Kufa Journal of Engineering
Vol. 17, No. 1, January 2026, P.P. 96-131
Article history: Received 3 November 2024, last revised 2 January 2025, accepted 11 January 2025

A REVIEW ON ZEOLITES: PROPERTIES, PREPARATION METHODS AND APPLICATIONS

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https://doi.org/10.30572/2018/KJE/170106

ABSTRACT

Zeolites are a particular type of crystalline aluminosilicate minerals that stand out for their remarkable chemical characteristics and distinctive porous architectures. This work offers a thorough summary of the characteristics, procedures for preparation, synthesis parameters, and various uses of zeolites. Zeolites are particularly useful in catalysis, adsorption, and separation processes because of their large surface areas, great heat stability, and ion-exchange capabilities. Their characteristics can be adjusted by a variety of preparation procedures, including ion-exchange operations, sol-gel methods, and hydrothermal synthesis. The achievement of particular material properties depends critically on modifications to synthesis parameters, such as temperature, pH, and precursor concentrations. Zeolites are particularly useful in the petrochemical industry for isomerization and cracking, in environmental engineering for air purification and wastewater treatment, and in agriculture as soil conditioners. The importance of maximizing synthesis conditions to improve zeolites efficiency and selectivity for certain applications is emphasized in this review.

KEYWORDS

Zeolites, Crystalline aluminosilicate, Porous structures, Hydrothermal synthesis, Catalysis, Adsorption.

1. INTRODUCTION

Zeolites are microporous crystalline aluminosilicates with channels and enclosed cages the size of molecules (Auerbach et al., 2004; Jiri Cejka, 2010, 2007; Santi Kulprathipanja, 2010; Scott M. Auerbach, 2003; Valentin Valtchev, 2011). Zeolites are employed in energy and environmental applications due to their narrow pore size distribution and potent catalytic active sites (Ennaert et al., 2016; Valtchev and Tosheva, 2013; Verboekend et al., 2016). The size range of zeolite crystals is micrometers to nanometers. The manufacture of zeolite membranes is one of the many uses for nanometer-sized zeolites (less than 100 nm) (Gascon et al., 2012), sensing technologies (Zheng et al., 2012), catalysis (Mintova et al., 2013), photocatalysis (Del-Pilar et al., 2015), and biomedical diagnostics (Platas-Iglesias et al., 2002).

Since zeolites have a unique structure with many open gaps and channels, they exhibit characteristics common to nanoporous materials. They can absorb and lose up to 30% of their dry weight in water (Ahmadi and Shekarchi, 2010). The tetrahedra of silicon [SiO4]and aluminum [AlO4], connected by common oxygen atoms, are the fundamental building blocks (PBU) of zeolites. Zeolites are crystals with a well-organized structure (Hrachovcová et al., 2020), producing what are referred to as supplementary building units. Löwenstein's rule states that aluminum-oxygen tetrahedra can only be connected to silicon-oxygen tetrahedra (Si–O–Al), while silicon-oxygen tetrahedra can be next to one another (Si–O–Si) (Larin, 2013). When Al3+ is substituted for the Si4+ cation in the tetrahedral position, an excess of electrons, or a negative charge, is created. So-called exchangeable cations as Na+, K+, NH4+, H+, Sr2+, or Mg2+ usually counteract this (Wang and Peng, 2010). These off-grid cations can freely travel within the mineral and easily interact with other ions in the surrounding environment because they are present in the aluminosilicate skeleton's open gaps. Water molecules are positioned next to these cations (De Magalhães et al., 2022). A diverse distribution of tetrahedra gives zeolites their distinctive internal structure. At room temperature, the water molecules inside these tetrahedra form a system of varying-sized structural chambers and channels. This water is known as zeolitic water (Bandura et al., 2022). Thermal treatment easily eliminates this water without changing the zeolite's crystal structure Fig.1. Water molecules or other adsorbates may fill the liberated pores (Kuldeyev et al., 2023; Wang and Peng, 2010). A basic FAU, LTA, and MFI zeolite cell and channel system is shown in Fig. 2.

Axel Fredrick Cronstedt, a Swedish mineralogist, first documented zeolites in 1756. Cronstedt gave them a name that was derived from the Greek terms lithos, which means "stone," and zeo, which means "to boil" (Mastinu et al., 2019). It goes without saying that the most prevalent zeolites analcime, chabazite, clinoptilolite, erionite, ferrierite, laumontite, mordenite, and phillipsite are found widely throughout Cenozoic and Mesozoic crustal strata (K. Margeta, 2013). Naturally formed zeolites are crystalline, hydrated aluminosilicate minerals that contain alkali or alkaline earth metal cations, arranged within a three-dimensional framework built from interconnected [SiO4]4− and [AlO4]5− tetrahedra linked through oxygen atoms. Because of the extra negative charge on the zeolite surface, which causes Si to be isomorphically replaced by Al in the basic structural unit, they are classified as cation exchangers (K. Margeta, 2013).

Natural zeolites have gained significant interest due to their distinctive physicochemical characteristics, such as high ion-exchange ability without altering their structure, substantial pore volume, reversible water loss, capability to adsorb molecules, and catalytic functionality. (Velarde et al., 2023). The cation exchange capacity (CEC) measures the ability of natural zeolites to exchange cations, and their CEC typically ranges from 1 to 4 mmol M^+ per gram of zeolite, depending on the degree of aluminum substitution for silicon in the framework (Belviso, 2020). The geological deposits are closely linked to the physicochemical characteristics. The structural features of zeolites influence their notable cation exchange capacity and high internal surface area, enabling effective interactions with charged species and chemical adsorption of various compounds, which makes these natural minerals well-suited for applications in soil and water remediation (Belviso, 2020). The natural zeolites themselves, however, still face a number of drawbacks, comprising (i) their availability near mining activities, (ii) contaminants, and (iii) a cation exchange capacity within the typical range of 24 meq/g. Moreover, the hydrophilicity of natural zeolites, such as clinoptilolite, is limited due to their higher Si/Al ratio and limited hydroxyl groups, which results in poor ion adsorption performance (Dionisiou and Matsi, 2016). Any natural zeolites adsorption properties are determined by the adsorbent's physicochemical and structural characteristics, as well as by the type, content, number, and location of cations and the Si/Al ratio. Chemical modification, such as acid and alkaline treatment or surfactant impregnation, and single or combination heat treatment are often used techniques to enhance the characteristics of raw materials such as increasing their porosity, surface area, chemical reactivity, and thermal stability, which would make them better suited for particular uses.

Zeolites are mostly found in sedimentary rocks in nature, and they must be activated by at least some mechanical action. Active centers found in zeolites' cavities and channels are crucial for the adsorption of various materials, including heavy metals. As the Si/Al ratio rises, zeolites' exceptional heat stability increases. Natural zeolite typically exhibits minimal structural change up to 300 °C, but at temperatures between 350 °C and 550 °C, its structure begins to break down. Active centers are modified to give them additional properties, greatly increasing their application (Vesna Krstić, 2021). Modifications to the physico-chemical properties of natural zeolites provide the foundation for improving their adsorptive qualities. When zeolites are exposed to an inorganic salt or acidic solution, the exchangeable cations in their framework are usually substituted by other cations, such as H^+ or Na^+, from the contacting solution. The zeolite surface may develop oxi-hydroxides with a preference for anions in solution as a result of alteration with an inorganic salt solution, such as FeCl (K. Margeta, 2013).

All continents have natural zeolite deposits that exhibit a variety of mineral kinds and contents, although precise global reserves statistics are lacking. There are over 70 different kinds of natural zeolites in the globe, and over 250 synthetic zeolites that resemble the natural ones have been produced. Slovakia, Bulgaria, Greece, Italy, and the United States. are the primary natural zeolite suppliers. Under different geochemical conditions, volcanic glass was converted to create natural zeolites (Velarde et al., 2023). The chemical formula of zeolites can be expressed as ((M+x, M2+ y) [Al(x+2y) Sin _ (x+2y) O2n ×mH2O, where M+x and M2+y represent monovalent and divalent metal ions, [Al(x+2y) Sin _ (x+2y) O2n] represents the basic zeolite framework, and m denotes the number of water molecules present (Piergiulio Cappelletti a, 2017). The natural zeolite framework consists of an infinite three-dimensional lattice of tetrahedra, where silicon and aluminum atoms are interconnected by oxygen atoms (I.C. Marantos, 2012). The total lattice is negatively charged because to the presence of Al in this structure [39], and the zeolite characteristics are significantly influenced by the Si/Al ratio (Silaghi et al., 2016). Their internal structure includes cages and channels that carry cations like Na+, K+, Ca2+, and Mg2+ as well as H2O molecules, which balance the three-dimensional lattice's negative charge. In ion-exchange operations, these cations may be substituted by other cations in the zeolite structure (Jiménez-Castañeda and Medina, 2017). Natural zeolites are widely used in a variety of fields, such as waste management, pollution control, biotechnology, agriculture, animal husbandry, medicine, and cosmetics (Cadar et al., 2022). Natural zeolites have a lesser specific area than manufactured zeolites because of contaminants, which makes them less suitable for environmental cleanup. However, the stability of the zeolite structure clearly limits the effectiveness of several methods for eliminating contaminants thereby increasing the specific surface area and porosity of natural zeolites (Ates and Hardacre, 2012).

In recent decades, numerous studies have focused on modifying natural zeolites to enhance their specific surface area or to improve their selectivity toward a particular drug or group of substances. Common activation methods for natural zeolites include chemical treatments (using acids, bases, or inorganic salts), surfactant modification, metal oxide modification, and thermal treatments, applied individually or in combination. When selecting modification procedures, it is important to take into account both the intended use and the financial viability (Vesna Krstić, 2021).

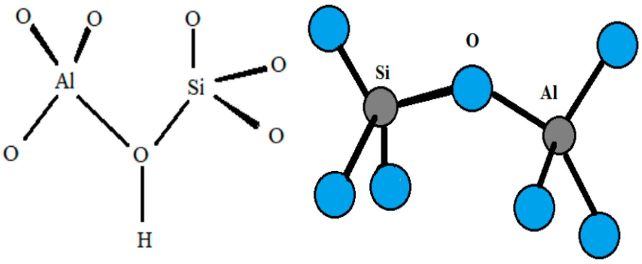

Fig. 1. Zeolite structural model of silicon and aluminum tetrahedra (personally developed based on Khaleque et al., (Khaleque et al., 2020)).

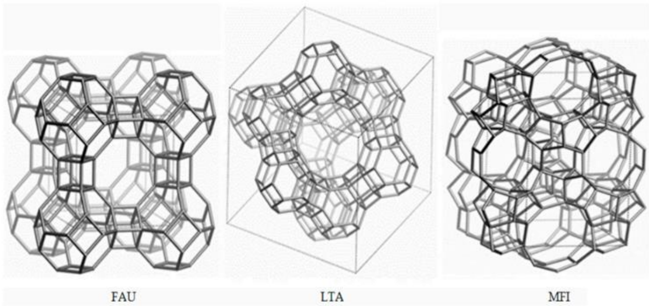

Fig. 2. The Database of Zeolite Structures maintained by the International Zeolite Association is the source of the elemental cell and channel system for FAU, LTA, and MFI zeolites. ("Database of Zeolite Structures", n.d.).

2. PROPERTIES OF ZEOLITES

Synthetic zeolites are highly suitable for specialized industrial applications because they are uniformly sized crystals and extremely pure. Natural zeolites, on the other hand, contain a variety of foreign substances with irregular crystal sizes. In contrast to natural zeolites, which can take from several days to decades to form, synthetic zeolites can be produced in a laboratory setting in a matter of hours or days and have high thermal stability, tunable pore size, and adsorbent surface properties. But compared to naturally occurring zeolites, this produces a far more homogeneous product at a somewhat greater cost. It is possible to create synthetic zeolite from a variety of sources with varying chemical compositions and physical-chemical characteristics. Synthetic zeolites typically have crystal sizes between 1.0 and 10.0 µm and densities between 2.0 and 23.0 g/cm^3. The bulk specific gravity of synthetic zeolites typically ranges between 0.80 and 0.90 g/cm^3 (Breck, 1973). From an optical standpoint, synthetic zeolites have refractive indices ranging from 1.47 to 1.52, and their water absorption capacity lies between 45.0 and 75.0 mL per 100 g (Smit and Maesen, 2008). A desirable level of thermal stability can be attained by lowering the Al content or by keeping the Si/Al ratio higher (Metintas et al., 2010; Zhao et al., n.d.). The quantity of aluminum (as alumina), which can alter the primary distinction between synthetic zeolite types A, P, X, and Y lies in their ion-exchange selectivity and crystal structure. In general, as the alumina and sodium contents rise, so do the ion-exchange capacity and rate of dissolution. Furthermore, zeolites may hydrolyze at pH values lower than 4.0, which could lead to the destruction of their crystal structure by the release of sodium ions, silicic acid, and aluminum salt. On the other hand, the zeolite aqueous suspension is discovered to be in the alkaline range (pH range of 10–10.5). Zeolite A is made up of cuboidal-shaped crystals with double 4-ring connections between sodalite cages. Zeolite type P, which is a member of the gismondine family, has special qualities. The faujasite-type structure (FAU) family includes the zeolite types X and Y. Zeolite type Y has a greater Si/Al ratio >1-1.5 than zeolite type X. These zeolites, however, have a more spherical shape. Their cuboctahedron construction components are connected by hexagonal prisms to a faujasite framework. Their pore diameter is around 0.74 nm, and their surface area is greater. As a result, they can exchange more ions, such as magnesium and calcium. There are numerous industrial uses for them (S. P. Zhdanov, 1990). The properties of zeolite are shown in the Table 1.

Table 1. Summary of Zeolite Properties.

Property	Natural Zeolite	Synthetic Zeolite	Reference
Crystal size	Irregular	1.0-10.0 µm	(Breck, 1973)
Purity	Contains impurities	Very pure	(Breck, 1973)
Formation Time	Days to decades	Hours to days	(Breck, 1973)
Thermal Stability	Lower	Higher	(Breck, 1973)
Porosity and Pore Size	Not Adjustable	Adjustable	(Breck, 1973)
Density	Not specified	2.0-23.0 g/cm3	(Breck, 1973)
Specific Gravity	Not specified	0.80-0.90 g/cm3	(Breck, 1973)
Optical Indices	Not specified	1.47-1.52	(Smit and Maesen, 2008)
(Refractive)	Not specified	45.0-75.0 ml/100 g	(Smit and Maesen, 2008)
Water Absorption	Not specified	Adjustable, higher ratios enhance thermal stability	(Smit and Maesen, 2008)
Capacity	Not specified	Prone to hydrolysis, releasing sodium ions, silicic acid, and aluminium salts	(S. P. Zhdanov, 1990)
Silica to Alumina Ratio (Si/Al)	Not specified	Alkaline (10-10.5)	(S. P. Zhdanov, 1990)

3. PREPARATION METHODS OF ZEOLITES

A variety of synthesis techniques, each with specific benefits and drawbacks, have been investigated for the preparation of zeolite from geopolymers (Mawlod and Ibrahim, 2021). A combination of alkaline liquids and geopolymer precursors is heated to high temperatures and pressures during the hydrothermal synthesis process. Using the alkalinity of geopolymer precursors to induce zeolite formation, alkali fusion and hydrothermal treatment (Davidovits, n.d.), as well as the sol-gel, microwave, and ultrasonic energy methods, are approaches for alkali activation.

3.1. Hydrothermal treatment

The earliest and most widely used method for creating zeolite, which has held a significant position thus far (Yanan Zhang, 2020), is hydrothermal synthesis, which uses temperature ranges of 100 to 240 ºC as illustrated in Fig.3. Because the reaction occurs in a controlled environment, the products of the hydrothermal treatment synthesis have high purity, generally represent low energy consumption, and have a little environmental impact (Yanan Zhang, 2020). Hence, is among the most often used processes for producing zeolite from alkaline solutions (Altmetric Review A mini-review on coal fly ash properties, 2020). The generally used synthesis procedure often involves the use of a sealed vessel in a steel autoclave, typically constructed of polypropylene or Teflon. This approach requires a lower synthesis temperature than other methods (Khaleque et al., 2020b). Traditionally, hydrothermal synthesis requires the use of a sealed vessel, often a polypropylene autoclave lined with PTFE (Sangeetha and Baskar, 2016). This technique is carried out at a reduced temperature. For this reason, compared to other ways, this one is much simpler and less expensive. Zeolites are usually made via a hydrothermal process (Cundy and Cox, 2003), due to a few benefits that have been acknowledged by several researchers (K. Byrappa, 2012), such as low energy consumption, high reactant reactivity, simplicity in solution management, lower air pollution, formation of metastable phases, and development of unique condensed phases. The effectiveness of any hydrothermal process can be influenced by a wide range of variables such as batch composition, temperature and pressure, reactant materials, overall alkalinity, aging time, template conditions, and seeding (E.B.G. Johnson, 2014). One of the benefits of this procedure is that it can activate or remove dangerous components without the need for pre-treatment. Unfortunately, the stringent requirements of sustainability are not addressed by the traditional hydrothermal process (Hyunjoo Lee, 2003; Xiangju Meng and Feng-Shou Xiao, 2014). They immediately construct and fill the pore volume of produced zeolites using structural guiding agents, which requires high temperature combustion to be eliminated continuously. As a result, high temperature burning increases the likelihood of producing greenhouse gases and other dangerous substances (Xiangju Meng and Feng-Shou Xiao, 2014).

3.2. Leaching and alkali-fusion techniques

In zeolite production, the alkali fusion technique is employed Fig. 4 which is a general methodology for breaking down materials rich in silica or alumina when alkali is available. The alkali acts as an activator, promoting the formation of soluble aluminate and silicate ions.

Alkali, such as NaOH, is also employed in solvothermal procedures; however, solvothermal and alkali fused processes differ in several ways which is used in solution form before any solvent is used in the solvothermal method. In the alkali fusion method, the alkali functions as a mineralizer in the reaction medium, preventing the formation of multiple phases and enabling the fusion of raw materials in the solid state. In the alkali-fusion procedure, the hydrothermal treatment usually comes after the primary material has undergone fusion with an alkali (such as NaOH) (Claudia Belviso a, 2017). When undergoing hydrothermal treatment, the fused product is mixed with water and heated to an appropriate temperature to promote crystallization and zeolite formation (Berend Smit, 2008). Alkali-fusion techniques are influenced by the following factors: (i) the ratio of silicon to aluminum in the primary materials; (ii) the concentration of the alkaline reaction medium; (iii) temperature; and (iv) the crystallization rate (Ma et al., 2010; Ma et al., 2010).

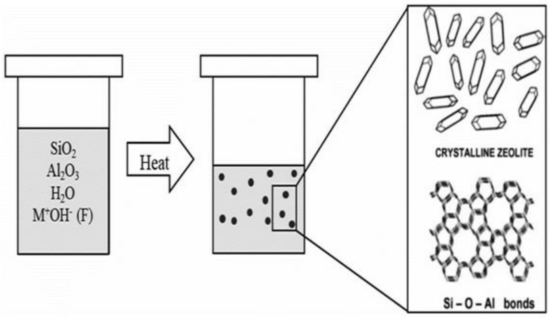

Fig. 3. Schematic of hydrothermal synthesis of zeolite (Nazir et al., 2020).

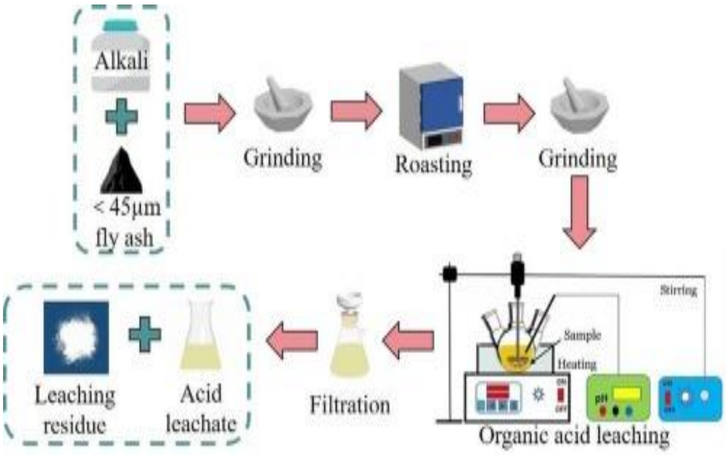

Fig. 4. Diagram showing the alkali fusion process for the manufacture of zeolites (Chen Li a, 2024).

3.3. Sol-gel method

To form a three-dimensional network structure, a physicochemical process called gelation of the inorganic colloidal suspension (sol) in a continuous liquid phase (gel) is required (Ul Haq et al., 1997). The conversion of a solution system from a liquid "sol" phase to a solid "gel" phase is known as "sol-gel process" as illustrated in Fig. 5. Better technique control is possible with this procedure, leading to increased porosity and more consistent particle size (Dongyuan Zhao a, 1998). There are a number of variables that could affect how well this strategy works. The key parameters involved are: (i) pH, (ii) temperature, (iii) heating rate, and (iv) hydrolysis rate (Metintas, 2010; S. P. Zhdanova, 1990). This method's main benefit is that it doesn't require any expensive or specialist equipment (Jatuporn Wittayakun, 2008). Because of the molecular mixing involved in this process, a high-quality homogenous product is produced (Hench and West, 1990). In addition to the many benefits, there are several drawbacks that will need to be addressed in the future, like the price of precursors (Hench and West, 1990).

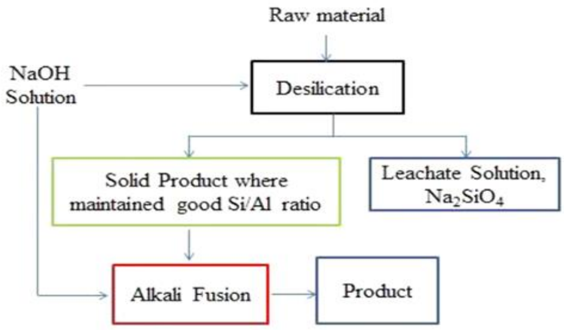

Fig. 5. Alkali leaching method for synthesis of zeolite.

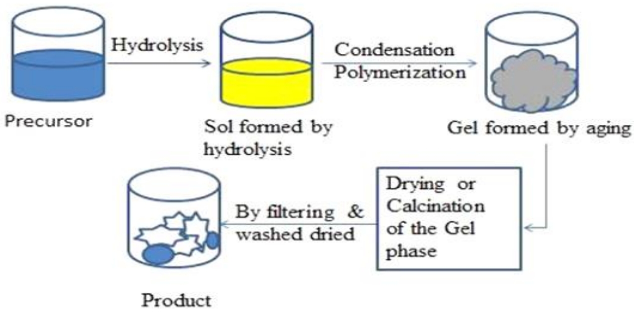

Fig. 5. Zeolite synthesis using the sol-gel method (Khaleque et al., 2020).

3.4. Microwave method

Microwave heating is a fast and energy-efficient technique that utilizes microwave radiation to treat zeolites (Rao et al., 1999). This method employs microwaves as high-frequency electromagnetic fields that carry out the reaction by eventually producing heat (Li and Yang, 2008). Therefore, either resonance or relaxation will cause the energy to be transferred from the microwave source to the reactant material (Arafat et al., 1993; Rao et al., 1999; Xu et al., 2000). The use of microwave techniques demonstrated in Fig.6 has numerous benefits. For instance, it provides brief duration, which results resulting in small particle sizes and the production of high purity zeolite (Xu et al., 2000). The SiO_2/Al_2O_3 molar ratio (Si/Al), alkalinity, the wavelength produced by the magnetron, the zeolization time and temperature, and the crystallization time and temperature are the factors that affect the microwave process

(Arafat et al., 1993). The majority of the time, solvothermal, ionothermal, and hydrothermal processes are used in conjunction with microwave assisted zeolite synthesis (Hwang et al., 2004; Le et al., 2019; Ou et al., 2017; Somani et al., 2003; Umer Khalil a b, 2016; Xiaochun Xu, n.d.). Kim et al. (2004), for instance, synthesized synthetic zeolite Beta in a fluoride medium using microwave irradiation. In their work, they demonstrated the function of seeding to lower particle size due to increased nucleation and fluoride mineralization under microwave (Jong-Chull ShonKaun-Beuk OhSo-Hyun LeeWon-woo Lee, 2004).

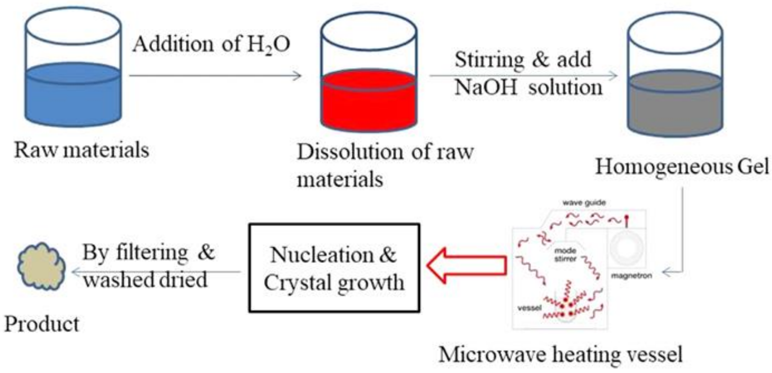

Fig. 6. Microwave synthesis of zeolite (Khaleque et al., 2020).

3.5. Ultra-sound energy method

Sonochemistry, a branch of ultrasonic technology with frequencies ranging from 20 kHz to 2 MHz, is extensively employed in synthetic chemistry (Timothy J Mason, 2002). In many synthesis scenarios, including the synthesis of distinct amorphous or crystalline materials and polymerization reactions, ultrasound has a major impact (Amara et al., n.d.). The use of ultrasound in the synthesis of zeolites has drawn a lot more interest due to its strong influences on crystallization. The benefits of this approach are its extreme simplicity, quick reaction time, lack of complicated facility requirements, high rate of crystal development, appropriate particle size distribution and morphology, along with the capability to control the nucleation process (Andaç et al., 2005; Gora et al., 1997). Cavitation is created by ultrasound, and it is caused by tiny bubbles that build and burst explosively (Boels et al., 2010). During the cooling crystallization process, the occurrence of cavitation can boost the rate of secondary crystal formation and enhance crystal quality (K.S. Suslick, 1990; Mccausland, 2001). Fig.7 illustrates the ultrasonic energy approach that provides tunable zeolite synthesis due to the wide range of traditional and emerging uses of synthetic zeolites. The type and properties of the zeolite produced are primarily influenced by three variables: temperature, reaction time, and reactant molar ratio. The synthesis of zeolites has made considerable use of the ultrasound energy technique.

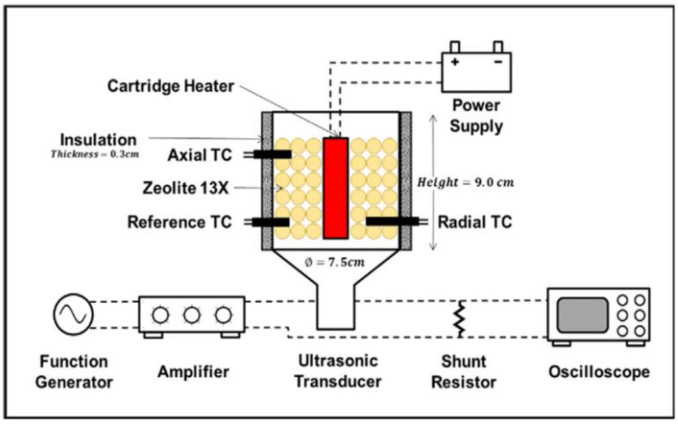

Fig. 7. Ultra-sound energy method (Daghooghi-Mobarakeh et al., 2020).

4. APPLICATIONS OF ZEOLITES

Zeolites are widely used in many contemporary scientific and industrial domains because of their distinct physicochemical characteristics and distinctive structure as microporous materials (Cadar et al., 2022b). such as adsorbents for environmental protection (Yan et al., 2024), molecular sieves, soil additives for agriculture, and catalysts for the petroleum industry. They seem to have innovative and promising applications in biotechnology and medicine. According to Hadžija and Paveli´c, (Auerbach et al., 2003). Natural and engineered zeolites alike have the potential to significantly advance the biological and pharmaceutical sciences due to their vast array of biomedical applications.

4.1. Applications of zeolite in water treatment

Zeolites are frequently regarded as an inexpensive heavy metal removal adsorbent due to the disadvantages and high cost of other well-known adsorbents including silica, alumina, and activated carbon. (Fenglian Fu a, 2011; Karnib et al., 2014). Zeolites' unique ion exchange and adsorption properties make them ideal for water treatment processes (Abraha et al., 2023; Efe et al., 2024; Fatma A. IBrahim et al., 2024; Nadjat Chouat, 2024; Pires, 2024), excellent thermal stability and porosity (Moreno et al., 2001; Yuna, 2016). Furthermore, as Pb, Cd, Zn, Fe, Cu, and Mn ions demonstrate, the exchangeable cation balances their net negative charge (Breck, 1964; Walid Elshorbagy, 2013). These ions are especially significant because of the detrimental impacts they have on the environment and human health (Walid Elshorbagy, 2013). An overview of the use of both natural and synthetic zeolites in the removal of various chemical pollutants from water and wastewater is given by Wang and Peng (Shaobin Wang, 2010). Jimenez-Castaneda et al. provide an overview of zeolites modified with surfactants which are employed to eliminate heavy metals from water (Danina Krajišnik, 2018), Howard et al. (Peter J. Reeve, 2018), Erdem et al. (E. Erdem a, 2004), and Blanchard et al. (G Blanchard, 1984). The zeolites used to cleanse wastewater from a range of sources, as shown in Fig. 8, these include metal-finishing wastewater and various natural, industrial, agricultural, and municipal wastes containing metal ions (Sb, Cr, Cu, Pb, Zn, Co, Ni) [56]. Via exchanging of cations at the zeolite's extra-framework exchange-active positions, the dissolved cations are extracted from the water (Jiahui Shi; Zixuan Yang; Hongliang Dai; Xiwu Lu; Lihong Peng; Xiangyi Tan; Lijun Shi; Raana Fahim, 2018). Tsitsishvili et al. and Wang and Pen (Wang and Peng, 2010) investigated the removal of toxic metals (Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, Mo^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}) from industrial waters using a variety of natural zeolites (clinoptilotite, mordenite, philtipsite, and chabasite); these zeolites are very selective for NH4+ ions even when competing cations are present (Fattahi et al., 2019). The authors discovered that the zeolite exchange sites remove harmful metal ions from water and substitute them with cations that are acceptable to the body, including Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, or H^{+}. (Ajenifuja et al., 2012). Pitcher et al. [60] investigated the use of synthetic zeolite to remove heavy metals from storm water from motorways. Zeolite effectively removes heavy metals; however, its effectiveness depends on the solution's pH (Bauer and Berger, n.d.). Zeolite alumina groups undergo protonation under highly acidic conditions while hydroxyl ions deprotonate them at high pH values. Protonated or neutral alumina groups react with the heavy metal ions. Hui et al. (Hui et al., 2005) demonstrated a comparison of commercial zeolite 4A and zeolites made from coal fly for the removal of heavy metals from aqueous solutions (Hui et al., 2005). They concluded that zeolites derived from coal fly ash can serve as an alternative adsorbent for removing heavy metal ions from wastewater; at pH 4, both the sorption efficiency and metal ion uptake are high (Derbe et al., 2021; El Gaidoumi et al., 2018; Hui et al., 2005).

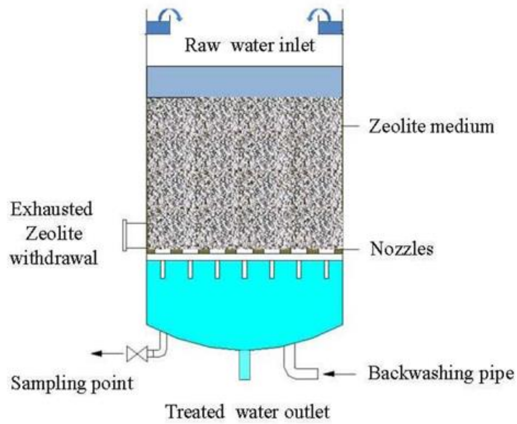

Fig. 8. Schematic representation of zeolite applications in water treatment (Vacca et al., 2010).

4.2. Adsorption of Harmful Substances

Zeolites have been utilized as detoxifying materials to eliminate dangerous compounds, including pesticides, heavy metals (David et al., 2024; Senila and Cadar, 2024) such as (mercury, arsenic, and cadmium), and mycotoxins. Their large surface area makes them highly effective as metal ion adsorbents, as illustrated in Fig. 9. Certain types of cancer and heart disease are facilitated and accelerated by these factors. Therefore, removing a sizable amount of those components from internal circulation blood likely lowers the risk of cancer. This theory that biomaterial adsorption is dependent on metal ion concentration, contact time, and zeolite to chitosan ratio was validated in 2014 when chitosan-zeolite combinations in varying proportions were used to absorb hazardous elements like copper and lead. The study also revealed that a 1:1 ratio results in maximum porosity and enhanced metal ion uptake. About 89% of the entire concentration was absorbed by the copper ions, compared to roughly 60% by the lead ions. Investigations into the absorption rate at various concentrations likewise showed that the amount of absorption increased as concentrations rose, with the maximum absorption occurring at 150 mg/l (Zhang et al., 2015). Basha et al. demonstrated that mice exposed to lead dioxide could have their neurons protected by clinoptilolite (Basha et al., 2013). Three-week-old mice received intraperitoneal injections of lead acetate (100 mg/kg body weight/day) for 21 days, followed by a two-week treatment with EDTA and clinoptilolite (100 mg/kg body weight). As a result, the researchers found that lipid peroxidation decreased, antioxidant systems were activated, and glutathione peroxidase, catalase, superoxide dismutase, and glutathione activity increased.

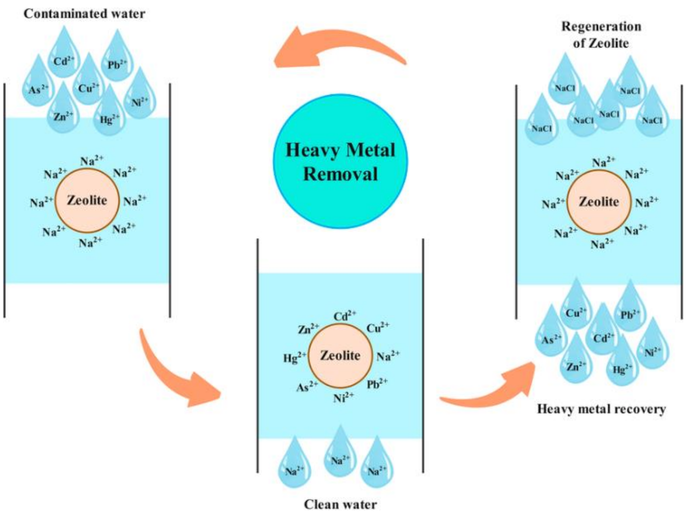

Fig. 9. Zeolite is used in an ion exchange process to remove heavy metal ions from water (Hama Aziz et al., 2023).

4.3. Engineering Bone Tissue

Zeolites are also utilized in tissue engineering (Li et al., 2022), when producing antibacterial compounds, fungicidal dressings, and implant coatings (Neidrauer et al., 2014). The materials exhibit biocompatible (Serati-Nouri et al., 2020a) and possess a highly porous structure (Alhusseny et al., 2023), This makes them ideal for bone tissue cells' adhesion and growth (Zarrintaj et al., 2020a). Bones are organs of dual origin, composed of both organic and inorganic tissues, including minerals, collagen, and fibrous elastin. Bone tissue can simultaneously mend itself and initiate the process of bone tissue regeneration when this organ is damaged. To repair bone tissues, bone grafts autografts, allografts, and xenografts are frequently used. In the early phases of bone remodeling, matrix and osteoclast resorption occurs. Osteoblasts are accommodated by mononuclear cells at the resorption site, where they produce the new matrix. The matrix becomes mineralized during the last step of bone remolding, and some osteoblasts undergo osteocyte differentiation (KREŠIMIR PAVELIĆ, 2019). Their introduction into the human body, however, may result in some issues, such as immunological reactions or trauma effects. A new route for bone regeneration through tissue engineering has recently been established by biomaterial scaffolds and biological components that would directly interact with cells, as represented in Fig. 10. Zeolites, inorganic aluminosilicates with high porosity, large surface area (Morteza Servatan a, 2018), and minimal cytotoxicity, can contribute to the development of effective grafts and coatings, as implants and scaffolds serve as primary frameworks to protect cells and promote their growth and proliferatio (Mohammad Reza Derakhshandeh, 2018). For bone implant applications, calcium-loaded zeolite/poly (amino acid) (CaY/PAA) composites with hemostatic properties were prepared via in situ melt polymerization. In this study, faujasite-type zeolite NaY was converted into zeolite loaded with Ca using an ion exchange chemical pathway (Verboekend et al., 2016). According to the results, the CaY/PAA composites have a reasonable mechanical strength for load-enduring bone replacement since their measured compressive strength, following zeolite incorporation, primarily falls between 145 and 186 MPa. Additionally, zeolites' porous nature allows for the customization of the encapsulation point and release profile of the resultant composites, which control the fluid adsorption characteristics. Additionally, coagulation studies indicated that the CaY/PAA composites perform better at inducing blood coagulation than other composites under study, have a shorter clotting period, and have increased hemostatic activity (Yu Zhong, 2018). Iqbal et al. used a microwave-assisted wet precipitation approach to create a bioactive molecule based on zeolite/hydroxyapatite. Nanostructured zeolite-HA composites accelerated the development of thick layers in tissues and demonstrated appropriate bioactivity and cell compatibility (Iqbal et al., 2014). It was observed that incorporating acid-treated zeolite A into the bone region effectively decreased the number of pits per osteoclast 24 hours post-treatment, and also reduced cathepsin B enzyme activity. One of the most used zeolite materials for altering the surface of bones in a variety of applications is LTA-type zeolite. Pit count per osteoclast following 48 hours of zeolite A calculation of an entrance into the media revealed a similar significant decrease. However, this effect was found to be temporary for the cathepsin

B enzyme, whose rate of reduction either slowed or nearly stopped. Zeolite A structures have a tetrahedral, cage-like structure. Si(OH4) and Al^{3+} are released when the compounds partially dissociate in water solutions with low pH, as applied in this study. Solutions including silica and/or aluminum cations were unable to increase the zeolite's impact. Adding to bone samples. Based on the findings, the residual structure of zeolite-A or a specific subcomponent is likely the primary factor behind the decrease in osteoclast resorptive activity (Schutze et al., 1995). It was observed that administering ZA to homogenous human osteoblast-like cell strains increased the percentage of cells in mitosis and the amount of control DNA synthesis in a dose-dependent manner (Keeting,' Merry et al., 1992; Zarrintaj et al., 2020).

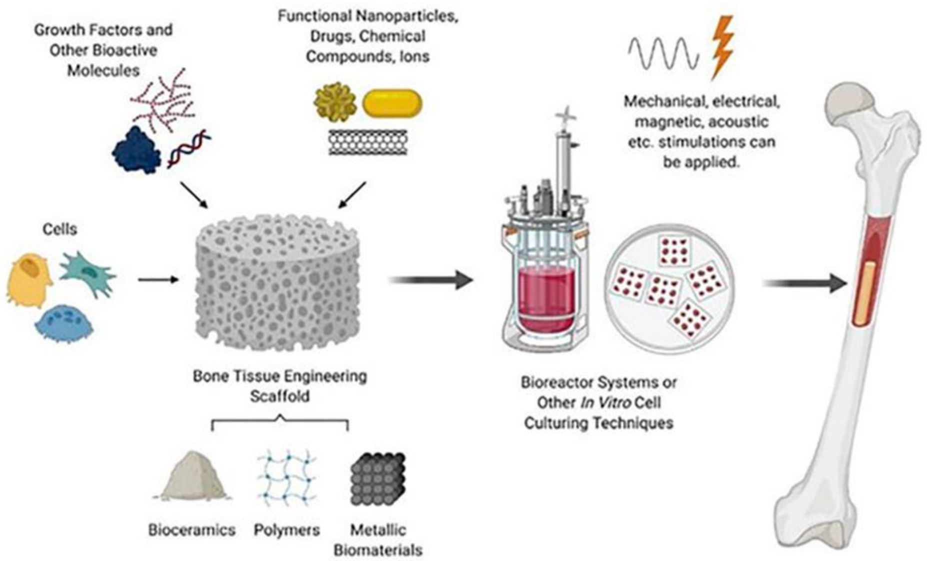

Fig. 10. Techniques for bone tissue engineering (Collins et al., 2021).

4.4. Carriers of Bioactive Compounds

Zeolites are a great biomaterial for drug delivery systems as a result of their high surface-to-volume ratio, stability, and flexibility. These characteristics enable the controlled release and encapsulation of physiologically active substances, Linares et al (Linares et al., 2004; Serati-Nouri et al., 2020b; Zarrintaj et al., 2020b), conducted research to determine the drug's hydrolytic stability and use the zeolite cancrinite as an acetylsalicylic acid carrier. Fig. 11 illustrates zeolite as a platform capable of delivering various types of drugs. However, due to their small size, the drugs are rapidly released from the framework. Therefore, the zeolite's pore size needs to be adjusted to suit the target medication (Horcajada et al., 2004) Moreover, the drug-loading capacity of zeolites can be constrained by the hydrophilic nature of certain pharmaceuticals, although this limitation can be overcome by surface modification of the zeolite (Salim and Malek, 2016). Thus, the surface of a zeolite can be tailored according to the specific drug to be delivered. Zeolite can simultaneously serve as a carrier for acetylsalicylic acid and function as an antacid as evidenced by the fact that none of the two chemicals lost its therapeutic properties. An investigation was carried out by Arruebo et al. (Arruebo et al., 2006). Commercial Na-Y zeolite was mechanically activated during high-energy milling at room temperature to produce magnetite and zeolite nanocomposites. In cancer treatment, the antibiotic doxorubicin is frequently used. Its high capacity and specific surface area (442.9 m2 g−1) allow it to be absorbed, retained, and released in large amounts. When an internal or external magnetic field is applied, the drug carrier can be directed precisely to tumor cells for release. This allows for a reduction in the administered therapeutic dose and minimizes the side effects of the drug (Shan et al., 2006). Zeolites can also be used to carry antimicrobial substances. The effectiveness of an antibacterial ointment with nitric oxide integrated into zeolite-A as the active ingredient for managing both acute and chronic wounds was investigated by Neidrauer et al. (Neidrauer et al., 2014).

The zeolite that was loaded with nitric oxide and exposed to participate in ion exchange with Zn^{2+} ions gradually released it over the course of three hours after coming when exposed to water on the skin, the researchers discovered that the tested ointment's minimum microbicidal concentrations (MMC). The minimum amounts required against yeast C. albicans (5×10^4 c.f.u.) were 50 mg, whereas the MMC against bacterial strains (5×10^7 c.f.u.) ranged from 50 to 100 mg. Compared to the control, the viability of both bacterial and fungal cells decreased after 8 hours of exposure to the zeolite ointment (by 5–8 log cycles and 3 log cycles, respectively). In addition to its medicinal properties, zeolite has the ability to hasten the healing of wounds infected by bacteria. The precise mechanism underlying the antibacterial activity of zeolites is unknown, however it most likely depends on indirect catalysis, physical adsorption, and ion exchange (Matusiak et al., 2023; Muhammad Zubair Mohsin a 2, 2023, 2023). The physical adsorption of microbes by zeolites renders them immobile on their surface, ultimately leading to their demise (Kubota et al., 2008). For example, when zeolites chemically interact with microbes, they release reactive oxygen species (like hydrogen peroxide) or positively charged metal ions (like copper and silver) into the environment from their structures (Chen et al., 2018). This results in microbial cell death and destruction, membrane and cell wall degradation, and membrane potential loss. Reactive oxygen species (like hydrogen peroxide) (Inoue et al., 2002) or positively charged metal ions (like copper and silver) into the environment from their structures (Chen et al., 2018). Consequently, microbial cells can be killed, their walls and membranes damaged, and their membrane potential disrupted. As a result, zeolites have several applications. Applications related to agricultural with a notable focus on decreasing environmental pollution.

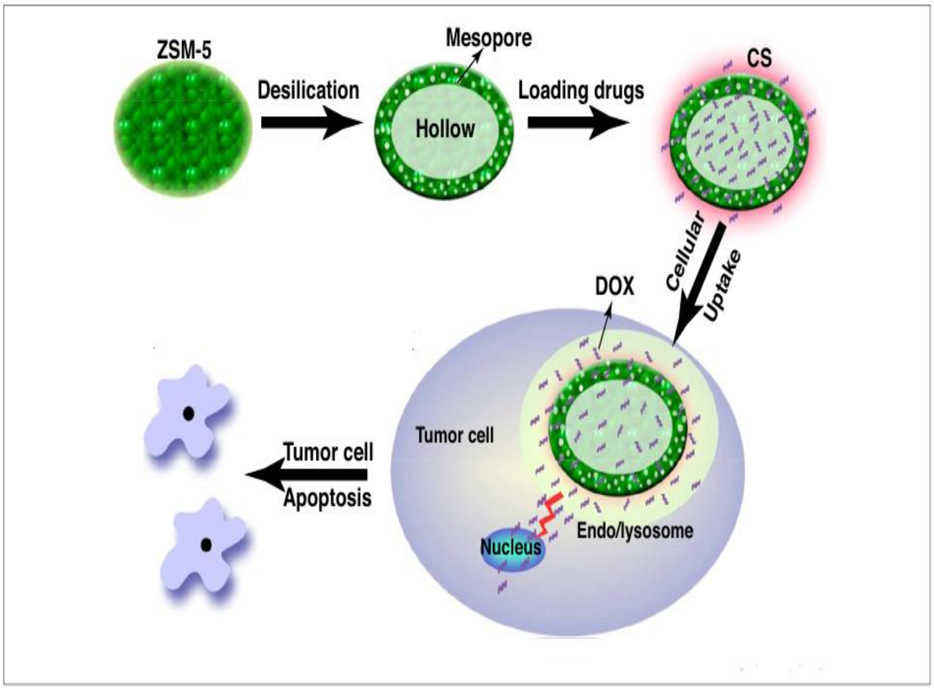

Fig. 11. Zeolite-Based Mechanisms for Drug Delivery (Xi Wen, 2017).

4.5. Antimicrobial and antibacterial

Biocompatible materials are becoming increasingly important in the treatment of diseases due to bacterial resistance to antibiotics (Kucherenko et al., 2022) and a variety of therapeutic plants are regarded as adjunctive therapies in addition to the elimination of pathogenic pathogens. As shown in Fig. 12, zeolites often have an antibacterial impact and have been combined with other complimentary components to strengthen their antimicrobial qualities (Liliana Ferreira a, 2016). In order to accomplish this, scientists in 2015 ionized zeolite Y with sodium, copper, zinc, and silver to compare its antibacterial level. They then utilized two indicators in this regard, which were Saccharomyces cerevisiae yeast and E. coli bacteria. The Zn/Ag element pair demonstrated superior antibacterial capabilities, however the materials supplied had good antibacterial qualities based on these experiments. Their antibacterial activity went as follows: Zn0.05Ag-Y > AgZn0.05-Y > AgCu-Y = CuAg Y > Zn0.05Cu-Y = CuZn0.05-Y = NaY (Chen et al., 2017). The antibacterial effect of gentamicin combined with ZSM-5 zeolite is approximately four times greater than that of gentamicin combined with hydroxyapatite alone. This is because putting antibiotic medications inside zeolites increases the antibacterial action of the medicine. Therefore, there is less bacterial development in that kind of zeolite (Yu et al., 2013). Zeolite and silver were used by Zhou et al. to improve the antibacterial qualities of dental materials. Escherichia coli and Staphylococcus aureus had minimal inhibitory values of 1 and 3.5, respectively, when 365.73 mg of loaded silver per g of zeolite was used. Additionally, 3.5 and 5 were the lowest bactericidal concentrations, respectively (B. Dong, 2014).

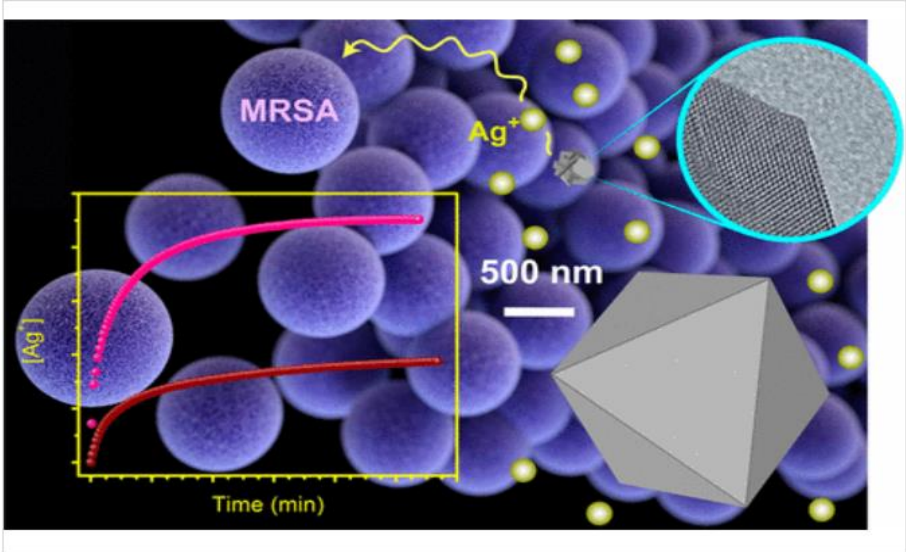

Fig. 12. antimicrobial silver-ion-exchanged zeolites (Chen et al., 2017).

5. CONCLUSIONS

zeolites represent a highly adaptable group of materials with special properties that make them indispensable in a variety of environmental and industrial applications. Their unique porous structures and exceptional chemical characteristics, including as high thermal stability and effective ion-exchange capacities, enable them to be employed in a range of processes, from adsorption and catalysis to environmental remediation. Zeolite preparation techniques, such as hydrothermal synthesis, sol-gel, and ion-exchange processes, offer flexibility in tailoring their properties for specific applications. To achieve the required material properties and performance, it is essential to comprehend and optimize synthesis factors like temperature, pH, and precursor concentrations. Because zeolites increase operational efficiency and lower energy consumption, they greatly improve industrial processes, which benefits the economy and the sustainability of resources. They are also essential for solving environmental issues worldwide, efficiently cleaning water, eliminating contaminants, and enhancing air quality. Energy storage and improving the effectiveness of catalytic processes in the chemical industry are just two of the problems that zeolites' adjustable qualities provide for the creation of novel solutions.

Future research and development efforts should focus on creating new applications and further refining synthesis conditions in order to increase the functionality and efficiency of zeolites. In line with global sustainability goals, the sustainable use of zeolites promotes the development of eco-friendly materials. Taking everything into account, zeolites continue to be a very important area of research due to their numerous applications and revolutionary potential across many industrial and scientific fields.

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