

A Comprehensive Review of Natural and Surfactant-Modified Zeolites and Their Applications

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Abstract: The present review provides an overview of the fundamentals and diverse applications of zeolites as reported in recent literature. Zeolites are crystalline microporous oxide materials with well-defined pores of molecular dimensions within their structure. Natural zeolites have garnered significant attention for their extensive environmental remediation and restoration applications. They are utilized as effective cation exchangers for removing pollutants from industrial wastewater and radioactive contaminants from nuclear power plant waters. Additionally, zeolites exhibit capabilities in decomposing indoor air ozone and enhancing peroxide bleaching of thermal-mechanical pulp, contributing to air and water quality improvement efforts. The review also sheds light on biomedical applications that harness natural and synthetic zeolites, highlighting their potential in diverse medical contexts. Overall, this review encapsulates the multifaceted nature of zeolites and their significant contributions across environmental, industrial, and biomedical domains.

Keywords: zeolites; ion exchange; catalysis; microporous structure; adsorption.

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1. Introduction

In 1756, the Swedish mineralogist Axel Fredrik Cronstedt observed that the mineral stilbite released steam when heated. This observation prompted him to coin the term "zeolite," derived from the Greek words "zeo" (to boil) and "lithos" (stone). Consequently, zeolites are also referred to as "boiling stones" [1]. Today, it is known that zeolites are three-dimensional crystalline microporous hydrated aluminosilicate minerals with the orderly framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral units sharing oxygen atoms between every two consecutive components, as shown in Figure 1. The presence of $[\text{AlO}_4]^{5-}$ tetrahedra imparts a negative charge to the framework, which is balanced by extra-framework cations or transition metal ions to maintain the overall neutrality of the structure. In aluminosilicates, silicon and aluminum atoms are referred to as T-atoms.

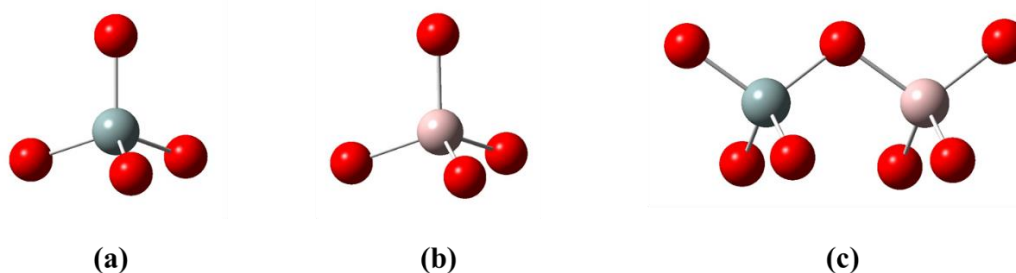


Figure 1. (a) $[\text{SiO}_4]^{4-}$; (b) $[\text{AlO}_4]^{5-}$ are primary building units of zeolite structure; (c) secondary building units of zeolite structure.

Since the 1960s, zeolites have been used in heterogeneous catalysis as shape-selective acid catalysts, for example, in petrochemical processes, especially the fluid catalytic cracking (FCC) processes, and for the conversion of methanol to gasoline and isomerization of hydrocarbons. Altogether, catalysis is the principal application of zeolites in terms of the financial market size (not in terms of tonnage), with an estimated market volume of about one billion US dollars per year [2].

In the present article, we have summarized the types, properties, and some significant applications of zeolites reported in the past. It also includes a discussion on the properties of nanocrystalline zeolites. The applications of zeolites span environmental remediation, catalysis, cation exchange, dye removal, and various industrial and medicinal fields. These materials' continued development and optimization will likely expand their applications and enhance their performance, contributing to sustainable industrial practices and environmental protection.

2. Types of Zeolites

Zeolites are majorly classified as natural and synthetic ones. Natural zeolites occur in nature and are mined for various applications, while synthetic zeolites are purposefully created in controlled environments to meet specific industrial needs. Both types have unique advantages and are valuable in different contexts.

2.1. Natural zeolites.

Natural zeolites are primarily formed through hydrothermal processes and originate predominantly from volcanic sources. They manifest in crystallized structures present in igneous and metamorphic rocks and in the form of smaller diameter grains that accumulate within sedimentary rocks [3]. Over the past few decades, natural zeolites have been utilized in various processes, including catalysis, gas adsorption, ion exchange, the building industry, agriculture, and energy applications [4]. In the last 200 years, more than 40 different types of natural zeolites have been discovered. Common natural zeolites include mordenite, clinoptilolite, Chabazite, phillipsite, analcime, stilbite, and laumontite, while rarer types include offretite, paulingite, barrerite, and mazzite. Among these, clinoptilolite is the most abundant and commonly mined natural zeolite. Toxicological studies have demonstrated that clinoptilolite is a non-toxic and safe material for use in human and veterinary medicine [5]. Due to their properties and significant global occurrence, natural zeolites have garnered renewed research interest for environmental applications. Recently, natural zeolites and their modified forms have been reported for their effectiveness in removing anions and organics from water systems. Natural zeolites exhibit varied ion exchange capacities for cations such as

ammonium and heavy metal ions [6]. This ion exchange capacity is influenced by factors such as temperature, pH of the solution, the availability of competing cations and complexing agents, the dimensions of hydrated dissolved species relative to the openings of zeolite channels, and external surface activity [7].

Since the structure of zeolites is fundamental to their properties and applications, different zeolites are distinguished based on their framework types, as shown in Table 1. The framework type indicates the dimensionality of the channels and cavities. According to the rules established by the IUPAC Commission on Zeolite Nomenclature, each framework type is identified by a unique three-letter code [8].

Table 1. Structural properties with several topologically inequivalent T-atoms (Q), i.e., tetrahedrally coordinated framework atoms, for some natural zeolites (Inspired from [6, 9]).

Zeolite	Chemical formula	Structure type	Q	Symmetry
Chabazite	$(Ca, Na_2, K_2)_2Al_4Si_8O_{24} \cdot 12H_2O$	CHA	1	Triclinic or Rhombohedral
Clinoptilolite	$(K_2, Na_2, Ca)_3Al_6Si_{30}O_{72} \cdot 21H_2O$	HEU	-	Monoclinic
Ferrierite	$(Na_2, K_2, Ca, Mg)_3Al_6Si_{30}O_{72} \cdot 20H_2O$	FER	4	Monoclinic or Orthorhombic
Mordenite	$(Na_2, Ca)_4Al_8Si_{40}O_{96} \cdot 28H_2O$	MOR	4	Orthorhombic
Scolecite	$Ca_4Al_8Si_{12}O_{40} \cdot 12H_2O$	NAT	-	Monoclinic
Phillipsite	$K_2(Ca, Na_2)_2Al_8Si_{10}O_{32} \cdot 12H_2O$	PHI	2	Monoclinic
Stilbite	$Na_2Ca_4Al_{10}Si_{26}O_{72} \cdot 30H_2O$	STI	4	Monoclinic
Laumontite	$Ca_4Al_8Si_{16}O_{48} \cdot 16H_2O$	LAU	3	Monoclinic
Analcime	$Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$	ANA	1	Cubic
Erionite	$(Na_2K_2MgCa_{1.5})_4Al_8Si_{28}O_{72} \cdot 28H_2O$	ERI	2	Hexagonal

2.2. Synthetic zeolites.

Chemical processes are used to synthesize synthetic zeolites, leading to a state that is more uniform and purer compared to natural zeolites. This is evident in the consistency of their lattice structure and the dimensions of pores and cages within their frameworks [10]. Pure chemicals high in silica and alumina, naturally occurring minerals, and industrial byproducts like coal fly ash can be used as the raw material for their synthesis [11]. The formation of zeolite types is contingent upon several factors, including temperature, solution pH, activation process, silica and alumina levels in the raw materials, alkaline concentration during synthesis, and duration of treatment [12].

Sumari and co-workers (2018) synthesized NaY zeolite using local sand as a source of silica and studied the effect of different temperatures. The synthesis was carried out at three different temperatures, i.e., 80, 100, and 150°C. The authors reported that the NaY zeolite was formed better at 80°C as compared to that of 100 and 150°C [13]. Further, Ryu and group (2019) synthesized hydroxyapatite-zeolite from blast furnace slag at four different temperatures, *viz.* 50, 90, 120 and 150°C. The authors reported that the hydroxyapatite-zeolite was formed at all considered temperatures, whereas faujasite-type zeolite was formed at only 90 and 120°C. In addition, at 150°C, the faujasite type zeolite was replaced by the hydroxy sodalite [14].

Kang and co-workers (2013) synthesized Sn-Beta zeolite by employing a steam-assisted conversion method and studied various factors that affect the Sn-Beta zeolite formation like crystallization temperature, gel drying temperature, crystallization time, and amount of water at the bottom of the autoclave. The authors reported that the high-quality Sn-Beta zeolite is formed in the crystallization temperature range of 433 – 473 K and gel drying temperature range of 333 - 373 K [15].

It has been reported that the yield of zeolite T increases with an increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the mixture. Further, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio depends on the alkalinity of the composition. High alkalinity crystallization is favored for zeolite T. The evolution of the zeolite L (LTL type) and zeolite W (MER type) species will begin as the relative alkalinity rises. The alkalinity of the medium depends on the amount of water added. Furthermore, altering the water content of the medium allows for pH adjustments. When the amount of water decreases, the hydroxide ions from mineralizer components of Na_2O and K_2O are released, and therefore, the alkalinity and pH of the medium increase [16-18].

Based on the Si/Al molar ratio, zeolites can be classified as low silica zeolites, intermediate silica zeolites, and high silica zeolites, with ≤ 2 , 2 to 5, and >5 , as their Si/Al ratio, respectively [10]. Some of the common minerals included in low silica zeolites are Analcime (ANA), Na-X (FAU), Phillipsite (PHI), Sodalite (SOD), Cancrinite (CAN), Natrolite (NAT); intermediate silica zeolites includes Chabazite (CHA), Mordenite (MOR), Faujasite (FAU), Na-Y (FAU), and high silica zeolites includes Zeolite- β (BEA) and ZSM-5 (MFI).

Synthetic zeolites have the benefits of high purity, regulated composition, and the opportunity to enhance crucial biological and mechanical aspects of drug delivery [19]. Because of their controlled and known physicochemical properties, most synthetic zeolites are used in laundry detergent powders.

A simplified structural representation of some of the most significant natural and synthetic zeolites is shown in Figure 2, illustrating their unique pore structures and frameworks. These structures are essential in determining their applications and functionalities.

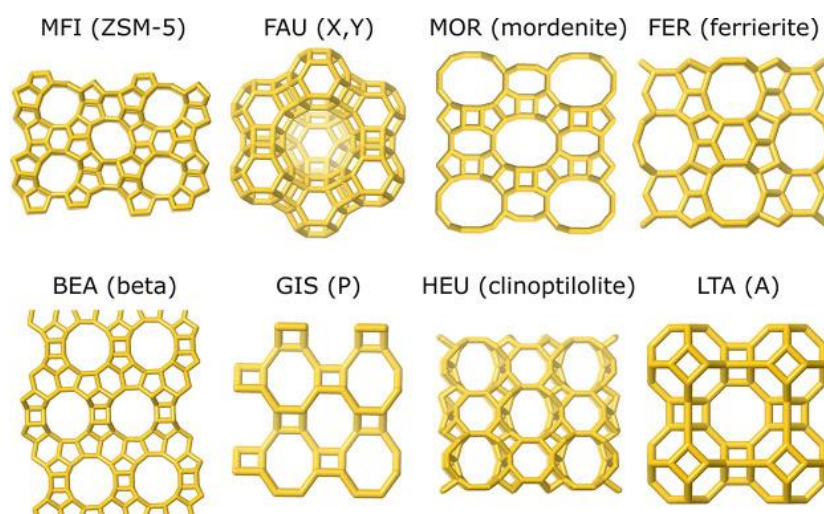


Figure 2. Front view of some selected natural and synthetic zeolites. The common name of the zeolite is indicated in parentheses. Adapted from [20]. Copyright © 2022 The Authors under CC BY 4.0 DEED License.

3. Nanocrystalline Zeolites

The importance of the atomic arrangement on a solid surface is widely acknowledged as a significant factor driving numerous processes, in contrast to those occurring within the bulk. Therefore, two primary strategies are commonly employed to enhance the presence of atoms on the solid surface: reducing the size of dense particles and establishing an open pore network within the solid's bulk. These approaches lead to the development of nanoscale zeolites with consistent pore sizes [21].

Nanoscaling reduces the size of zeolite crystals from micrometers to the nanometer range, typically less than 100 nm, resulting in a higher external surface area per gram of the

sample [22]. As a result of the increased number of active sites on the sample surface, the zeolite's total catalytic activity rises [23].

Figure 3 illustrates the remarkable properties of nanocrystalline zeolites. Their extensive surface area, a characteristic of nanosized zeolites, contributes to their diverse morphology. Other significant attributes include finely adjusting bulk properties, modifying surface properties, and facilitating rapid diffusion of various species within the zeolite cavities [24].

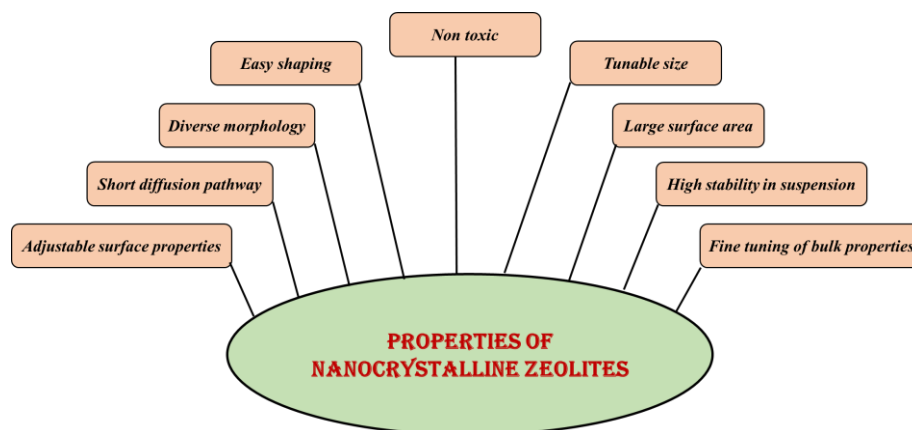


Figure 3. Properties of nanocrystalline zeolites (Inspired from [24]).

4. Properties of Zeolites

Zeolites have been extensively utilized as catalysts, ion exchangers, and adsorbents since their industrial breakthrough in the 1950s. They remain at the forefront of adsorbent technology in numerous separation processes. Moreover, their unique properties position them as preferred materials for developing and emerging separation applications.

Zeolites and related materials exhibit high thermal stability and moderate to high chemical stability. The most crucial property of zeolites, which underpins their use as catalysts, adsorbents, and ion exchangers, is their structural porosity. This characteristic and their narrow and highly regular pore size distribution make them particularly valuable for applications requiring size or shape selectivity. The structural diversity of zeolitic frameworks leads to a wide range of properties, including geometric characteristics such as connectivity, channel dimensionality, and pore space, all of which are essential for applications involving adsorption. Additionally, this diversity influences physical properties, including mechanical behavior [25-27].

Moreover, the acidic protons present in zeolites are known to show migratory behavior at elevated temperatures [28]. From impedance measurements [29,30] and quantum chemical calculations [31] on H-ZSM-5, it has been observed that the acidic proton migrates or hops from one site to other neighboring sites instead of being attached to a specific oxygen site in the zeolite [32,33]. Experimental studies of dehydrated H-ZSM-5 zeolite showed that acidic protons migrate between the four oxygen atoms that surround the tetrahedral aluminum. The mobility of proton in H-ZSM-5 was examined using Density functional theory (DFT) calculations using the cluster formalism, with and without the addition of hydrogen-bearing species RO-H in the gas phase, where R may be H, CH₃, CH₃CH₂, and R-H, where R may be H, CH₃, C₂H₅, C₃H₇, C₆H₅. It was found that the polarizability of the species RO-H causes an increase in the activation barrier. Still, the deprotonation energy of the interacting species R-H causes an increase in the activation energy for the R-H series [28,34].

5. Applications of Zeolites

5.1. Natural and surfactant-modified zeolites as environmental remediators.

Natural zeolites offer a wide range of applications in environmental remediation owing to their ion exchange characteristics [35,36]. The utilization of natural zeolites presents numerous advantages over alternative materials, including their affordability, favorable mechanical and thermal properties, and abundant availability in large quantities. Additionally, they do not introduce any additional environmental contamination. It is well established that ion exchange occurs between cations within zeolites, and several factors influence the uptake of cations from the solution, including temperature, pH of the solution under study, the presence of competing cations, and complexing agents [37]. Thermodynamic studies have revealed that zeolites exhibit enhanced selectivity towards monovalent ions (such as Cs^+ , NH_4^+ , etc.) compared to bivalent cations like Sr^{2+} , Pb^{2+} , etc. [38,39].

Another area of possible environmental use for natural zeolites is the removal of heavy metals (such as Fe, Pb, Cd, and Zn) from acid mine drainage [40-43]. Lead, cadmium, and nickel were successfully removed from contaminated soils using phillipsite and faujasite [44]. Zeolites and humic acids combined with artificially lead-polluted soil significantly decreased the amount of lead in plants while marginally increasing the number of water-soluble lead compounds in the soil [45]. To protect poplar plants grown in contaminated soil, clinoptilolite was examined as a lithium sorbent. Due to its direct traceability using nuclear magnetic resonance (NMR) spectroscopy, lithium was chosen as a model contaminant [46].

Natural zeolites have been extensively studied for their ability to adsorb heavy metals from aqueous solutions. The adsorption process can be carried out using various contact methods, depending on the application and the nature of the adsorbate. These methods include batch systems, fixed bed processes, pulsed beds, fluidized beds, and moving mat filters [47-49].

In batch systems, a fixed amount of adsorbent is added to a known volume of contaminated solution. The solution is then mixed for a certain amount of time to allow for adsorption to occur. The solution is then separated from the adsorbent, and the adsorbate's concentration is measured. This method is useful for laboratory-scale experiments and for testing the effectiveness of different adsorbents.

In fixed bed processes, the contaminated solution is passed through an adsorbent-fixed bed. The adsorbent is held in a column, and the contaminated solution is pumped through the column. The adsorbate is adsorbed onto the adsorbent, and the treated solution is collected at the other end of the column. This method is useful for large-scale applications such as water treatment.

Pulsed bed processes involve alternating the flow of the contaminated solution and the regenerated solution through the adsorbent bed. This method is useful for removing fouling agents that may accumulate on the surface of the adsorbent.

In fluidized bed processes, the adsorbent particles are suspended in a fluid and are kept in motion by the flow of the fluid. The contaminated solution is passed through the fluidized bed, and the adsorbate is adsorbed onto the adsorbent. This method is useful for large-scale applications and removing adsorbates that tend to foul the surface of the adsorbent.

In moving mat filter processes, the adsorbent is placed on a moving belt, and the contaminated solution is passed over the adsorbent. The adsorbate is adsorbed onto the

adsorbent, and the treated solution is collected at the other end of the belt. This method is useful for continuous flow applications and for removing adsorbates that tend to clog fixed bed filters.

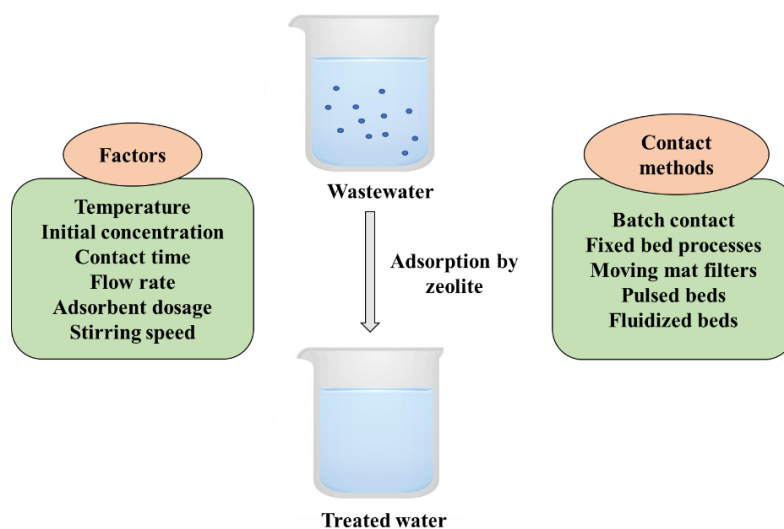


Figure 4. Factors affecting the adsorption process by zeolite (Inspired from [49]).

Several factors influence the adsorption process by zeolites, and optimizing these factors can help improve the efficiency and effectiveness of zeolite-based adsorption processes. These factors include pH, temperature, contact time, adsorbent dosage, concentration of the adsorbate, particle size and surface area, and presence of other ions [49,50]. A schematic representation is illustrated in Figure 4.

Surfactant-modified zeolites have been considered for use as decontaminating agents for soils and water basins, backfill and sealing materials in waste repositories, and as permeable reactive barriers for the cleaning of waters. These materials combine natural zeolites' enhanced cation sorption properties with the capacity to sorb anionic and non-polar organic species from aqueous streams [51]. Quaternary amines, notably hexadecyl-trimethylammonium (HDTMA), octadecyl-trimethylammonium (ODTMA), and N-cetyl pyridinium, are the most commonly utilized modifying agents because they change the surface charge of zeolite by forming a bilayer-like structure on its surface [52]. Laboratory-scale investigations indicated that surfactant-modified zeolites can bind anionic species of metals like iodides, chromates, perchlorates, nitrates, arsenates, etc. [53-57]. Moreover, they demonstrate the capacity to bind pathogens from sewage, such as *Escherichia coli* [58].

5.2. Zeolites for dye removal.

Effluents containing dye residues from diverse coloring or textile industries can pose toxicity risks to microbes and vertebrates. Various chemical, physical, and biological processes have been employed to address the removal of these dyes from effluents [59]. Among these methods, physical adsorption stands out as the most effective in reducing dye concentrations in the effluent. While activated carbon has traditionally been the go-to adsorbent for this purpose, its high production and regeneration costs have increased attention towards alternative adsorbents such as zeolites [60].

Balköse et al. (1996) investigated the adsorption behavior of methylene blue on polyvinylchloride (PVC) composites and noted a decrease in the ability of adsorption of zeolite embedded within the composites [61]. Similarly, Meshko et al. (2001) explored the adsorption of basic dyes from aqueous solutions using granular activated carbon and natural zeolite, <https://nanobioletters.com/>

concluding that the adsorption capacity of granular activated carbon exceeded that of natural zeolites [62]. Subsequent research examined the efficacy of natural and modified zeolites for removing reactive dyes from aqueous solutions, revealing that natural zeolites exhibited limited adsorption capacity for reactive dyes [63-64].

The MCM-22 zeolite has emerged as a highly efficient adsorbent for eliminating dyes like crystal violet, methylene blue, and rhodamine B from aqueous solutions, owing to its unique properties such as an uncommon framework topology, expansive surface area, and remarkable adsorption capacity [65]. Additionally, recent years have witnessed reports of its utilization in other applications, including adsorption and catalysis, highlighting its versatility and potential in various fields [66-68].

5.3. Natural zeolites as cation exchangers.

Each zeolite is characterized by its rigid crystalline anionic framework, generating an electric field. Different cations exhibit distinct interactions with zeolite frameworks and the associated electric fields. Utilizing naturally occurring minerals containing zeolites for cation exchange offers an effective means of removing polluting cations such as ammonium, heavy metal cations from industrial wastewaters, and radionuclides from nuclear power plant waters, particularly in the presence of interfering cations [69,70].

Several physical-chemical methods have been explored in the quest to remove ammonium ions, including selective ion exchange, air-stripping, and breakpoint chlorination. Among various methods, selective ion exchange emerges as the most advantageous for the removal of NH_4^+ from wastewater. Once a suitable exchanger is identified, this method offers advantages over alternatives. For instance, in air stripping, the volatility of ammonia decreases with lower temperatures, leading to a process with low efficiency and high costs. Breakpoint chlorination, on the other hand, produces unintended side effects, and the byproducts generated have a substantial negative impact on the environment.

Additionally, this method involves ammonia oxidation to molecular nitrogen [71-74]. Then, in response to the expensive nature of the selective ion exchange procedure, Mercer and the group recommended using clinoptilolite, a natural zeolite. The calcium and sodium forms of this zeolite showed high selectivity for NH_4^+ ions [74-76].

Addressing the removal of heavy metal cations from industrial wastewater has become a significant concern due to their extensive industrial utilization and adverse impacts on both plants and animals. Initially, the conventional approach involved the direct addition of soda or lime to facilitate the precipitation of heavy metal cations as their hydroxides [77,78]. However, challenges such as the prolonged settling process of metal hydroxides and the disposal of resulting sludge prompted the introduction of natural zeolites as an alternative solution.

Numerous zeolites have been investigated for their capacity to adsorb transition metal ions such as iron, copper, zinc, manganese, nickel, chromium, lead, and others [79,80]. Multiple research teams have scrutinized Chabazite and phillipsite, two commonly occurring zeolites, as potential cation exchangers for eliminating zinc, copper, chromium, and lead from aqueous waste solutions [81-83]. Effective removal of manganese, nickel, and cobalt ions has been achieved using ammonium-modified clinoptilolite [84].

Zeolites offer a valuable application in separating radioactive nuclides from liquid radioactive wastes. Even in low-level liquid waste scenarios, the ion exchange method facilitated by zeolites enables decontaminating water tainted with radioactive nuclides. Studies have highlighted sulfur-modified Chabazite as a particularly effective zeolite for extracting

trace amounts of cesium and strontium from waters in nuclear power plants [85]. Moreover, the literature provides data on removing numerous other radioactive elements, including zirconium, americium, niobium, thorium, and hafnium, among others [86-90].

5.4. Zeolites-driven indoor air ozone decomposition.

Ozone, a hazardous substance present in the Earth's atmospheric layers, poses a significant challenge in indoor air pollution. Its widespread use in various industrial processes, such as soil and water cleaning, textile bleaching, and waste gas oxidation, underscores the urgency of managing ozone levels [91]. Sources contributing to ozone formation include devices like laser printers, photocopiers, and fax machines [92]. Given the potential lung damage from prolonged exposure to ozone, effective removal and decomposition methods are imperative [93,94]. While activated carbons have historically been utilized, their flammability poses limitations [95].

Natural and synthetic zeolites have emerged as viable options for removing gaseous ozone from contaminated indoor air in recent years. Their extensive internal surface area facilitates adsorption and catalytic processes [2]. Additionally, transition metal ions such as copper, iron, and cobalt, along with their oxides, have shown promise as alternative substances for enhancing ozone decomposition [94]. A common method for incorporating transition metals into zeolites is aqueous ion exchange. This process alters the chemical characteristics of zeolites, rendering them effective catalysts for a range of redox reactions.

Recent studies indicate that the ozone removal efficiency of Fe-ZSM-5 and Cu-ZSM-5, reaching 90% and 70%, respectively, surpasses that of the parent ZSM-5 at around 40%. This underscores the significant enhancement in catalytic activity achieved by depositing transition metal ions into zeolites [91].

5.5. Advancing peroxide bleaching of thermal-mechanical pulp with magnetically recyclable zeolite ZSM-5.

Industries involved in paper and pulp production have long been identified as sources of pollution [96]. Various bleaching technologies and chemicals, including hydrogen peroxide, ozone, and oxygen, have been explored to replace chlorine and chlorine dioxide [97]. Among these, hydrogen peroxide is preferred for bleaching mechanical pulp due to its cost-effectiveness and eco-friendly properties. However, a significant drawback of hydrogen peroxide is its catalytic decomposition by transition metal ions such as manganese and copper [98]. To mitigate this issue, chelating agents like ethylenediaminetetraacetic acid (EDTA) and stabilizing agents such as magnesium sulfate and sodium silicate are utilized to form stable complexes with transition metal ions [99].

Nevertheless, these chemicals pose limitations, including the poor biodegradability of chelating agents [100]. Stabilizing agents are released as bleaching effluents post-process, potentially causing environmental pollution. Therefore, a promising solution to these challenges lies in the use of zeolites like ZSM-5, which are non-toxic and environmentally friendly. These zeolites diminish the catalytic activity of peroxide decomposition by binding transition metal ions via internal anionic sites [101]. However, incorporating zeolites into pulp presents challenges regarding their reusability, which directly impacts the bleaching process's cost.

Magnetic separation emerges as a highly efficient and rapid method for recycling and removing magnetic species by applying a magnetic field [102]. Recently, magnetically recyclable ZSM-5 zeolite particles have been employed for alkaline hydrogen peroxide bleaching of thermal-mechanical pulp from *Acacia mangium* to enhance the bleaching process. These zeolite particles demonstrate high efficiency in adsorbing transition metal ions like manganese and copper, thereby preventing hydrogen peroxide decomposition during bleaching and resulting in increased pulp brightness post-bleaching. Moreover, they exhibit significant catalytic activity for various organic reactions [103].

5.6. Catalytic applications of zeolites.

Zeolites have been used as catalysts in various industrial chemical reactions. Presently, zeolites are the most significant heterogeneous catalysts in the petrochemical and oil-refining sectors. The bronsted acid sites in the zeolite framework play a crucial role in the catalytic reactions. The zeolite-catalyzed petroleum refining processes chiefly include olefin alkylation, reforming, cracking, and hydrocracking [104,105].

The principal function of the cracking component is to reduce high molecular weight hydrocarbons into fractions with lower boiling points (particularly gasoline). Catalytic cracking is preferred over thermal cracking as the gasoline produced in the catalytic cracking is of a high-octane number along with a high yield. Fluid catalytic cracking (FCC) is known to be one of the fundamental applications of zeolite catalysts. The crucial reactions in catalytic cracking include isomerization, dehydrogenation, hydrogen transfer, cyclization, and condensation. FCC yields hydrocarbons with high anti-knock characteristics and lowers the production of methane and olefinic hydrocarbons [106,107].

Reforming the heavy naphtha fraction into mixtures where aromatic chemicals (in particular benzene, toluene, and xylenes) are the major components is one of the most crucial operations in refining. Reforming involves the conversion of saturated cyclic and acyclic hydrocarbons into aromatic compounds through dehydrogenation without significantly lowering the proportion of carbons in the products to those in the substrates. The primary goal of reforming is to produce aromatics because they have octane numbers above 100 and, when added to a gasoline pool, significantly raise the octane number of the final blend. Since the principal process involved in reforming is dehydrogenation with hydrogen evolution, acidity is not required for the catalyst; instead, it comprises noble metals with excellent dehydrogenation/hydrogenation activity as its key active component. Thus, the majority of commercial reforming catalysts rely on Pt supported on large surface areas materials like metal oxides or non-acidic zeolites [4,105,108].

On a broad scale, one commonly employed process for converting heavier hydrocarbons into lighter fractions involves hydrocracking crude oil, vacuum oil, and oil derived from coke into lighter compounds. This process aids in reducing the boiling point of residual oil. In terms of the efficacy of zeolites in hydrocracking, research indicates that higher acid strength contributes to an elevated proportion of naphtha formation during hydrocracking, albeit at the expense of middle distillates [109,110].

5.7. Biomedical applications of zeolites.

Zeolites have found numerous biomedical applications due to their unique properties, including drug delivery, wound healing, tissue engineering, biomedical imaging, hemodialysis, and antibacterial and antiviral applications [111,112].

Zeolites have found applications in drug delivery owing to their large surface area, ion exchange properties, and controlled release capabilities. The zeolites' porous structure allows for the encapsulation of drugs, which can be released slowly over time. In drug delivery systems, zeolites can be carriers for hydrophobic and hydrophilic drugs. The drug can be loaded into the zeolite's pores through various methods, such as adsorption, ion exchange, or covalent bonding. The release of the drug can be controlled by adjusting the pH, temperature, or other external stimuli [113].

Zeolites have a wide range of features, allowing them to serve as molecular sieves with long-term chemical and biological stability, promote ion exchange, and absorb gas and water molecules [5]. Several toxicological investigations on the natural zeolite clinoptilolite revealed that it is non-toxic and can be used as an adjuvant in cancer treatment [114]. It has also been found to be effective in the treatment of diabetes. Copper-ion-containing zeolites exhibit effective antibacterial properties against gram-positive and gram-negative bacteria [115]. In magnetic resonance imaging (MRI), gadolinium zeolite is a good contrast material for improving the gastrointestinal system [116]. According to Liu and colleagues, the hydrophilic characteristics of zeolites allowed for the retention of the soluble enzyme and methylene green, considerably enhancing the sensor's stability [117].

Zeolite A, which is a synthetic zeolite, can stimulate bone formation. Zeolites also have exterior uses in dermatology and cosmetics because they can shield polymers from UV deterioration. Moreover, they have been shown to speed up the healing of surgical incisions and wounds. In medicines, zeolites like clinoptilolite are used as antidiarrheal agents for treating skin wounds and ammonia removal from body fluids in kidney dialysis [111,112,118,119]. Apart from these, zeolites have found a huge number of biomedical applications, as shown in Figure 5.

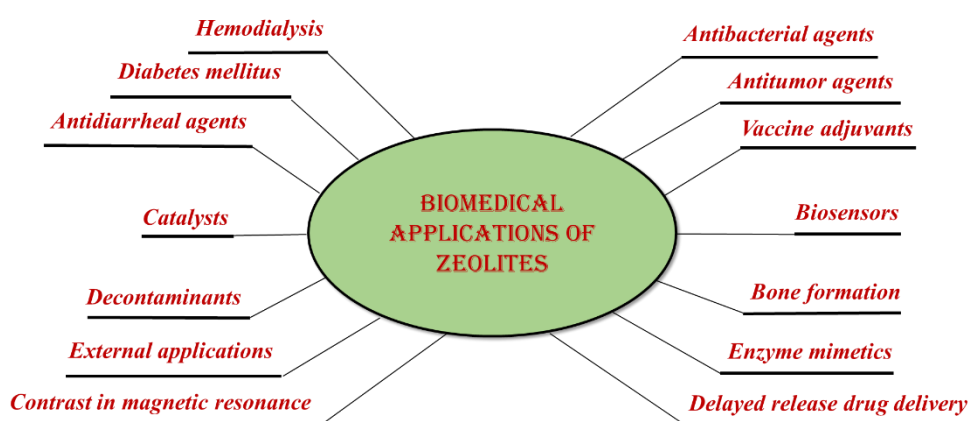


Figure 5. Biomedical applications of natural and synthetic zeolites (Inspired from [120]).

Research has demonstrated that zeolites possess antibacterial properties against a diverse array of bacterial species, encompassing both gram-positive and gram-negative species. The antibacterial activity of zeolites is thought to be due to several mechanisms, including ion exchange, adsorption, pH regulation, and release of metal ions. Studies have shown that zeolites can be effective against various bacterial infections, such as skin, respiratory, and

urinary tract infections. Zeolite-based materials have been developed for use in wound dressings, antibacterial coatings for medical devices, and as a potential alternative to traditional antibiotics [121].

Overall, zeolites typically exhibit antibacterial effects and have been employed alongside other complementary elements to enhance their antimicrobial properties. In 2015, multiple research groups ionized zeolite Y (FAU type) with zinc, copper, silver, and sodium to assess and compare their antibacterial efficacy. Two indicators, *Saccharomyces cerevisiae* yeast and *E. coli* bacteria, were utilized in the study. The results indicate that the combination of zinc and silver demonstrated superior antibacterial activity. [122,123]. Further, the antibacterial effect of the drug could be enhanced by inserting an antibiotic drug into the zeolite. Gentamicin combined with zeolite ZSM-5 has an approximately four-fold greater antibacterial activity than gentamicin combined with hydroxyapatite alone [124].

Zeolites have been investigated as potential filters for hemodialysis fluids due to their ability to remove toxins and waste products from the blood while maintaining essential electrolyte balance. The zeolites' porous structure efficiently removes uremic toxins and other waste products from the blood during hemodialysis. Zeolites have been shown to have high ion exchange capacity, which removes excess electrolytes from the blood while maintaining proper electrolyte balance. Additionally, zeolites have been investigated as a potential replacement for traditional dialysis membranes due to their ability to selectively remove toxins while retaining essential nutrients and proteins in the blood [125].

6. Conclusions

The comprehensive review of the scientific literature presented in this study underscores the diverse applications of natural zeolites in addressing environmental challenges. Surfactant-modified zeolites, in particular, emerge as effective tools for removing harmful anions and organic contaminants. Additionally, incorporating various transition metals into zeolites enhances their catalytic activity, as evidenced by the superior ozone removal efficiency of iron and copper-loaded ZSM-5 compared to the parent zeolite ZSM-5. Furthermore, nanocrystalline zeolites' expanded exterior surface area enables them to serve as reactive surfaces for adsorption and catalysis, enhancing their efficacy in various applications.

Zeolites play pivotal roles as catalysts in numerous petrochemical and oil-refining processes, showcasing their versatility in industrial contexts. Moreover, their applications extend to biology and medicine, reflecting their broad utility beyond traditional environmental remediation. With their inherent ion exchange properties facilitating the removal of contaminating ions from diverse solutions, zeolites offer a promising array of prospective applications.

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Conflicts of Interest

The authors declare no conflict of interest.

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