

# Fabrication and characterization of zeolite and its application in heavy metal capture

# **Research project**

Submitted to the department of Chemistry College of education in partial fulfillment of the requirements for the degree of BSc.

**By** Payam Othman Taha

# **Supervised by** Dr. Suad Najmaldin Mohiaedin

# **Supervisor recommendation**

I am the student's supervisor, -----student full name----Payam Osman Taha— I support that the student has completed all the requirements for submitting the research drawn entitled -------title of project-- Fabrication and characterization of zeolite and its application in heavy metal capture -according to the numbered administrative order 3/1/5/1972 on 9<sup>th</sup> oct. 2022 in accordance with the instructions of Salahaddin university quality assurance and it is ready for discussion.

Supervisor full name with Signature with date :

 $\phi$ 

Dr. Suad Najmaldin Mohiaedin

Research project lecturer Dr. Dler D. Kurda

#### ACKNOWLEDGMENTS

First of all, I address my utmost thankful to God for his blessing and empowered me to be able to complete this vital study and help me to accomplish it successfully.

I deeply would like to extend my infinite gratitude to **Dr**. **Suad Najmaldin Mohiaedin** who assisted me in order to conduct this remarkable research project under the name of (**Fabrication and Characterization of Zeolite and its Application in Heavy Metal capture**) and inspired me throughout this entire significant process.

I sincerely express my thankful to my dear colleagues and those dedicative participants who took part in this highly crucial cooperation and committed themselves to fulfil this project.

To conclude, I was really contented to come across hugely modern information about this particular topic and obtained lots of Relevant stuff to it.

# Table of content

1.INTRODUCTON
2.History
2.1Natural occurrence
3. Properties
4. Characteristics of zeolite
4.1Porosity
4.2 Isomorphous substitution
4.3 Framework structure
5. Production
5.1 Synthetic Zeolites:
5.2 Synthesis of zeolites and zeolite films:
5.3. Methods of synthetic zeolite synthesis
5. 3.1. Solvothermal method
5. 3.2. Hydrothermal method
5. 3.3. Ionothermal method
5. 3.4 Solvothermal method
5.3.5 Alkali-fusion and leaching method
Factors affecting the alkali-fusion methods are:
The factors that affect the alkali leaching method are:
<b>5.3.6.</b> Sol-gel method
5.3.7. Microwave method
5.3.8. Ultra-sound energy method
6. Applications of synthetic zeolite:
6.1. Heavy metal, cation and anion removal
6.2. Removal of radioactive substances
6.3. Synthetic zeolite for gas adsorption
6.4 organic synthesis
6.5. Ion exchange and softeners
6.6.Catalysis:
6.7 Gas separation and storage
6.8 Solar energy storage25
6.9.Light emission

6.10.Cat litter	26
6.11. Soil treatment	26
6.12.Aquaria	26
7.conclusion	
8. Future recommendations	29
9. References:	

# Table of figures

Figure	ıre Title							
1	Comparison of framework structures of LTA-type zeolite and FAU-type zeolite .							
2	2 Zeolite A framework type and SEM image and zeolite P framework type and SEM.							
3	all solvothermal method (including hydrothermal and ionothermal) for the synthesis of zeolite.	15						
4	representation of zeolite synthesis via alkali fusion.							
5	Alkali leaching method for synthesis of zeolite.							
6	Sol-gel method for synthesis of zeolite.							
7	Microwave methods for synthesis of zeolite.							
8	Partitioning of a mixture of toxic chromate anions and perchloroethylene during their combined sorption by a surfactant- modified zeolite (SMZ).	24						
9	Gas separation and storage.	25						

## Abstract

Zeolite have a framework structure that encloses interconnected cavities occupied by large metal cations (positively charged ions) and water molecules. The essential structural feature of a zeolite is a three-dimensional tetrahedral framework in which each oxygen atom is shared by two tetrahedra. All zeolites are made up of the aluminosilicate framework where silicon and aluminums are tetrahedrally coordinated. Silicon cation and aluminum cations are enclosed by four oxygen anions (O2-). The tetrahedral structure of SiO4 and AlO4 forms the building block of zeolite. A zeolite mineral is a crystalline material with a structure consisting of connected tetrahedra, each of which contains four O atoms surrounding a cation. Open cavities in the form of channels and cages can be found in this system. These are normally occupied by H2O molecules and typically exchangeable extra-framework cations. Guest organisms can move through the channels because they are wide enough. Dehydration occurs in the hydrated phases at temperatures predominantly below 400 °C and is essentially reversible. (OH, F) groups will break the structure by occupying a tetrahedron apex that is not shared with neighboring tetrahedra. Because of their versatility and adaptability, zeolites have drawn a lot of interest from researchers and scientists over the years. Zeolites have been discovered to be strong adsorbents, ion exchangers, and molecular sieves. In particular, the molecular sieve properties of zeolites are widely used in industry.

Key words: Zeolite Silicon, Aluminum, aluminosilicate, tetrahedral, molecular sieve

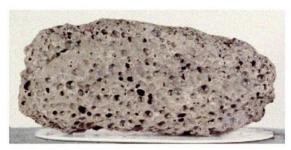
# **1.INTRODUCTON**

eolites are microporous, crystalline aluminosilicate materials commonly used as commercial adsorbents and catalysts. They mainly consist of silicon, aluminum, oxygen, and have the general formula  $Mn+1/n(AlO2)-(SiO2)_x \cdot yH2O$  where Mn+1/n is either a metal ion or H+. (Sanjana et al., 2022)These positive ions can be exchanged for others in a contacting electrolyte solution. H+ exchanged zeolites are particularly useful as solid acid catalysts.

zeolite, any member of a family of hydrated aluminosilicate minerals that contain alkali and alkaline-earth metals. The zeolites are noted for their liability toward ion-exchange and reversible dehydration. They have a framework structure that encloses interconnected cavities occupied by large metal cations (positively charged ions) and water molecules.

The essential structural feature of a zeolite is a three-dimensional tetrahedral framework in which each oxygen atom is shared by two tetrahedral. If all tetrahedral contained silicon the framework would be neutral; substitution of aluminum for silicon creates a charge imbalance and requires other metal ions to be present in relatively large cavities of the framework. In naturally occurring zeolites these metal ions are typically mono- or di-valent ions such as sodium, potassium, magnesium, calcium, and barium. Zeolites are similar to feldspar minerals except that cavities are larger in zeolites and water is generally present. Structurally, zeolites are classified by the types of structural units that compose the framework, such as rings or polyhedral types. The cavities formed by the framework units have diameters ranging from about 2 to 8 angstroms, which permits relatively easy movement of ions between cavities.

differences. Dehydration character varies with the way water is bound in the structure. For



specific structural properties.

those zeolites in which water is tightly bound, dehydration occurs at relatively high temperatures; by contrast, in certain zeolites with large cavities, some of the water can be released at low temperatures. The rate of ion exchange depends on the size and connections between cavities. Some ions are excluded because of Zeolite properties are exploited through commercial production of zeolites with particular structural and chemical features. Some commercial uses include separation of hydrocarbons, such as in petroleum refining; drying of gases and liquids; and pollution control by selective molecular adsorption.

Natural zeolites occur in mafic volcanic rocks as cavity fillings, probably as a result of deposition by fluids or vapors. In sedimentary rocks zeolites occur as alteration products of volcanic glass and serve as cementing material in detrital rocks; they also are found in chemical sedimentary rocks of marine origin. Extensive deposits of zeolites occur in all oceans. Metamorphic rocks contain a sequence of zeolite minerals useful for assigning relative metamorphic grade; these minerals form at the expense of feldspars and volcanic glass.

In the early 21st century the world's top producers were China, South Korea, Japan, Turkey, and Jordan.

# **2.History**

The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that rapidly heating a material, believed to have been stilbite, produced large amounts of steam from water that had been adsorbed by the material. Based on this, he called the material zeolite, (Nayak et al., 2020)from the Greek  $\zeta \hat{\epsilon} \omega$  (zéo), meaning "to boil" and  $\lambda \hat{i} \theta o \zeta$  (líthos), meaning "stone".

Zeolites occur naturally but are also produced industrially on a large scale. As of December 2018, 253 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known. Every new zeolite structure that is obtained is examined by the International Zeolite Association Structure Commission and receives a three letter designation

#### **2.1Natural occurrence**

A form of thomsonite (one of the rarest zeolites) from India Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite. An example of the mineral formula of a zeolite is: Na2Al2Si3O10·2H2O, the formula for natrolite.



Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are

rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.[citation needed] Zeolites transform to other minerals under weathering, hydrothermal alteration or metamorphic conditions. Some examples.

The sequence of silica-rich volcanic rocks commonly progresses from:

Clay  $\rightarrow$ quartz $\rightarrow$  mordenite

heulandite  $\rightarrow$  epistilbite  $\rightarrow$  stilbite  $\rightarrow$  thomsonite  $\rightarrow$  mesolite  $\rightarrow$  scolecite  $\rightarrow$  chabazite  $\rightarrow$  cal cite.

The sequence of silica-poor volcanic rocks commonly progresses from:

Cowlesite  $\rightarrow$  levyne  $\rightarrow$  offretite  $\rightarrow$  analcime  $\rightarrow$  thomsonite  $\rightarrow$  mesolite  $\rightarrow$  scolecite  $\rightarrow$  chab azite  $\rightarrow$  calcite.

#### Gemstones

#### **Polished thomsonite**



Thomsonites, one of the rarer zeolite minerals, have been collected as gemstones from a series of lava flows along Lake Superior in Minnesota and, to a lesser degree, in Michigan. Thomsonite nodules from these areas have eroded from basalt lava flows and are collected on beaches and by scuba divers in Lake Superior.

These thomsonite nodules have concentric rings in combinations of colors: black, white, orange, pink, purple, red, and many shades of green. Some nodules have copper inclusions and rarely will be found with copper "eyes". When polished by a lapidary, the thomsonites sometimes displays a "cat's eye" effect (chatoyancy).

# **3. Properties**

Properties of zeolites are alumina-silicates with an open structure composed of a threedimensional network of SiO4 and AlO4 tetrahedra sharing all the corners with each other. A general formula for the chemical composition may be expressed as:  $(M+, 0.5M2+)m[AlmSix-mO2x] \cdot nH2O$  where = extra framework cation.(Sanjana et al., 2022) The exchange of silicon for aluminum in the framework results in a net negative charge which must be compensated by extra framework cations. In general, these may be any alkali, alkaline-earth or rare earth cation as well as organic cations such as the tetramethylammonium ion. Water molecules are located in the channels and cavities, as are the neutralizing.

cations. Zeolites may be classified in various ways on the basis of structural differences, one of them being based on the size of the pore openings. Depending on the structure, the size of the pores is in the range 3 to 8 Å.

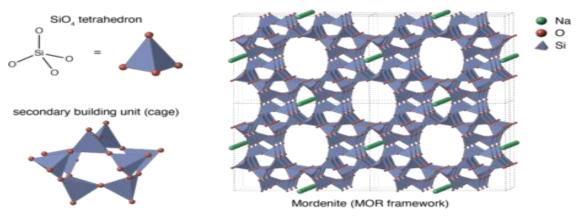
The Figure 1. The framework structure of Faujasite Figure 2. The framework structure of zeolite A. 2 apertures are bounded by oxygen atoms of connected tetrahedra. In general, these rings involve 6, 8, 10 or 12 oxygen atoms. (Marakatti and Halgeri, 2015) However, other factors are involved in determining the final pore size. For example, the location, size and coordination of the extra framework cations. The latter is a well-known parameter in the case of zeolite A, in which the channel aperture size can be tailored by using different sized extra framework cations. The interconnected regular three-dimensional network of micropores at a molecular scale and the extra framework cation content are the key factors determining the physical and chemical properties of zeolites. The size of the pores gives the zeolites molecular sieving properties, i.e if the molecule is larger than the pore size, it will not enter the structure. The shape of the pore may also influence the adsorption capability(Li et al., 2017). The extra framework cations are in many cases exchangeable, which allows for the introduction of acid sites bonded to the non-saturated oxygen atoms. Three different zeolite structures were investigated in this work: the faujasite [FAU] group zeolites (see Figure 1), zeolite A [LTA] (see Figure 2) and ZSM-5 [MFI]. All of them have found important applications and are therefore synthesized in an industrial scale. Zeolite X and Y are the synthetic analogues to the natural faujasite. The difference between these two zeolites is the Si/Al ratio which is 1-1.5 and 1.5-3 in zeolite X and Y, respectively]. The channel system has equidimensional channels intersecting in a perpendicular fashion. The free aperture diameter for the channels is 8 Å in

NaY. Zeolite A has a Si/Al ratio of ca. 1 . The three-dimensional channel system has, like in FAU-type zeolites, equidimensional channels intersecting perpendicular to each other. The free aperture diameter for the channels is 4 Å in zeolite NaA. ZSM-5 has a three dimensional pore system consisting of sinusoidal channels ( $5.1 \times 5.5$  Å) and intersecting straight channels ( $5.3 \times 5.6$  Å). ZSM-5 can be synthesized with a wide variety of Si/Al ratios, mainly in the range 5-100.

# 4. Characteristics of zeolite

Microscopic structure of a zeolite (mordenite) framework, assembled from cornersharing SiO 4 tetrahedra. Sodium is present as an extra-framework cation (in green). Si atoms be partially replaced by Al or other tetravalentetals. Zeolites can are the aluminosilicate members of the family of microporous materials, and mainly consist of silicon, aluminum, oxygen, and have the general formula Mn+1/n(AlO2)-(SiO2)x · yH2O where Mn+1/n is either a metal ion or H+. (Marakatti et al., 2014)The value of x (Si/Al molar ratio) is greater than 1 and y is the number of water molecules in the formula unit. Zeolites have microporous structures with a typical diameter of 0.3–0.8 nm and accommodate a wide variety of cations, such as Na+, K+, Ca2+, Mg2+ and others. These positive ions are often loosely held and can readily be exchanged for others in a contacting electrolyte solution. Cation exchanged zeolites possess different acidity and catalyze different reactions.[5][nonprimary source needed]. The Si/Al ratio is greater than 1 because zeolites have no Al-O-Al bond (Löwenstein rule). They are formed by the linking of the corner oxygen atoms of AlO4 and SiO4 tetrahedra to form covalent network structures. The general formula of zeolite, Mn+ 1/n(AlO2)-(SiO2) x, where the Mn+1/n(AlO2)- part is ionic bond-like and the (SiO2)x part is covalent bond-like. Zeolites therefore have both ionic crystal and covalent crystal properties, and the balance of these properties depends on the Si/Al ratio (x). Si/Al ratios below about 3 correspond to natural zeolites and some synthetic zeolites such as A-type and X-type zeolites. They are useful as ion-exchange agents because of their high ion-exchange capacity. Commercially available molecular sieve adsorbents often belong to this group.

Zeolites with a Si/Al ratios higher about 3 are classified as high-silica zeolites, which are rarely found in nature and are synthesized industrially. They possess high physical and chemical stability due to the large covalent bonding contribution. They have excellent hydrophobicity and are suited for adsorption of bulky, hydrophobic molecules such as hydrocarbons. In addition to that, high-silica zeolites are H+ exchangeable, unlike natural zeolites, and are used as solid acid catalysts. The acidity is strong enough to protonate hydrocarbons and high-silica zeolites are used in acid catalysis processes such as fluid catalytic cracking in petrochemical industry.



4.1Porosity

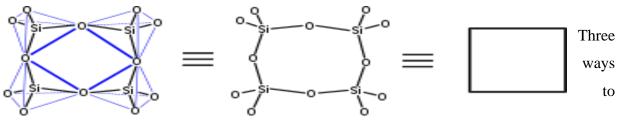
The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels. (Burrows et al., 2021)These are conventionally defined by the ring size of the aperture, where, for example, the term "eight-ring" refers to a closed-loop that is built from eight tetrahedrally coordinated silicon (or aluminum) atoms and eight oxygen atoms. These rings are not always perfectly symmetrical due to a variety of causes, including strain induced by the bonding between units that are needed to produce the overall structure or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical.

#### 4.2 Isomorphous substitution

Isomorphous substitution of Si in zeolites can be possible for some heteroatoms such as titanium, zinc and germanium. Al atoms in zeolites can be also structurally replaced with boron and gallium.

The silico alumina phosphate type (Alpo molecular sieve), in which Si is isomorphous with Al and P and Al is isomorphous with Si, and the gallogermanate and others are known.

#### 4.3 Framework structure



represent the oxygen 4-membered ring structure of silicate compounds.

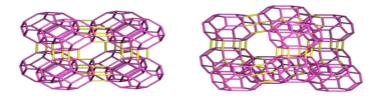


Fig. (1) Comparison of framework structures of LTA-type zeolite (left) and FAU-type zeolite (right)

As of December 2018, the framework structures of 253 different zeolites or their analogues are known, nearly 200 of which can only be synthesized artificially. For each structure, the International Zeolite Association (IZA) gives a three-letter code called framework type code (FTC). For example, the major molecular sieves, 3A, 4A and 5A, are all LTA (Linde Type A). Most commercially available natural zeolites are of the MOR, HEU or ANA-types.

An example of the notation of the ring structure of zeolite and other silicate materials is shown in the upper right figure. The middle figure shows a common notation using structural formula. The left figure emphasizes the SiO4 tetrahedral structure. Connecting oxygen atoms together creates a four-membered ring of oxygen (blue bold line). In fact, such a ring substructure is called four membered ring or simply four-ring. The figure on the right shows a 4-ring with Si atoms connected to each other, which is the most common way to express the topology of the framework.

The figure on the right compares the typical framework structures of LTA (left) and FAU (right). Both zeolites share the truncated octahedral structure (sodalite cage) (purple line). However, the way they are connected (yellow line) is different: in LTA, the fourmembered rings of the cage are connected to each other to form a skeleton, while in FAU, the six-membered rings are connected to each other. As a result, the pore entrance of LTA is an 8ring (0.41 nm) and belongs to the small pore zeolite, while the pore entrance of FAU is a 12ring (0.74 nm) and belongs to the large pore zeolite, respectively. Materials with a 10-ring are called medium pore zeolites, a typical example being ZSM-5 (MFI).

Although more than 200 types of zeolites are known, only about 100 types of aluminosilicates are available. In addition, there are only a few types that can be synthesized in industrially feasible way and have sufficient thermal stability to meet the requirements for industrial use. In particular, the FAU (faujasite, USY), \*BEA (beta), MOR (high-silica mordenite), MFI (ZSM-5), and FER (high-silica ferrierite) types are called the big five of high silica zeolites, and industrial production methods have been established.

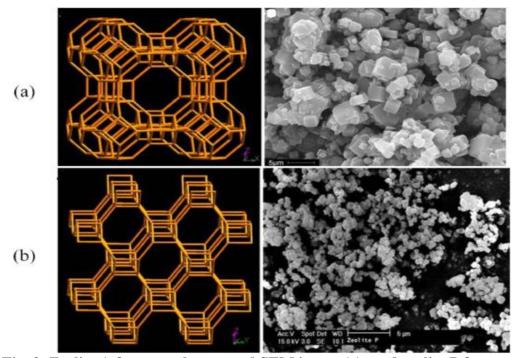


Fig. 2. Zeolite A framework type and SEM image (a); and zeolite P framework type and SEM image (b).

# **5. Production**

Industrially important zeolites are produced synthetically. Typical procedures entail heating aqueous solutions of alumina and silica with sodium hydroxide. Equivalent reagents include sodium aluminate and sodium silicate. Further variations include the use of structure directing agents (SDA) such as quaternary ammonium cations.

Synthetic zeolites hold some key advantages over their natural analogs. The synthetic materials are manufactured in a uniform, phase-pure state. It is also possible to produce zeolite structures that do not appear in nature. Zeolite A is a well-known example. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited .

#### Ore mining



Natrolite from Poland

Conventional open-pit mining techniques are used to mine natural zeolites. The overburden is removed to allow access to the ore. The ore may be blasted or stripped for processing by using tractors equipped with ripper blades and front-end loaders. In processing, the ore is crushed, dried, and milled. The milled ore may be air-classified as to particle size and shipped in bags or bulk. The crushed product may be screened to remove fine material when a granular product is required, and some pelletized products are produced from fine material.

As of 2016, the world's annual production of natural zeolite approximates 3 million tonnes. Major producers in 2010 included China (2 million tonnes), South Korea (210,000 t), Japan (150,000 t), Jordan (140,000 t), Turkey (100,000 t) Slovakia (85,000 t) and the United States (59,000 t).[8] The ready availability of zeolite-rich rock at low cost and the shortage of competing minerals and rocks are probably the most important factors for its large-scale use. According to the United States Geological Survey, it is likely that a significant percentage of the material sold as zeolites in some countries is ground or sawn

volcanic tuff that contains only a small number of zeolites. Some examples of such usage include dimension stone (as an altered volcanic tuff), lightweight aggregate, pozzolanic cement, and soil conditioners

#### **5.1 Synthetic Zeolites:**



#### Synthetic zeolite

There are over 200 synthetic zeolites that have been synthesized by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates. Many more such structures could theoretically be made

In addition to variations in structures, zeolites can also be made with a variety of other atoms in them to make them chemically interesting and active. Some examples of the so-called heteroatoms that have been incorporated include germanium, iron, gallium, boron, zinc, tin, and titanium One of the important processes used to carry out zeolite synthesis is sol-gel processing(Li et al., 2017). The product properties depend on reaction mixture composition, pH of the system, operating temperature, pre-reaction 'seeding' time, reaction time as well as the templates used. In the sol-gel process, other elements (metals, metal oxides) can be easily incorporated. The silicate sol formed by the hydrothermal method is very stable. The ease of scaling up this process makes it a favored route for zeolite synthesis.

#### 5.2 Synthesis of zeolites and zeolite films:

Generally, zeolites are crystallized by hydrothermal treatment of a clear synthesis solution or synthesis gel containing a silica source, an aluminum source and an alkali source (alkali hydroxide or/and organic bases).(Shamzhy et al., 2016) The composition of the synthesis mixture, the temperature during synthesis and synthesis duration are the main parameters determining which zeolite phase will be formed. In some cases, organic additives

are required in order to crystallize the desired product. For example, the molecular sieve Silicalite-1 is not possible to crystallize in the absence of organic additives. Moreover, the addition of organic additives to the synthesis gel of aluminum-rich zeolites results in the crystallization of more silica-rich structures. Frequently used additives are the tetramethylammonium (TMA)+ ion and the tetra propylammonium (TPA)+ ion.

The organic molecules become trapped in the pores of the zeolite and must be removed in order to render the structure microporous(Król, 2020). This is usually done by calcination which entails oxidation of the organic molecules at high temperature. In large-pore zeolites, such as the faujasites, the organic molecules can be removed by ion-exchange.

Zeolite membranes are most commonly synthesized on porous supports of alumina or steel. There are three main routes to synthesize continuous, supported zeolite films and membranes. The most common method is to treat the support directly with a molecular sieve precursor solution, called in-situ crystallization or direct synthesis in the literature.

#### **5.3.** Methods of synthetic zeolite synthesis

#### Zeolite synthesis from low-cost materials and environmental applications:

Zeolites can be synthesized from different raw materials which can be either natural or man-made. However, all raw materials are not suitable for synthesizing the zeolite from the economic point of view. Hence, raw materials should have some properties. They should be cheap, readily available, low production cost, selectivity, high production yield, and less abundance of foreign substances. Till now, various physicochemical and solvothermal methods have been adopted and developed to pro-

duce synthetic zeolites such as hydrothermal method alkali-fusion method, sol-gel method, and alkali-leaching method. However, the choice of the synthesis approach depends on which type of zeolite will produce. Each method has some advantages and few limitations which are represented in Table 2. Following subsections describe different synthetic routes of zeolite from various raw materials.

#### 5. 3.1. Solvothermal method

Solvothermal synthetic method is the general term of using a solvent by which zeolites can be synthesized. Water is by far the crucial solvent; hence there is a unique term "hydrothermal" to define its use. However, many organic solvents such as alcohols (e.g., methanol, ethanol, pentanol), ethylene glycol, hydrocarbons and pyridine have been used successfully for the synthesis of zeolite . (Shoppert et al., 2017)As with water these molecular solvents produce significant autogenous pressure at elevated temperature. The properties of the solvent used in this method can be either nonpolar or hydrophobic and hydrophilic polar solvent. In case of using ionic solvent (ionic liquids), this term is assigned as ionic thermal. Hence, all hydrothermal and ion thermal methods are basically solvothermal method, while all the solvothermal methods are not. A general schematic representation of solvothermal processes is shown in Fig. 3.

The solvothermal methods not only depend on the temperature and pressure but also on other factors such as reactant sources, composition, silica and alkali ratio, ageing time, alkalinity, stirring conditions, inorganic cations, seeding time, and solvent. Hence, this method offers easy and precise control of size, shape distribution, crystalline of the final zeolite product through the proper adjusting the parameters (Table 3). There have been multiple previous attempts to synthesis zeolite via a solvothermal method. For instance, reported the preparation of lithocyte (-LIT) type aluminosilicate zeolites by the solvothermal treatment of low-silica zeolite powders dispersed in alcohol-containing KOH, and the mixture was treated at 200–250°C for 15–120 h without stirring. developed zeolite omega from magadiite with well crystal structure and high purity via solvothermal approach. However, it is convenient to use different synthesis method combinedly such as hydrothermal-solvothermal and microwave-assisted solvothermal method.

#### 5. 3.2. Hydrothermal method

The hydrothermal technique is considered as the primary route of the synthesis of zeolites. This approach is nothing but solvothermal where water is used as a solvent, and a base is used as a mineralizer at different temperatures and pressures (Fig. 3). Conven- tonally, hydrothermal synthesis needs to use a sealed vessel usually

made of polypropylene and Teflon-lined (PTFE) steel autoclave (Fig. 2)

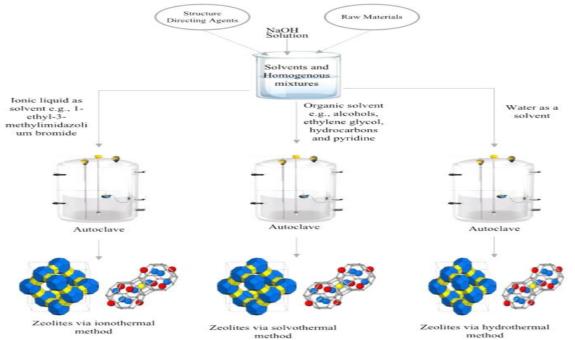
. In this method, a lower temperature is required. That is why, this method is very straight forward and cheaper in comparing to other methods. Zeolites are habitually synthesized via hydrothermal approach due to some advantages agreed by different researcher, which includes low energy consumption, the high reactivity of reactants, easy maintenance over the solution, lower air pol- lotion, formation of meta-stable phases and unique condensed phases(Cejka et al., 2017). There are many factors which can affect the performance of any hydrothermal method for example temperature and pressure, batch composition, silica and aluminum ratio, reactant materials, overall alkalinity, aging time, template condition, and seeding . To date, there have been multiple previous attempts to synthesis zeolites via conventional hydrothermal method.

#### 5. 3.3. Ionothermal method

Ionothermal synthesis refers to the use of ionic liquids and they are mainly based on the low vapor pressures compounds (Fig. 3). Hence, ionic liquids act as both the solvent and potential template or structure directing agent simultaneously in the formation of solids. Generally, hydrothermal, solvothermal and ionothermal methods are similar, except for the use of different solvents. Hence, these three methods have similar factors for the synthesis of zeolites. The ground-breaking of this area they used deep eutectic solvents (e.g.,1-ethyl-3-methylimidazolium bromide and urea/choline chloride) to prepare several distinct materials depending on the conditions. The crucial advantage of this method is that the solvent can act as template or structure-directing agent and after getting products it is relatively easy to remove them since both solvent and template are the same species. In addition, the ion thermal method produces a large size of crystals and the ability to create a crystalline phase. It is also easy to control the composition of growing crystals

#### 5. 3.4 Solvothermal method

Solvothermal synthetic method is the general term of using a solvent by which zeolites can be synthesized. Water is by far the crucial solvent; hence there is a unique term "hydrothermal" to define its use. (Setthaya et al., 2016)However, many organic solvents such as alcohols (e.g., methanol, ethanol, pentanol), ethylene glycol, hydrocarbons and pyridine have been used successfully for the synthesis of zeolite. As with water these molecular solvents produce significant autogenous pressure at elevated temperature. The properties of the solvent used in



this method can be either nonpolar or hydrophobic and hydrophilic polar solvent. In case of using ionic solvent (ionic liquids), this term is assigned as ionothermal. Hence, all hydrothermal and ionothermal methods are basically solvothermal method, while all the solvothermal methods are not. Nevertheless, basic difference among them solvents remain in molecular form in both solvothermal and hydrothermal while ionic in ionothermal synthesis method. The . A general schematic representation of solvothermal processes is shown in Fig3 **fig.3 general schematic of all solvothermal method (including hydrothermal and ionothermal) for the synthesis of zeolite** 

#### 5.3.5 Alkali-fusion and leaching method

In zeolite synthesis, alkali fusion method describes a general approach to decompose the material rich with silica or alumina in the presence of alkali which acts as an activator for the formation of soluble aluminate and silicate salts. Solvothermal methods also use alkali (e.g., NaOH) but there have some differences between solvothermal and alkali fused method. In alkali fusion method alkali is used to prevent multi- phase and fused in solid-state with raw materials before going to any sol- vent while in solvothermal method, alkali is used in terms of solution state and they act as mineralizer of the reaction medium. Generally, in the alkali-fusion method, the raw material is first fused with alkali (e.g., NaOH) before a hydrothermal treatment (Fig. 4). At the hydrothermal treatment, the fused product mixed with water and treat with the proper conditions like heating with appropriate temperature for the crystallization to form zeolite .

#### Factors affecting the alkali-fusion methods are:

- (i) silicon aluminum ratio of the raw material,
- (ii) concentrating the reacting alkali medium, But the drawbacks are the production of toxic chemicals and high operating time (Table 2).

Several studies have also been reported to syn- the size zeolites. For example, the first time, use of an ionic liquid or eutectic mixture as the solvent to produce synthetic zeolite. Recently, this method has received a growing interest among zeolite scientific community. There are many reports on the preparation of synthetic zeolites using this method.

For instance,(Shoppert et al., 2017)In a different study, ionothermal synthesis of German silicate zeolites. However, the more depth study is required to get a full judgement of this synthesis technology.

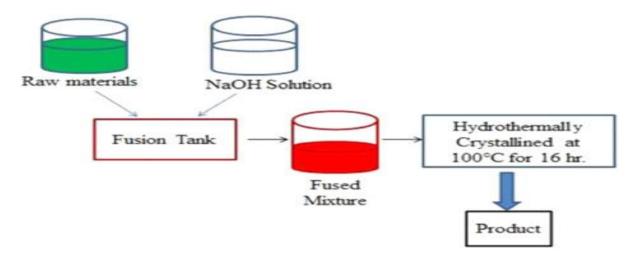


Fig. 4. A schematic representation of zeolite synthesis via alkali-fusion method.

Figure 4 illustrated the alkali fusion method to synthesize zeolite-A, zeolite-X and hydroxy sodalite from the BFS. In a previous study reported the synthesis of zeolite X from the lithium slag by hydrothermal reaction with alkali fusion. They mentioned excellent properties the zeolite. (Abdullahi et al., 2017)Moreover, in most of the processes, the alkali fusion technique is followed by a hydrothermal method of synthetic zeolite. Both methods require high temperatures, time, and pressures. The main sources for zeolite synthesis are commercial chemicals, which are very rich in alumina silicate, mineral resources in the earth's crust and industrial by-products. By varying the experimental conditions different types of zeolite products can be obtained, such as zeolite-X, zeolite- P, hydroxy sodalite, to be mohrite, and nepheline. This method allows low-grade raw materials without purification, and it offers the

anhydrous zeolite with high purity, which is considered as the advantages of this method. While it still has the problems of high energy consumption and the associated cost

. Alkali leaching is another approach where the leaching maintains the silica-alumina ratio out of the leachates such as NaOH solution The schematic representation of this method is shown in Fig. 5.

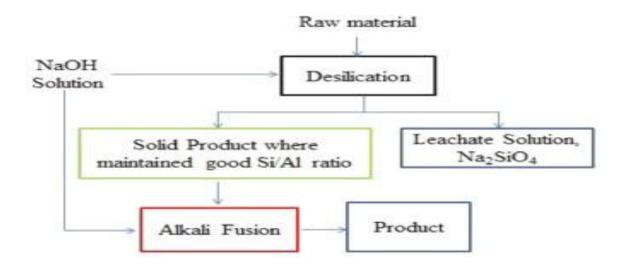


Fig 5 Alkali leaching method for synthesis of zeolit

## The factors that affect the alkali leaching method are:

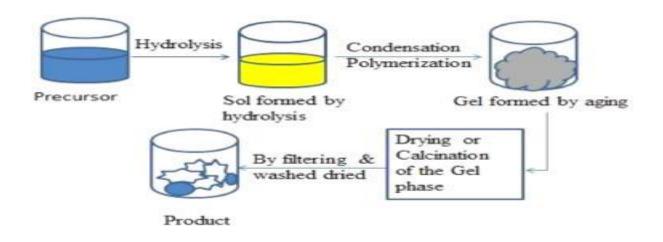
- (i) desalination rate.
- (ii) silica-alumina ratio of leachate free solid product.
- (iii) fusion temperature.
- (iv) concentration of leaching agent.
- (v) crystallization rate.

Several investigators have reported different zeolites synthesis via alkali leaching approach. For instance, synthesized the pure zeolites by alkaline leaching method from the silica extract which was obtained from the fly ash. Their synthesized A-X zeolite blends had the greatest potential for the sorption of cesium ion. Another group of researchers has reported the preparation of mesoporous ZSM-5 zeolite catalysts using(Wajima, 2014)

organic hydroxides by using alkali leaching and desalination methods. According to their finding's, the silicon dissolution in tetraalkylammonium hydroxides was much slower than in NaOH making the demetallation process highly controllable hence producing different quality of zeolite.

## 5.3.6. Sol-gel method

It is a physicochemical process that involves the formation of an in- organic colloidal suspension (sol), and the gelation of the sol in a continuous liquid phase (gel) to form a three-dimensional network structure (Fig. 6).



#### Fig 6 Sol-gel method for synthesis of zeolite.

The sol-gel process encompasses the transition of a solution system from a liquid "sol" into a solid "gel "phase. This method provides better control of the technique which ultimately provides higher porosity and definite particle size .(Le et al., 2019, Ou et al., 2017) There are several factors which can influence the performance of this method. They are:

- (i) hydrolysis rate.
- (ii) temperature.
- (iii) heating rate Meatal.
- (iv)

#### 5.3.7. Microwave method

Microwave heating is a fast and energy-efficient technique in where microwave radiation is applied for the synthesis of zeolites. (Ou et al., 2017)In this method, microwaves act as highfrequency electric fields which eventually produce heat to carry out the reaction. Hence, the energy transfer from the microwave to the

reactant material occurs either through the resonance or relaxation There are many advantages of using microwave methods. For example, it gives concise time, which leads to small particle size and high purity zeolite can be

obtained (Fig. 7)



Fig 7 Microwave methods for synthesis of zeolite. Factors that affect for the microwave method are: (i) SiO2/Al2O3 molar ratio (Si/Al), (ii) alkalinity, (iii) wavelength produced from the magnetron, (iv) zeroization time and temperature, (v) crystallization time and temperature.

In most of the cases, microwave- assisted synthesis of zeolite is applied in combination with other methods such as hydrothermal, solvothermal and ionothermal For example, liked microwave the irradiation for synthesis of synthetic zeolite beta in fluoride media. In their experiment, they showed the role of fluoride mineralization under microwave and seeding to reduce the particle size

due to higher nucleation. Recently, proposed a rapid microwave heating method for the liquid phase synthesis of Y-type zeolite under high-temperature conditions. The effect of microwave

heating temperatures, crystallization time and silica to alumina ratio on the syn- thesis of Ytype zeolite is systematically investigated.

From 1990 to on- wards, the major attempts on zeolitization of fly ash have been made by . Thereafter, several research works have been reported on the synthesis of zeolites from fly ash

#### 5.3.8. Ultra-sound energy method

The ultrasound with frequency 20 kHz to 2 MHz is the branch of termed sonochemistry which is widely used in synthetic chemistry. Ultrasound has significant influences in different types of synthesis cases such as various amorphous or crystalline materials synthesis and polymerization reactions(Jha et al., 2016). Because of high influences on crystallization, application of ultrasound has been received much more attention in the field of zeolite synthesis. The advantages of this method are very simple, rapid reaction, and do not need any complex facilities, high crystal growth rate, suitable particle size distribution and morphology and provide control on nucleation process (Table 2); . Ultra-sound develops cavitation, and this cavitation is the result of the growth and explosive collapse of microscopic bubbles. The cavitation can also raise the secondary nucleation rates and the crystal purity in the time of cooling crystallization . Usually, they are used as a pure powder which does not contain additive or clay binder. Various applications of synthetic zeolite are presented below.

# 6. Applications of synthetic zeolite:

## 6.1. Heavy metal, cation and anion removal

Zeolite exhibit great potential to remove cationic heavy metals (HMs) species from industrial wastewater. It is well known that HMs have many adverse effects on the environments and biological systems. (Petrus and Warchoł, 2005)Various adsorbents or ion exchange materials are used to treat HM contaminated water and wastewater. As a part of this, both naturally occurring zeolites and synthetic zeolites are successfully applied to adsorb a wide range of HM cations such as Cu2+, Cd2+, Cr6+, Zn2+, Pb2+ andHg2+ from various contaminated water streams. Among the different zeolite as sorbents, fly ash-based zeolites, particularly, are gaining popularity amidst researchers. Due to low-cost and bulk availability, presence of well-defined molecular and porous structure, high thermal stability, ion selectivity,

ion exchange capacity and high surface area]. The HM removal efficiency of fly ash zeolites was much higher compared to raw fly ash, which was mainly attributed to their mineralogical alteration

Fly ash has been found effective for the removal of Pb

Table 5								
Metal ion	Zeolite	Zeolite origin	Temperature (°C)	Time (h)	Initial concentration (mg/L)	S/L ratios (g/mL)	pH	Adsorption capacity, q(mg/g)
Cr <sup>3+</sup> and NaA	Blend of NaX	From mordenite	25	24	500	1/200		71.1
Cr3+ and NaP	Blend of NaY	From mordenite	25	24	500	1/200		83.2
Cr <sup>3+</sup>	NaP	From mordenite	25	24	500	1/200		52
Cr3+ te	Hydroxysodali	From kaolin	25	24	500	1/200		34.7
Cr3+	Zeolite 4A	From CFA	25	1	50-100	1/1000	3-4	38.7-56.4
Cr3+	NaP1	From CFA	22	6	100	1/100	4	43.6
Cd <sup>2+</sup>	Zeolite X	From kaolin	25	0.5	20	1/125	7.5	92
Cu <sup>2+</sup>	Zeolite A	From kaolin	25	0.5	20	1/125	7.5	41.6
Cu <sup>2+</sup>	Zeolite X	From kaolin	25	0.5	20	1/125	7.5	44.16
Cu <sup>2+</sup>	Zeolite 4A	From CFA	25	1	50-100	1/1000	3-4	39.8-72.0
Cu <sup>2+</sup>	NaP1	From CFA	22	6	100	1/100	5	50.5
Cu <sup>2+</sup>	NaX +-activated carbon	From CFA	25	24	500	1/500	7	101.7
Cd <sup>2+</sup>	NaX +; activated carbon	From CFA	25	24	500	1/500		129
Cd <sup>2+</sup>	Zeolite A	From kaolin	25	0.5	20	1/125	7.5	71
Cd <sup>2+</sup>	NaP1	From CFA	22	1	100	1/100	6	50.8
Pb2+	NaX +-activated carbon	From CFA	25	24	1000	1/500		228
Pb <sup>2+</sup>	Zeolite	From kaolin	25	0.5	20	1/250	7.5	213
Pb <sup>2+</sup>	Zeolite X	From kaolin	25	0.5	20	1/125	7.5	187
Zn <sup>2+</sup>	Zeolite A	From kaolin	25	0.5	20	1/125	7.5	28.6
Zn <sup>2+</sup>	Zeolite X	From kaolin	25	0.5	20	1/125	7.5	41
Zn <sup>2</sup> *	Zeolite 4A	from CFA	25	2	50-100	1/1000	3-4	19.6-40.4
Zn <sup>2</sup> *	NaP1	From CFA	22	1	100	1/100	6	32.6
Ni <sup>2+</sup>	Zeolite A	From kaolin	25	1	20	1/125	7.5	24.65
Ni <sup>2+</sup>	Zeolite X	From kaolin	25	1	20	1/125	7.5	24.89
Ni <sup>2+</sup>	NaP1	From CFA	22	1	100	1/100	6	20.1
Ni <sup>2+</sup>	Zeolite 4A	from CFA	25	1	50-100	1/1000	3-4	11.5-6.1
Ni <sup>2+</sup>	NaX +-; activated carbon	From CFA	25	24	500	1/500		132.1
C0 <sup>2+</sup>	Zeolite 4A	from coal flash	25	1	50-100	1/1000	3-4	5.5-16.8
C02+	Modified zeolite (MCP-GLU)	From Iran	25	6	600	1/100	6	29.38
Co2+ (NCP)	Modified zeolite	From Iran	25	6	600	1/100	6	19.05
Co <sup>2+</sup>	Modified zeolite (NCP-GLU)	From Iran	25	6	600	1/100	6	41.47

Table 1 summarizes the results of some studies on removing toxic HMs with different synthetic zeolites. Adsorption properties of chitosan/zeolite conjugate films were evaluated for removing Cr4+ ions and excellent adsorption capacity was observed (Johnson and Arshad, 2014).

The positive effect of zeolitic materials on adsorption of other HM cations has been studied thoroughly. For instance, the remediation of Cu2+ toxicity in Jawa tilapia by using a faujasite zeolite was reported. Moreover, many HMs have successfully been removed from water and wastewater streams which indicates the capability as well as the selectivity of zeolite materials toward HMs in summary, synthetic zeolites have higher potentials in the removal of HMs from water and wastewater.

Synthetic zeolites have great potential for the capture of cations from waste-water selectively. Zeolites prepared from the coal fly ash was found the most promising materials for the cation removal

#### 6.2. Removal of radioactive substances

Zeolite is one of the well-known inorganic ionic exchangers for decontaminating radioactive wastewater due to its unique characteristics such as high exchange capacity, thermal and mechanical stability and high resistance to radiation. nuclear waste disposal, more attention has been paid to the treatment and disposal of radionuclides. The study showed that the zeolite and mordenite had good adsorption capacity for 137Cs, 90Sr, and 60Co(Falyouna et al., 2020).

Recently, magnetic zeolite composite (Ze/FeO) was selected as the ideal adsorbent for treating cesium contaminated water in a lab-scale continuous treatment system. It was found that cesium removal capacity was 100% and generated clean effluents that were safely discharged to the environment without posing any environmental and health risks [36]. Recently, Y type nano zeolite NFA-Y was used for the adsorption of Cs+ from aqueous solution. The adsorption capacity of the NFA-Y was 167.12 mg g–1. Very recently, an aluminosilicate with CHA-type zeolite framework was synthesized and investigated for the adsorption of Sr2+ ions which removed 100% of these ions at very high concentration. Synthetic zeolite A was an efficient ion exchange material for the removal of 137Cs and 90Sr ions from waste aqueous. Hence, it is clear about the significance of synthetic zeolite in this field. However, some future studies should have been carried out regarding the applications such as adsorption mechanisms, surface modification of synthetic zeolites, safe handling of the adsorption process.

# 6.3. Synthetic zeolite for gas adsorption

Zeolites have tunable channels with a very rigid framework. This imparts zeolites with excellent shape selectivity and capabilities to- wards gas molecules.(Liang et al., 2020) Natural and synthetic zeolites are found potential for removing SOx, NOx, COx, H2S, and storing H2 gas. Recently, several numbers of reports have published on the adsorptive removal of CO2 using synthetic zeolites (Table 9). Zeolites and metal–organic frameworks are one of the most widely applicable classes of solid-porous adsorbents for CO2 capture. CO2 separation

selectivity and adsorption capacity for carbon capture and sequestration applications, recently a core-shell Zn/Co zeolitic imidazolate framework (ZIF) was synthesized which showed the maximum CO2 uptake (3.22 mmol/g at 273 K and 1 bar). This was 2.13 times higher than that of the raw core-shell Zn/Co ZIF. Nowadays, nitrogen doped carbons derived from core-shell Zn/Co ZIF was found the promising materials for solid CO2 separation from industrial power plant flue gas . The modification of zeolite substrates with catalytic nanoparticles is a suitable method for the removal of similar pollutants such as hydrogen sulfide. In a study, the effect of adding magnetite nanoparticles to zeolite ZSM-5 and Y substrates was investigated.(Tao et al., 2006) Hydrogen sulfide removal at high temperatures by the two substrates was compared. Some of the volatile organic compounds have also been captured by different zeolites Some recent studies suggest that understanding the flexibility of other zeolites and metal organic frameworks will lead to applications in selective separation and storage of small molecules. Still, the performance of these materials is quite limited because of their small pore size and restricted surface area. However, this could be improved by physicochemical modification of zeolite. There are still lots of challenges on

#### **6.4 organic synthesis**

In synthetic chemistry, homogeneous catalysts are preferred because of availability, low cost, and excellent catalytic activity as all the catalytic sites are readily available. But these homogeneous catalysts have several disadvantageous, such as being non-reusable, and require more than the stoichiometric amount. Also, some other drawbacks in its use include the potential dangers in handling, toxicity, corrosive nature, difficulty in separation and recovery, and disposal problems due to the acidic effluent(Jafari et al., 2020). In addition to that, hydrolysis and purification of the resultant complex results in corrosive by-products. So, the basic idea is to find alternative heterogeneous solid catalysts which are stable, reusable, and nature-friendly, and there has been much attention to finding new ones which will also allow a better work up of reaction products. Among these different solid catalysts, zeolites were found to be superior due to their shape selectivity, thermal stability, and reusability.

Freidel-Crafts alkylation and acylation using zeolites as catalyst are common in organic synthesis.

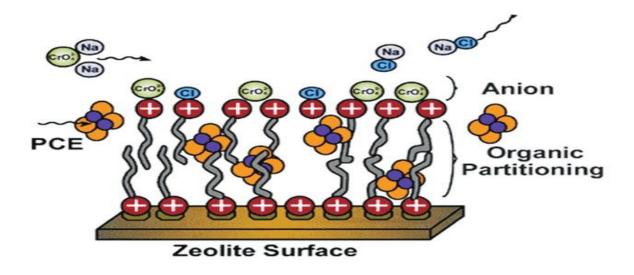


Fig.8. Partitioning of a mixture of toxic chromate anions and perchloroethylene during their combined sorption by a surfactant-modified zeolite (SMZ).

#### 6.5. Ion exchange and softeners

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications.

Earlier, polyphosphates were used to soften hard water. The polyphosphates forms complex with metal ions like Ca2+ and Mg2+ to bind them up so that they could not interfere in cleaning process.(Maiti et al., 2018) However, when this phosphate rich water goes in main stream water, it results in eutrophication of water bodies and hence use of polyphosphate was replaced with use of a synthetic zeolite.

The largest single use for zeolite is the global laundry detergent market. Zeolites are used in laundry detergent as water softeners, removing Ca2+ and Mg2+ ions which would otherwise precipitate from the solution. The ions are retained by the zeolites which releases Na+ ions into the solution, allowing the laundry detergent to be effective in areas with hard water

#### 6.6. Catalysis:

Synthetic zeolites, like other mesoporous materials (e.g., MCM-41), are widely used as catalysts in the petrochemical industry, such as in fluid catalytic cracking and hydrocracking. Zeolites confine molecules into small spaces, which causes changes in their structure and reactivity. The acidic forms of zeolites prepared are often powerful solid-state solid acids, facilitating a host of acid-catalyzed reactions, such as isomerization, alkylation, and cracking.

Catalytic cracking uses a reactor and a regenerator. Feed is injected onto a hot, fluidized catalyst where large gasoil molecules

are broken into smaller gasoline molecules and olefins. The vapor-phase products are separated from the catalyst and distilled into various products(Bezverkhyy et al., 2020). The catalyst is circulated to a regenerator, where the air is used to burn coke off the surface of the catalyst that was formed as a byproduct in the cracking process. The hot, regenerated catalyst is then circulated back to the reactor to complete its cycle.

#### 6.7 Gas separation and storage

Zeolites have the potential of providing precise and specific separation of gases, including the removal of H2O, CO2, and SO2 from low-grade natural gas streams. Other separations include noble gases, N2, O2, freon, and formaldehyde(Davis, 2014).

On-board oxygen generating systems (OBOGS) and oxygen concentrators use zeolites in conjunction with pressure swing adsorption to remove nitrogen from compressed air to supply oxygen for aircrews at high altitudes, as well as home and portable oxygen supplies.

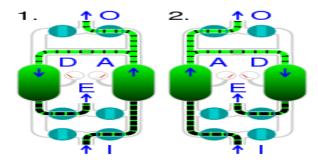


Fig.9Animation of pressure swing adsorption, (1) and (2) showing alternating adsorption and desorption. I compressed air input Adsorption oxygen output D desorption E exhaust Zeolite-based oxygen

concentrator systems are widely used to produce medical-grade oxygen. The zeolite is used as a molecular sieve to create purified oxygen from air using its ability to trap impurities, in a process involving the adsorption of nitrogen, leaving highly purified oxygen and up to 5% argon.

The German group Fraunhofer e.V. announced that they had developed a zeolite substance for use in the biogas industry for long-term storage of energy at a density four times greater than water.[40][non-primary source needed] Ultimately, the goal is to store heat both in industrial installations and in small combined heat and power plants such as those used in larger residential buildings.

Debbie Meyer Green Bags, a produce storage and preservation product, uses a form of zeolite as its active ingredient. The bags are lined with zeolite to adsorb ethylene, which is intended to slow the ripening process and extend the shelf life of produce stored in the bags.

Clinoptilolite has also been added to chicken food: the absorption of water and ammonia by the zeolite made the birds' droppings drier and less odoriferous, hence easier to handle. Zeolites are also used as a molecular sieve in cry sorption style vacuum pumps.

#### **6.8 Solar energy storage**

Zeolites can be used to thermochemically store solar heat harvested from solar thermal collectors as first demonstrated by Guerra in 1978 and for adsorption refrigeration, as first demonstrated by Tchernev in 1974 In these applications,(Amoni et al., 2019) their high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability is exploited. This hygroscopic property coupled with an inherent exothermic (energy releasing) reaction when transitioning from a dehydrated form to a hydrated form make natural zeolites useful in harvesting waste heat and solar heat energy. [non-primary source needed].

#### **6.9. Light emission**

Zeolites were discovered to help silver naturally emit light, which may compete with fluorescent lights or LEDs. Building materials Synthetic zeolites are used as an additive in the production process of warm mix asphalt concrete. The development of this application started in Germany in the 1990s. They help by decreasing the temperature level during manufacture and laying of asphalt concrete, resulting in lower consumption of fossil fuels(Ennaert et al., 2016).

, thus releasing less carbon dioxide, aerosols, and vapors. The use of synthetic zeolites in hot mixed asphalt leads to easier compaction and, to a certain degree, allows cold weather paving and longer hauls.

#### 6.10. Cat litter

Non-clumping cat litter is often made of zeolite (or diatomite), one form of which, invented at MIT, can sequester the greenhouse gas methane from the atmosphere

Hemostatic agent(Andrejkovičová et al., 2012).

Quik Clot brand hemostatic agent, which is used to stop severe bleeding, contains a calciumloaded form of zeolite found in kaolin clay.

### 6.11. Soil treatment

Experimental use of zeolite as soil stabilizer in San Miniato, Tuscany. Mixing composted waste matter from wine production with zeolites.

The microporous structure of the zeolites put into ground stabilizes water release and pH. In agriculture, clinoptilolite (a naturally occurring zeolite) is used as a soil treatment. It provides a source of slowly released potassium(Rhee et al., 2008). If previously loaded with ammonium, the zeolite can serve a similar function in the sl ow release of nitrogen.

Zeolites can also act as water moderators, in which they will absorb up to 55% of their weight in water and slowly release it under the plant's demand. This property can prevent root rot and moderate drought cycles.

#### 6.12. Aquaria

Pet stores market zeolites for use as filter additives in aquaria where they can be used to adsorb ammonia and other nitrogenous compounds. They must be used with some care, especially with delicate tropical corals that are sensitive to water chemistry and temperature. Due to the high affinity of some zeolites for calcium, they may be less effective in hard water and may deplete calcium. Zeolite filtration is also used in some marine aquaria to keep nutrient concentrations low for the benefit of corals adapted to nutrient-depleted waters. Where and how the zeolite was formed is an important consideration for aquarium applications. Most Northern hemisphere, natural zeolites were formed when molten lava came into contact with sea water, thereby "loading" the zeolite with Na (sodium) sacrificial ions. The mechanism is well known to chemists as ion exchange. These sodium ions can be replaced by other ions in solution, thus the take-up of nitrogen in ammonia, with the release of the sodium(Jamshidi et al., 2009). A deposit near Bear River in southern Idaho is a fresh water variety (Na < 0.05%). Southern hemisphere zeolites are typically formed in freshwater and have a high calcium content

## 7.Conclusion

Zeolite is an aluminosilicate mineral having tetrahedral building units made up of [SiO4] 4- and [AlO4] 5-. Since its introduction in the 1960's, it has been applied in a wide range of areas starting from its use as catalysts in catalytic cracking, water softeners and molecular sieves. The current trend in its application is in agriculture, medicine etc. and the application areas keep increasing. Its versatility is based on the fact that many different raw materials can and have been successfully used in its synthesis. The use of readily available, cheap and abundant raw materials in the synthesis of zeolite has been proven to produce good quality zeolites compared to the use of rather expensive chemicals that are also in use to produce them. . Zeolites have been classified into two major types depending on their source: natural zeolites – which are mined from the earth, and synthetic zeolites – which can be made in the laboratory. Natural zeolites are mostly found in volcanogenic sedimentary rocks, having been formed by chemical reactions of the volcanic ash and alkaline water a few thousand millennia ago. At least 60 species of natural zeolites are known to exist, occurring naturally in soils, sediments, and rocks, predominantly concentrated in those rocks and soils of volcanic origin.

Since the current applications of zeolites require more zeolites than can be mined worldwide, together with the fact that natural zeolites contain impurities (such as quartz which is found in most of the clinoptilolite deposits) often leading to a decrease in the zeolites' adsorption and ion exchange efficiency, a need for artificial production has arisen, resulting in synthetic zeolites. More than 200 synthetic zeolites have been reported and shown to have a more uniform composition than natural zeolites. Synthetic zeolites have higher surface areas, higher micropore volumes, lack impurities and can be specially manufactured for a specific task. A large number of different zeolites with varying functional groups have been synthetically produced for specific purposes.

Further research is necessary to tackle the yet undetermined parameters such as the exact behavior and mechanisms in zeolite-catalyzed reactions. Additional comprehension of mechanistic properties of contaminant-surfactant-zeolite interactions will allow advances in applicability of zeolites in providing new low cost, eco-friendly (green) solutions to industrial, agricultural, medicinal to mention but a few challenges.

#### 8. Future recommendations

Different forms of synthetic zeolites facilitate their applications into various fields. However, challenges associated with the synthesis and application of zeolite to need to overcome in future. Need to find out alternative synthetic routes to synthesize high sur face area, controllable molecular dimensions and high adsorption capacity of zeolite materials from different raw materials. Especially, more study requires to find out inexpensive raw materials for the zeolite synthesis.

- Need to study more about on how the nucleation growth during synthesis process of zeolite with the relevant kinetics study and energy calculation.
- Need to develop easy synthetic routes in order to reduce the cost of production.
- Synthetic zeolites need to apply for many new applications including electronic wearable materials development.
- Need to study on the performance of the regeneration of the synthetic zeolite for environmental applications.

Different aspects of the effective synthesis of synthetic zeolites from various raw materials have been critically reviewed. Besides this, the potential advantages and disadvantages of the different synthetic routes and different raw materials have been summarized. It was found that zeolites have versatile applications, although our discussion was limited in environmental applications only. This review results show that the readily available, cheap raw materials have been proven to produce good quality zeolites compared to the use of relatively expensive raw materials. These raw materials can maintain a uniform structure together with lowering the ageing time as well as the cost. However, different methods have some limitations which need to control properly in future. Furthermore, environmental applications of synthetic zeolites have great potential as they have a wide range of applications. Still now, here are a few observations which need to address in the future for the full application of synthetic zeolites in a commercial scale.

- ABDULLAHI, T., HARUN, Z. & OTHMAN, M. H. D. 2017. A review on sustainable synthesis of zeolite from kaolinite resources via hydrothermal process. *Advanced Powder Technology*, 28, 1827-1840.
- AMONI, B. D. C., FREITAS, A. D. L. D., LOIOLA, A. R., SOARES, J. B. & SOARES, S. D.
  A. 2019. A method for NaA zeolite synthesis from coal fly ash and its application in warm mix asphalt. *Road Materials and Pavement Design*, 20, S558-S567.
- ANDREJKOVIČOVÁ, S., FERRAZ, E., VELOSA, A., SILVA, A. S. & ROCHA, F. 2012. Air lime mortars with incorporation of sepiolite and synthetic zeolite pellets. *Acta Geodyn Geomater*, 9, 79-91.
- BEZVERKHYY, I., PUJOL, Q., DIRAND, C., HERBST, F., MACAUD, M. & BELLAT, J.-P. 2020. D2 and H2 adsorption capacity and selectivity in CHA zeolites: Effect of Si/Al ratio, cationic composition and temperature. *Microporous and Mesoporous Materials*, 302, 110217.
- BURROWS, A., HOLMAN, J., LANCASTER, S., PARSONS, A., OVERTON, T., PILLING,
  G. & PRICE, G. 2021. *Chemistry3: Introducing inorganic, organic and physical chemistry*, Oxford university press.
- CEJKA, J., CORMA, A. & ZONES, S. 2017. Zeolites in Catalysis, Royal Society of Chemistry.
- DAVIS, M. E. 2014. Zeolites from a materials chemistry perspective. *Chemistry of Materials*, 26, 239-245.
- ENNAERT, T., VAN AELST, J., DIJKMANS, J., DE CLERCQ, R., SCHUTYSER, W., DUSSELIER, M., VERBOEKEND, D. & SELS, B. F. 2016. Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. *Chemical Society Reviews*, 45, 584-611.
- FALYOUNA, O., ELJAMAL, O., MAAMOUN, I., TAHARA, A. & SUGIHARA, Y. 2020. Magnetic zeolite synthesis for efficient removal of cesium in a lab-scale continuous treatment system. *Journal of colloid and interface science*, 571, 66-79.
- JAFARI, M., ZENDEHDEL, R., RAFIEEPOUR, A., NAKHAEI POUR, M., IRVANI, H. & KHODAKARIM, S. 2020. Comparison of Y and ZSM-5 zeolite modified with magnetite nanoparticles in removal of hydrogen sulfide from air. *International Journal* of Environmental Science and Technology, 17, 187-194.

- JAMSHIDI, R., AFZALI, Z. & AFZALI, K. 2009. Modified natural zeolites as sorbents for separation and preconcentration of traces amount of metal ions. *Asian Journal of Chemistry*, 21, 3381.
- JHA, B., SINGH, D. N., JHA, B. & SINGH, D. N. 2016. Basics of zeolites. *Fly Ash Zeolites: Innovations, Applications, and Directions*, 5-31.
- JOHNSON, E. & ARSHAD, S. E. 2014. Hydrothermally synthesized zeolites based on kaolinite: A review. *Applied Clay Science*, 97, 215-221.
- KRÓL, M. 2020. Natural vs. synthetic zeolites. Crystals, 10, 622.
- LE, T., WANG, Q., PAN, B., RAVINDRA, A., JU, S. & PENG, J. 2019. Process regulation of microwave intensified synthesis of Y-type zeolite. *Microporous and Mesoporous Materials*, 284, 476-485.
- LI, Y., LI, L. & YU, J. 2017. Applications of zeolites in sustainable chemistry. *Chem*, 3, 928-949.
- LIANG, J., LI, J., LI, X., LIU, K., WU, L. & SHAN, G. 2020. The sorption behavior of CHAtype zeolite for removing radioactive strontium from aqueous solutions. *Separation and Purification Technology*, 230, 115874.
- MAITI, S., RAJ, H., BISHT, R., MINOCHA, A., PANIGRAHI, S., ALEXANDER, S. & SINGH, M. 2018. X—ray photoelectron spectroscopy study on adsorption property of harmful air pollutants on zeolite prepared from fly ash. *Materials Research Express*, 5, 085507.
- MARAKATTI, V. S. & HALGERI, A. B. 2015. Metal ion-exchanged zeolites as highly active solid acid catalysts for the green synthesis of glycerol carbonate from glycerol. *RSC advances*, 5, 14286-14293.
- MARAKATTI, V. S., RAO, P. V., CHOUDARY, N. V., GANESH, G. S., SHAH, G., MARADUR, S. P., HALGERI, A., SHANBHAG, G. V. & RAVISHANKAR, R. 2014. Influence of alkaline earth cation exchanged X-zeolites towards ortho-selectivity in alkylation of aromatics: Hard-soft-acid-base concept. *Advanced Porous Materials*, 2, 221-229.
- NAYAK, Y. N., NAYAK, S., NADAF, Y., SHETTY, N. S. & GAONKAR, S. L. 2020. Zeolite Catalyzed Friedel-Crafts Reactions: A Review. *Letters in Organic Chemistry*, 17, 491-506.
- OU, X., XU, S., WARNETT, J. M., HOLMES, S. M., ZAHEER, A., GARFORTH, A. A., WILLIAMS, M. A., JIAO, Y. & FAN, X. 2017. Creating hierarchies promptly:

Microwave-accelerated synthesis of ZSM-5 zeolites on macrocellular silicon carbide (SiC) foams. *Chemical Engineering Journal*, 312, 1-9.

- PETRUS, R. & WARCHOŁ, J. K. 2005. Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems. *Water Research*, 39, 819-830.
- RHEE, P., BROWN, C., MARTIN, M., SALIM, A., PLURAD, D., GREEN, D., CHAMBERS, L., DEMETRIADES, D., VELMAHOS, G. & ALAM, H. 2008. QuikClot use in trauma for hemorrhage control: case series of 103 documented uses. *Journal of Trauma and Acute Care Surgery*, 64, 1093-1099.
- SANJANA, M., VASUBABU, A. & SRINIVASARAO, G. 2022. Zeolites Commercial Applications–A Review. *Mathematical Statistician and Engineering Applications*, 71, 8786-8790.
- SETTHAYA, N., CHINDAPRASIRT, P. & PIMRAKSA, K. Preparation of zeolite nanocrystals via hydrothermal and solvothermal synthesis using of rice husk ash and metakaolin. Materials Science Forum, 2016. Trans Tech Publ, 242-247.
- SHAMZHY, M. V., ELIAŠOVÁ, P., VITVAROVÁ, D., OPANASENKO, M. V., FIRTH, D. S. & MORRIS, R. E. 2016. Post-Synthesis Stabilization of Germanosilicate Zeolites ITH, IWW, and UTL by Substitution of Ge for Al. *Chemistry–A European Journal*, 22, 17377-17386.
- SHOPPERT, A., LOGINOVA, I., CHAIKIN, L. & ROGOZHNIKOV, D. 2017. Alkali fusionleaching method for comprehensive processing of fly ash. *KnE Materials Science*, 89-96.
- TAO, Y., KANOH, H., ABRAMS, L. & KANEKO, K. 2006. Mesopore-modified zeolites: preparation, characterization, and applications. *Chemical reviews*, 106, 896-910.
- WAJIMA, T. Synthesis of zeolite from blast furnace slag using alkali fusion with addition of EDTA. Advanced Materials Research, 2014. Trans Tech Publ, 124-127.