical industry. The Clinoptilolite Zeolite is already showing the ability to enhance the immune system of the body against the antigen. It can be used for diarrhea treatment. In artificial kidney, Zeolites are also beneficial due to the eradication of uremic toxins like urea, uric acid, creatinine, p-cresol and indoxyl sulfate from the blood. The Zeolite have other numerous applications such as in bone formation, contrast agent in a Magnetic resonance imaging machine, an antibacterial agent, enzymemimetics, hemodialysis, decontaminates and in diabetes mellitus [32].

Shaghayegh Rahmani et al (2016) prepared nanozeolitesodalite for the application of drug delivery. Without using any organic materials, they synthesized nanozeolitesodalite from perlite as Si source and sodium aluminate as Al source in a stainless steel chamber at 170°C by hydrothermal method. Then, the prepared nanozeolitesodalite was tailored with cationic surfactant named as hexadecyltrimethylammonium bromide (HDTMAB). They investigated the adsorption of drug cetirizine onto nanozeolitesodalite as a transporter of the drug UV-Vis spectroscopy. The result was successful and this carrier is used to reduce the toxicity, to enhance the therapeutic effectiveness of drug and also useful for control release of drug in the body [33].

Mingfei Pan et al (2017) adopted nanozeolite molecular sieve to prepare a portable oxygen concentrator using pressure-vacuum swing adsorption (PVSA) cycle which could be favorable for patients having the chronic obstructive pulmonary disease (COPD). With 90sec cycle time, the oxygen concentrator produced 90 vol% of refined oxygen through adsorption and desorption mechanism. The 13X nanozeolite which exchanged by Li^+ ion is used as an adsorbent to absorb nitrogen from the atmosphere. The dimension of the adsorption column is 20cm in length and 3cm in diameter. Now a day's cryogenic distillations, membrane separation processes are used as air separation in oxygen plant but these are high energy consuming. So the above method is highly effective, economical as well as convenient [4, 34].

Toxic heavy metals, tobacco smoke, abundant use of pesticide in agriculture, use of antibiotics for a disease, synthetic cosmetics creates various disorder in our health such as reduction of immunity, skin allergy, hair loss, hormone imbalance, cardiovascular disorder, neurological disorder and imbalance in sugar level. To counter such, Zeolites in the various forms are highly useful. The natural Zeolite Clinoptilolite is modified with FeSO_4 , which can reduce the sugar from blood after consuming with water. The modified Zeolite can be used as an anticancer therapeutic agent [32, 35].

D. Zeolites in Petroleum Refining Processes

In petroleum refining, the focus area is to get high-quality fuels from the efficient conversion of crude oil. All the gasoline throughout the world is produced or upgraded through Zeolites. The fuels i.e. gasoline, aviation jet fuel and diesel which are coming out from crude oil, are in the increasing order molecular weight. The fuel fractions which having high molecular weight like gasoil and asphalt, go for thermal cracking, catalytic cracking to get gasoline and to get jet fuel catalytic hydrocracking is processed. In 1957, Rabo discovered strong acid catalytic activity of X and Y Zeolite which laid the foundation for application of Zeolite as a molecular sieve in cracking, hydrocracking and isomerization of hydrocarbon. In Fischer-Tropsch reaction, methanol is the principal product. This methanol can be effectively converted into high octane fuels with the help of ZSM Zeolite as catalysts. [4, 36, 42].

In the fluid catalytic cracking process, the crude oil also known as heavy gas oil or vacuum gas oil having high molecular weight is converted into low molecular weight and lighter hydrocarbon like gasoline, LPG distillate, and C3 olefin when a hot powered catalyst containing Y Zeolite come with contact with crude oil. Many researchers have proved that Zeolite Y is only Zeolite which gives huge gasoline with high octane number and highest degree of catalytic stability. A small quantity of ZSM-5 Zeolite is also added to enhance the octane number of gasoline [4, 38].

Commonly FCC catalysts constitute following elements (a) Zeolite crystal with the required content of rare earth. Low rare earth contents i.e. less than 3 weight% of Zeolite Y permits the Zeolites to be dealuminated which will lower hydrogen transfer capability as well as lower the acid site density. Whereas Zeolite Y with high rare earth content i.e. up to 15% restricts the Zeolite from dealuminating which maintain high site density and high hydrogen transport rate. Mainly, the addition of rare earth content to Zeolite Y is to improve the hydrothermal stability in FCC regenerator and continuous performance of Zeolite Y. The lanthanum and cerium are the rare earth elements which are used to stabilize Zeolite activity and enhance hydrothermal stability. (b) To breakdown the large molecule into small molecules, an active matrix with required composition and porosity is essential. This is done on the presence of highly acidic porous structure

Zeolite. This process is the synergy between Zeolite and matrix. (c)Kaolin clay is acting as a heat sink and filler and to maintain the cohesiveness and adhesiveness of dried sprayed particle a binder is used [36, 37, 38].

Due to escalating demand for high octane and high compression ratio gasoline, low freezing point jet fuel and diesel, the Zeolite based hydrocracking catalysts boost the hydrocracking process. Catalytic cracking and hydrogenation are the two steps for the hydrocracking process in which hydrocarbon molecules and hydrogen gas pass over the Zeolite catalyst with high pressure and temperature. In this process, high molecular weight petroleum breaks down into low molecular weight fuel fraction. The main advances in Zeolite-catalyzed hydrocracking are clean fuel production as well as low aromatic and sulfur in gasoline and in diesel. The commercial hydrocracking catalysts are partly dealuminated and having low sodium content or high silica content Y type Zeolite in hydrogen [4, 37, 38].

In winter or in a cold environment the flow of fuel i.e. diesel or lube oil becomes difficult due to the presence of paraffinic component. So it is necessary to remove waxy elements for low-temperature application by the process called catalytic dewaxing a selective method for hydrocracking process. Recently SAPO-11/31 molecular sieve catalyst Zeolite consisting of platinum and ZSM-22/23 Zeolite crack the long chain paraffin to shorter chain or nonwaxy molecules. The pore dimension of mention Zeolite is given in the table-13 [4, 37].

Zeolite name	Zeolite type index	Pore Dimension (Å)
ZSM-22	TON	4.6×5.6
ZSM-23	MTT	4.5×5.2
SAPO-11	AFI	4.0×6.5
SAPO-31	ATO	5.4×5.4

Table 13:- Value of pore dimension of Zeolite [37]

ZSM-5 Zeolite at liquid phase is used for the synthesis of ethylbenzene which is a basic chemical for polystyrene products. In para-xylene production, an ion-exchanged form of synthetic FAU Zeolite is used along with desorbent liquid to recuperate 97% of para-xylene at high purity from mixed C₈ aromatics. TA-4 catalyst, which is based on zeolite disproportionate toluene into benzene and mixed xylene. It has another function such as transalkylation of toluene and trimethylbenzene to mixed xylene which further added to Parex unit to produce paraxylene. M.V Choudary et al (2011) reported that successful design of UZM-n-type Zeolite which leads to an exploration of ITQ-30 molecular sieve. UZM-n family has UZM-4, UZM-5, UZM-8, UZM-9, UZM-15, and UZM-17 types Zeolites. From these, UZM-8 has a unique

structure and having a high amount of acidic sites which is suitable for the production of mono-alkyl-aromatics [4, 37].

E. Zeolite for Environmental Protection

The natural Zeolites play a major role in environmental remediation due to cation exchange properties. Some modification of Zeolite is also done to make it into an anion exchanger. Temperature, pH of the solution, the presence of competing cations, pore size and outer surface activity afflicts the Zeolite for withdrawal of metal cations from solutions. The various experiment indicated that Zeolite has more selectivity towards monovalent cations like Cs⁺ and NH₄⁺ than divalent cations like Sr²⁺ and Pb²⁺. The absorption of transition elements and actinides by Zeolites is dependent on the aqueous chemistry and hydrolysis reaction of different soluble and insoluble products that is connected with Zeolite. The adsorption and ion exchange removal mechanism are essential for the extraction of metals from solutions along with surface precipitation [4, 39].

L.L Ames in 1961 was the pioneer who first developed the environmental application of Zeolite for the handling of high-level alkaline wastes from PUREX processing of used nuclear fuel. It has experimented that natural Zeolite having improved sorption properties are used as nuclear waste management. The natural Clinoptilolite paralyzes the movement of cationic radioactive cesium (¹³⁷Cs) and strontium (⁹⁰Sr) isotopes from nuclear power plant wastewater at the nuclear industry [39, 41, 42].

Removal of heavy metal like iron, ink, cadmium, and lead from acid water in the mining area is done by Zeolites. Then these Zeolites can be regenerated by Ethylenediaminetetraacetic acid (EDTA), NaCl, NaNO₃, NaHCO₃ etc in case of Zink adsorption. The stabilization of lead, cadmium, and nickel is done by Phillipsite and faujasite Zeolite. Also, a mixture of Zeolite and humic acids reduces the lead concentrations in soil compared with the single use of Zeolite. Due to the absurd use of fertilizer in agriculture, the flow of chemical water through soil and various human activities, the agricultural soil become polluted absorbing heavy metals. Hence, both natural and synthetic Zeolite with another additive can diminish the bioequivalence of heavy metals from soil. From numerous experiments, it has been found that the use of Zeolite in acidic soil, the pH is increasing; consequently affects the devaluation insolubility of heavy metals and bioavailability for plants [39, 40].

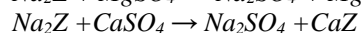
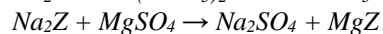
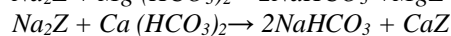
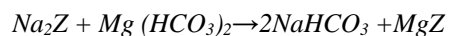
It has been pragmatically possible to adsorb lithium from contaminated soil by Clinoptilolite for the growing of popular plant. This lithium can be detected through nuclear magnetic resonance. Presence of Zeolite in dull soil restores a familiar environment for biota, which will lead to fertile soil for agriculture after removing toxic metal elements like Zn, Pb, and Cu. After utilization of Zeolite in wheat cultivation, the wheat reduces to pick up cadmium and lead from soil [39, 40].

Wastewater from industry and urban areas can be purified by natural Zeolitic materials. Zeolites were used as sorbent material of ammonium and heavy metals from urban wastewater and dye from industrial water. Treatment of wastewater through natural Zeolite is in operating mode in various countries. In many kinds of literature, it has been reported that nutrient species like NH_4^+ , $\text{H}_2\text{PO}_4^{2-}$ can be removed in an effective manner by Zeolitic materials [39, 41].

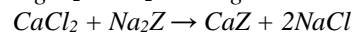
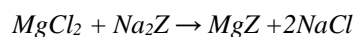
For environmental remediation surfactant modified Zeolites (SMZ) are used as a decontamination agent for soil and water basin. After surface modification, the Zeolites will have hybrid properties of both cation and anion sorption. The modifying agents are quaternary amines like HDTMA, ODTMA, N-cetyl pyridinium, which modify Zeolite into a bilayer structure of opposite charges. This bilayered Zeolite can be applied for the cultivation of the plant as artificial soils termed as zeoponics plant growth system. In 1990, this technology is adopted by NASA for the growth of the plant in space which is beneficial for human survival in space. Also, polymer modifier like polyhexamethyleneguanidine is used to enhance for binding of anionic species. Surfactant modified also acts as sorption agent for volatile petroleum hydrocarbon such as BTEX, Xylene, toluene, Benzene etc. and also use as wastewater treatment from a petroleum refinery. A laboratory column having 30 cm height and 2.5 cm radius filled with SMZ having diameter 1.4-2.4mm has been studied by Robert S. Brown. This column showed better results for purification oilfield wastewater after removing benzene, toluene, ethylbenzene, and p-, m- and o-xylene (BTEX). So the surfactant-modified Zeolite (SMZ) is efficient for sorption of cation, anions and non-polar organic molecules from contaminated water [39- 42].

Zeolite particles can carry bacteria from wastewater in the treatment plant and also increase sedimentation activity. Experimentally, it is found that antibody-like *E. Coli* bind by surfactant modified Zeolite and SMZ have the ability to extract 99 to 100% of bacteria and viruses from sewage drainage. Schulze Makuch et al set up a unit of ten piezometers for injection and sampling. The dimension of the model was $109 \times 40 \times 2 \text{ cm}^3$. They performed two experiments; one is controlled run not including barrier and treatment barrier with a 10 cm wide barrier containing SMZ of size 1.4-2.4 mm in the middle of the model. Then bacteriophage MS2, pathogen like *E. Coli* and bromide (NaBr) injected to a constructed side of wetland which receives sewage effluent. The outlet water they got was pathogen free. Copper and Silver exchanged Zeolites are highly effective as an antimicrobial source in a dust mask, plastic films and antifouling coating for the boat to prevent small sea creature with the shell to tightly stick [39 -42].

To maintain the equilibrium of the aqua system, the phosphate should ban to flow into the large aqua environment like pond and lake. These phosphates are found in detergent powder which removes the Ca^{2+} and Mg^{2+} ions from hard water to make it soft. The sodium Zeolite has the same properties which adsorb the calcium and magnesium ion from hardness causing salt present in water. The following reaction explains how the reaction of Zeolite with hard water occurs. Z stands for Zeolites.



When all calcium and magnesium ions are captured by Zeolite, it becomes dormant. For further use, it needs to be regenerated by the brine solution. The reactions are as follows.



The soft water we get in this Zeolite process only for laundry purpose but not for the boiler in power plant. Because soft water contain NaHCO_3 , which produces CO_2 when water heated and this is corrosive for the turbine blade in a power plant. Out of 1.4 million metric ton production of synthetic Zeolite in the world, 80% synthetic Zeolites are adopted in laundry detergent. Many developed and developing countries are adopting Zeolite instead of phosphate [4, 30, 39, 42].

Today emission control from automotive is a major issue. The lean-burn diesel engine radiates nitrogen oxide (NO_x) which is a serious challenge to the environment. Hence, Zeolites with an extensive cluster of combined base and precious metals, as catalysts to permit NO_x reduction, hydrocarbon storage, oxidation of both hydrocarbon and CO and particulate control. 90% of hydrocarbon emission occurs by gasoline used vehicles at the time of cold start period i.e. within 3 minutes. Hence, a mechanically, thermally and hydrothermally reliable Zeolite molecular sieve with added catalyst adsorbed should be used to capture the emitted hydrocarbon. Then catalytic converters oxidize the HC. Then harmless emission will release to the atmosphere [4].

F. Some Advance Application

Kyungsu Na et al (2011) synthesized a series of mesoporous (2 to 50nm) which has a zeolite structure with crystalline microporous walls. They reported that using different types of surfactants, the mesoporous size, wall thickness, and framework topologies can be controlled. As compared to conventional zeolite and amorphous mesoporous materials, these types of molecular sieves are highly efficient for catalysts in different types of acid-

catalyzed reactions of the bulky molecular substrate [46]. Mi Young et al (2017) developed ultra-selective high-flux membrane from directly synthesized zeolite (MFI type) nanosheets. They prepared MFI nanosheets by hydrothermal growth of MFI seeds (30 nm dia) following bottom-up technique in the presence of bis-1,5(triethyl ammonium) pentamethylenediiodide. These versatile architectures provide efficient mass transfer properties for specific catalysis and adsorption applications. The aspect ratios of these nanosheets are very high which can be used to fabricate thin and defect-free coating which covers the porous substrate potentially. This coating further intergrowth to prepare high-flux and ultra-selective MFI membrane as compared to other existing MFI materials i.e. exfoliated nanosheets or nanocrystals [47]. Karin Möllar et al(2011) assembled the thin wall of crystalline zeolites into hexagonal nanoporous networks which can be understood that pores within pores. In the dualtemplating technique, the advantages of zeolite and mesoporous oxide are merged. Apart from molecular zeolite templates, the large assemblies also did with help of surfactant micelles, polymers of carbon fiber to create mesoporosity. Another approach which develops very thin slices of zeolite crystals from large molecules of zeolite pore and the entire pore surface can be used for adsorption. This technique creates a large surface area and also eliminates the necessity of internal pore diffusion [48,51].

IV. CONCLUSION

It may be concluded that natural Zeolite, as well as synthetic Zeolite, are the most important material for mankind without any adverse effect on the environment. The synthetic zeolites as molecular sieve have numerous applications in the production of fuels, petrochemicals and other designed products which is beneficial for the human race. Zeolites have the ability to cut down the pollution due to stable ion exchanging property. It can be used in water treatment, agriculture, aquaculture, animal nutrition, metal processing, and biomedical engineering and in various environmental remediations to maintain the equilibrium of ecosystems. The best part is, various types of zeolites can be synthesized from wastes like fly ash, blast furnace slag, municipal solid waste fly ash, rice husk ash, kaolin, lithium slag, and paper sludge ash etc.

From future prospective of zeolites are those preparations of high efficient nano zeolites because in the nanosize the reactivity of zeolites toward any substance is very high as the surface area to volume ratio increases. The natural zeolite should be used in the cement preparation as filler in paper, an energy supplier in solar refrigerator etc. Research is under progress to make zeolite materials user-friendly for the common man who can save more energy in term of water treatment, sewage management, and air purifier and in many potential applications.

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