



Review

Zeolites as Carriers of Nano-Fertilizers: From Structures and Principles to Prospects and Challenges

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Abstract: The world is facing immense challenges in terms of food security, due to the combined impacts of the ever-increasing population and the adversity of climate change. In an attempt to counteract these factors, smart nutrient delivery systems, including nano-fertilizers, additives, and material coatings, have been introduced to increase food productivity to meet the growing food demand. Use of nanocarriers in agro-practices for sustainable farming contributes to achieving up to 75% nutrient delivery for a prolonged period to maintain nutrient availability in soil for plants in adverse soil conditions. In this context, sieve-like zeolites and the diversity in their structural morphologies have attracted increasing interest over recent years. Engineered nano-porous zeolites, also called aluminosilicates, are defined based on the presence of micro- (<2 nm), meso- (2–50 nm), and macropores (>50 nm), which can be employed as carriers of fertilizers due to their enhanced ion-exchange properties and adsorption capabilities. In this study, we provide a detailed overview of the production and optimization of hierarchical zeolite structures within the size range from micro- to nanometers, as well as the various top-down and bottom-up approaches which have been used to synthesize zeolites with a large surface area, tunable pore size, and high thermal stability, which make them an excellent candidate to be used in agronomy. The delivery of pesticides, insecticides, and fertilizers by loading them into nano-zeolites to manage the crop production without disrupting the soil health is discussed, as well as future perspectives of zeolites in the perpetual maintenance of soil productivity.

Keywords: engineered nano-zeolites; controlled-release fertilizers; toxic effects

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1. Introduction

The world's food demand is rapidly growing due to a rapid increase in the global population, which is expected to rise to 9.6 billion by 2050. It is estimated that the annual grain production should increase by 70% to meet the food demand of the world's population [1,2]. Over the past few decades, extensive use of agrochemicals has enhanced agricultural productivity, but also compromised human and soil health, disrupting food supplies due to the reduced agricultural yield [3]. At present, fertilizer contributes to improving 50% of total agriculture production, but increasing the dose of fertilizers does not always guarantee an increased crop production and yield. These agricultural practices demand excessive use of nutrients such as N, P, K, Ca, Mg, Fe, Zn, Mo, and B to enhance soil fertility and productivity, but might lead to soil contamination [4]. Despite the increased use of fertilizers, the rate of nutrient removal from the soil is much higher, resulting in a net-negative soil nutrient balance of about 10 million tons, and widespread economic loss to farmers [4]. Nutrient deficiency is a major contemporary problem. Nutrients contained in chemical fertilizers are not readily available to plants due to their macro size; thus, crops

use as little as half of what is applied [5]. Furthermore, most macronutrients are insoluble in soil, and the unused fractions run off, contributing to the soil and water pollution. Overuse of chemical fertilizers has short-term gains in terms of an increase in crop yield or production, but poses long-term detrimental effects on the ecosystem.

Most developing and underdeveloped countries do not have proper legislation for using chemical fertilizers. In most cases, the chemical fertilizers are sprayed or drizzled onto plants without considering the nutritional conditions of the plant or soil. As a result of non-targeted strategies of conventional fertilizer application, the amounts of nutrients reaching the plant are much less than that lost through leaching and spillage from the agricultural fields to the water bodies and the soil. The other challenges of using conventional fertilizers include economic losses, environmental impacts including damaged microflora, disruption of ground food webs which leads to genetic mutations, changes in ecosystem ecology, reduced nitrogen fixation, and an increased number of pathogens and pests eventually affecting the soil flora and fauna [6].

The challenges of nutrient deficiency can potentially be addressed through nanotechnology-based solutions, and specifically targeted nutrient delivery through engineered nanoscale materials. Nanomaterials have the potential to revolutionize the agriculture sector by changing the food system, improving crop yield, preserving ecological balance, and fostering environmental sustainability [7]. With their small size, large surface area, high solubility, and mobility, these particles can be well dispersed in soil, and easily diffuse across plant cell membranes by soil or foliar treatment. Nanoparticles (NPs) can easily translocate in plants, promoting the release of nutrients through nano-fertilizers, and can also provide better protection using nano-pesticides and nano-herbicides.

A strong candidate to be employed as a carrier of nutrients are porous aluminosilicates known as zeolites. They are naturally occurring or can be synthesized chemically, whereby their porosity can be tuned on nanoscales, depending upon the application requirements. Naturally available zeolites include clinoptilolite, mordenite (MOR), erionite, phillipsite, analcime, lind type A (LTA), chabazite (CHA), beta-structured (BEA), sodalite (SOD), etc. They have different pore sizes, ion exchange properties, and bulk densities [8]. On the other hand, synthetic zeolites are prepared using different methodologies (template-assisted, template-free, hydrothermal treatment, etc.), with the advantages that their size, shape, and other physiochemical properties can be modified [9].

The unique properties of zeolites enable the prolonged and controlled introduction of necessary nutrients such as potassium, ammonium, and phosphates into the soil [10]. Studies have also shown that zeolites serve as slow-release sources of nutrients when they are pre-charged with ammonium–nitrogen ($\text{NH}_4 = \text{N}$) and iron (Fe^{2+}), then selected as components in soilless media [11]. In order to minimize nitrate leaching and volatilization, slow-release fertilizers with zeolites are needed to support the increasing demand of nitrogen in soil [12]. Both natural and synthetic zeolites are studied for their capability to load fertilizer and use as delivery molecules [13,14].

Other review articles describing the use of zeolites in agriculture including the use of zeolites as an addition to fertilizers [15], zeolites enhancing soil health, crop productivity and environment safety [16], zeolite-based composites as slow-release fertilizers [17], and applications of zeolites in agriculture and other potential uses [18] have recently been reviewed. This review describes the performance characteristics of zeolites as nutrient delivery systems, furthering understanding of what nano-zeolites are and their associated synthesis methodologies, and how the physicochemical properties of the nano-zeolites such as size, porosity, and thermal stability can be fully exploited in agriculture as carriers of nutrients, pesticides for enhanced delivery, and their long-lasting effects as compared with conventional fertilizers.

2. Smart Nutrient Delivery: Nano-Fertilizers and Their Mode of Action

Nano-fertilizers function as smart fertilizers which are either modified or synthesized from traditional fertilizers and bulk materials. They are of three different types:

- i. Nanoscale fertilizers (nanoparticles of silica, iron, etc., which contain nutrients);
- ii. Nanoscale additives (established fertilizers with nanoscale additives);
- iii. Nanoscale coatings (fertilizers coated with nanoscale materials).

Nanotechnology in the agriculture sector is still in its infancy, as compared with medical and engineering applications. Nanoparticles have the potential to act as carriers of nutrients, leading to the concept of nanoscale fertilizers as smart nutrient delivery systems. Nano-fertilizers have advantages over routine agrochemical methods due to their large surface area, controlled release of nutrient formulations to match uptake patterns of the crops, increased nutrient uptake efficiency, solubility, and dispersion of micronutrient-directed release modes, and reduced loss rate of nutrients [6]. Nanocarriers have many advantages (Figure 1) because of their physicochemical properties, including their stability in media, their size, and biocompatibility, which helps to increase their shelf life in soil, resulting in efficient mixing of the fertilizer solution. Ordinary fertilizers, if used in excess, can have harmful effects on humans. However, the use of these delivery molecules helps to mitigate the drastic effects of ordinary fertilizers [19]. The encapsulation of fertilizers for the controlled release will not only protect the active ingredient, but will also affect the diffusion rate, the interactions of compounds with the environment, and their activity [20].

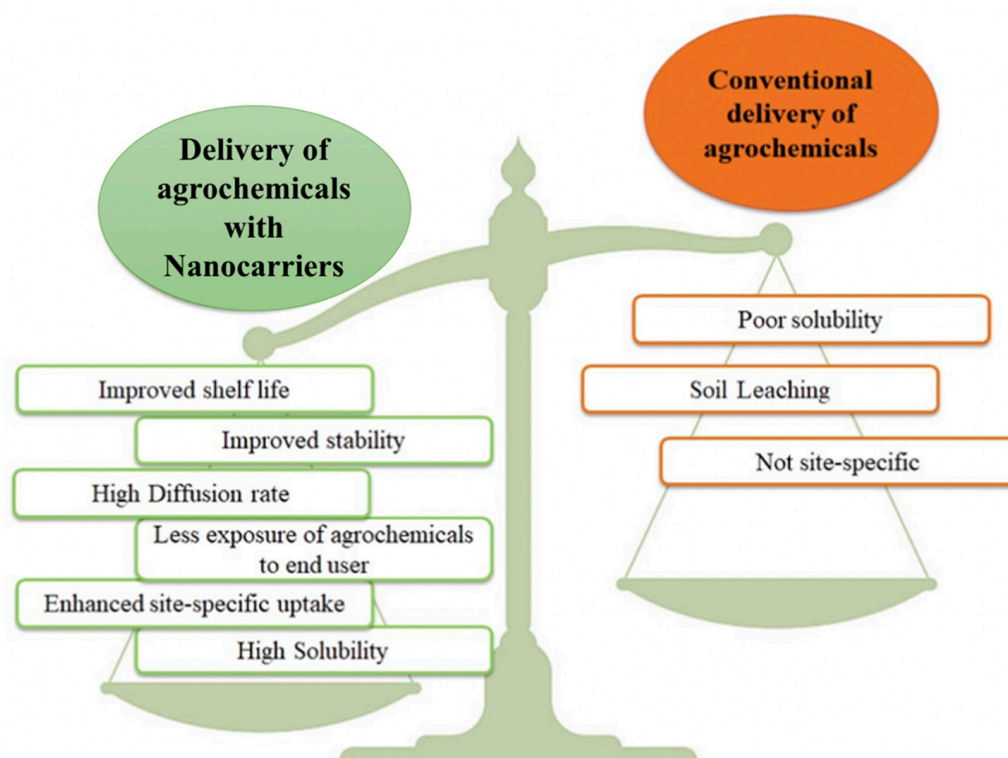


Figure 1. Advantages of delivery of agrochemicals using nanocarriers over conventional delivery.

Nanoscale fertilizers are smaller than the sizes of pores in the roots and leaves of plants, which increases their absorption and the uptake of nutrients in the plant body. Nano-zeolites can release nutrients to the plant body at a slow rate, which increases the availability of nutrients in crops and prevents the loss of nutrients from denitrification, volatilization, and leaching [21]. The surface coating of nanoparticles with various biocompatible polymers helps to slow the release of compounds; alternatively, the surface can be made more porous so that some of the nutrient content can be retained for a longer period. The nutrient release rate required by slow-release fertilizers (SRFs) is different, depending upon the requirements of crops. The European standardization committee task force has defined the criterion for SRFs that not more than 15% of nutrients are released within 24 h, with the remaining 75% within 28 days of application of the fertilizer [22].

The release of nutrients from nano-fertilizers is divided into three major stages: the lag period, linear period, and decay period [23,24]. In the lag stage, the water in the soil enters through the surface of the nano-fertilizers and slowly penetrates the core. During this stage, no fertilizer is released, and the vapor–pressure gradient created acts as the driving force. The lag is established to create a flux of water entering and a flux of solute leaving. In the second stage, the water level inside continues to increase, such that more fertilizer is dissolved, because of which osmotic pressure in the core builds, leading to slow release of the fertilizer through the pores [25]. The last stage is decay, during which the majority of the fertilizer has been released, reducing the concentration gradient, driving force, and increasing the release rate. The mechanism is described using a sigmoidal, S-shaped curve (Figure 2). If the internal pressure increases too rapidly in the lag phase, it may lead to a burst release of the nutrients, which is explained as a failure (dotted line); however, if the internal pressure increases linearly with time, then the nutrient molecules adsorbed in the pores will facilitate the slow-release mechanism depicted as the green sigmoidal curve. The prolonged release of nutrients from the source to the plants will promote growth, maintaining soil health.

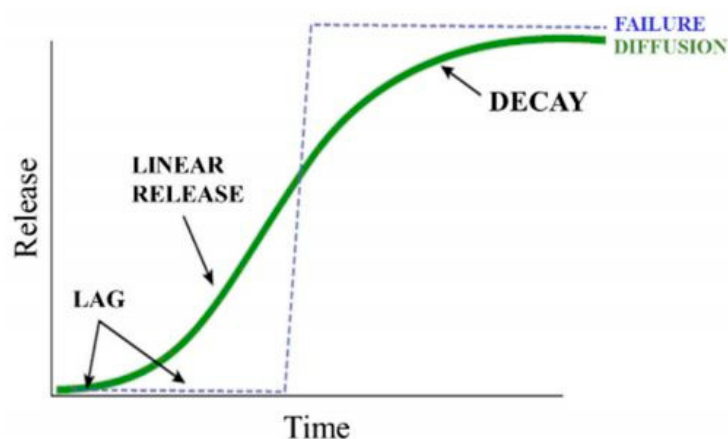


Figure 2. Sigmoidal curve for slow-release fertilizer (green) and failure release (blue). Reproduced from [26].

Nanoparticles such as zeolites have a high adsorption capacity to accumulate N, P, K, and S nutrients from precursor solutions due to their porous structure. They not only carry the nutrients, but also facilitate prolonged release as compared with bare nutrients provided to the plants. The enhanced micronutrient use efficiency with zeolite supplementation is also reported in many studies [22,26,27]. The improved availability of nutrients in the soil with the application of zeolites will ultimately facilitate enhanced nutrient availability to the plants.

3. Zeolites: Potential Candidates for Modern Agricultural Practices

Zeolites, often referred to as molecular sieves, are crystalline, hydrated alumina silicates of alkali and alkaline earth cations. They have a three-dimensional lattice which defines an inner network of interconnected pores and channels (Figure 3). The term ‘zeolite’ was coined by Swedish mineralogist Axel Fredrik Crönstedt in 1756, who observed that, upon rapid heating, this material produced steam from water which it had adsorbed [28]. Based on this, he called the material “zeolite”, which originates from the Greek word ζέω (zéō), meaning “to boil” and λίθος (líthos), meaning “stone”. These molecular sieves are composed of $\text{TO}_{4/2}$ tetrahedra, where T stands for Si, Al, Si, P, Ga, Ge, and B [28]. The basic structures of zeolites and their composing units are depicted in Figure 3. These materials have inbuilt channels and cages that crisscross the entire structure and make the crystalline framework accessible to foreign species. Appropriate hydrothermal conditions can lead to the crystallization of zeolites, linking Al (Si) tetrahedra (primary building blocks) into a

corner-sharing network (secondary building network) through oxygen (O) atoms integrated by rings and prisms of different sizes. The combination of such units generates a structure with regular distribution of pores and cavities, with the pore size ranging from micropores (<2 nm), to mesopores (2–50 nm), to macropores (>50 nm). In a zeolite framework, Si and Al (being tetravalent and trivalent) give rise to SiO_4 electro-neutral tetrahedra and AlO_4 negatively charged tetrahedral, whereby this charge is compensated by extra cations provided by alkali and alkaline earth metals. The composition of a hydrated zeolite can be expressed by the formula:

$$\text{M}_{x/n} (\text{H}_2\text{O})_z [(\text{AlO}_2)_x (\text{SiO}_2)_y]$$

where M is an extra framework cation with valence n, and x and y are the values of molar concentrations of Al and Si, respectively, in the zeolite structure. Z is the molar concentration of H_2O [4]. Due to their unique physicochemical properties, zeolites have found a diverse range of applications, such as in water purification [29], chemical and radioactive waste remediation [30], catalysts in organic reactions [31], pesticide and herbicide management agents, etc. [32].

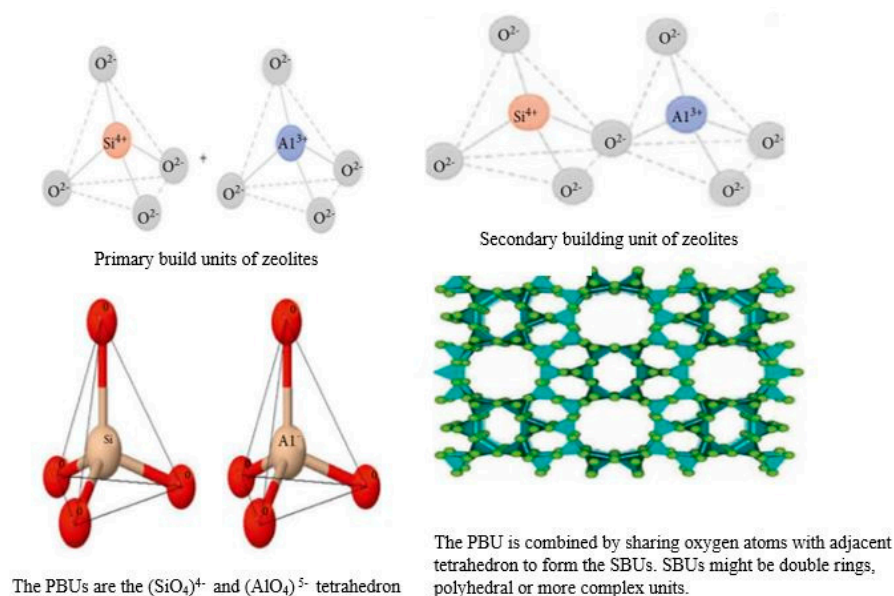


Figure 3. Structures of zeolite frameworks. Reproduced from [33].

Zeolites are mainly classified according to their silica/aluminium ratio into the following categories [27]:

1. Zeolite with a low Si-Al ratio (1–1.5): zeolite 4A, X, UZM-4 and UZM-5, etc.
2. Zeolite with intermediate Si-Al ratio (2–5): mordenite, LTA type, etc.
3. Zeolite with a high Si-Al ratio (10–several thousand): ZSM-5, ZSM-12, etc.

Zeolites also have a high void volume (50%), low mass density (2.1–2.2 g/cc) [29], high cation exchange capacity (CEC) of 150–250 cmol (+)/g, cation selectivity, for cations such as ammonium, potassium, cesium, etc. In a multi-component system, the selection of a zeolite depends upon various factors, including the hydration ratio, the exchangeable cation exchange capacity, the Si/Al ratio of zeolite, and the complementary ions as well as the temperature [33].

Zeolites are attractive materials due to their superior adsorption capacity and biocompatible nature [34]. Zeolites can have diverse applications, including:

- Industry: catalysis (shape-selective, acid catalyst, etc.), water softeners in laundry detergents [35], purification and separation of the volatile compounds [36].
- Horticulture: grass soil amendment [37], hydroponics experiments, and greenhouses.

- Agriculture: carrier of nutrients [38], organic manure [39] and soil conditioners [40]
- Environmental applications: decontamination, radionuclide applications [41], wastewater treatment (heavy metal and ammonia removal, etc.)
- Aquaculture: filtering ammonia in fish hatcheries and as biofilter media.
- Pharmaceutical industry: for the removal of toxins [42] and in drug-delivery systems, biomedical applications including tissue engineering, wound dressing, etc. [43].

These materials can be used as carriers, with optimized physicochemical and biological properties, which can permeate cell membranes more easily than large molecules; thus, they can be used as delivery tools of bioactive compounds [44]. The potential usage of zeolites for drug release [45] and biomedical applications can be improved by providing proper support to zeolite particles, to secure adhesion to tissues [46] and tailor drug release kinetics [47]. Due to their documented adsorption and ion exchange properties, zeolites can potentially be used for the cost-effective removal of pollutants from water, air, and soil [23]. Comparing natural and synthetic zeolites, the latter are preferred due to their enhanced texture parameters and diverse physicochemical properties [48]. Among natural zeolites, clinoptilolite is commonly used in agriculture and environmental applications, and its sorption and exchange properties can be modified by physical and chemical treatments [49,50]. However, the full potential of zeolites to remove toxic and harmful contaminants has not been explored to date [51].

Fertilizers play a significant role in agriculture; however, to further enhance the efficiency of nutrient use and control the long-term problem of eutrophication, nanofertilizers have been identified as a potential route for significant development [52]. In this context, zeolites have been employed as carriers for the slow and targeted release of essential macro- and micronutrients to plants [53]. They reduce nitrogen loss due to leaching and allow selective release linked to time or environmental conditions. Nanoporous zeolites have also been used as carriers in pest management, herbicide delivery, and as sensors in pest detection [54–56]. Improvement in soil physical properties, by reducing the bulk density, which, in turn, improves the water holding capacity and soil air porosity, is a benefit of applying zeolites in agricultural applications [39]. Zeolites are also considered water reservoirs, retaining soil moisture for a longer time during dry periods and enabling plants to survive during such conditions. It has been reported that soil amelioration with zeolites increases the water availability to plants by 50% [56]. This property was exploited by Moritani et al. [57], such that the incorporation of 10% of artificial zeolites in sodic soil resulted in improved wet aggregate stability. Different types of natural zeolites (mordenite, clinoptilolite, and stilbite) and synthetic zeolites have demonstrated positive changes in the soil properties, when applied to various textural classes of soil (sandy, loamy, clay, etc.), including water content, infiltration rate and hydraulic conductivity [58].

Increasing the use of zeolites leads to more demand for feasible methods for the development of hierarchical porous zeolites. Depending upon the desired properties, such as zeolite size, ordered channels, and defined pore diameter, the synthesis methods can be tuned [59]. Some methods employed for the fabrication of zeolites with enhanced physicochemical properties are discussed in the forthcoming section.

4. Synthetic Preparation of Porous Nano-Zeolites

The reduction in the size of porous materials offers additional potential for their usage in many agronomic applications. A decrease in size enhances the crystal quality and increases the surface area which, in turn, leads to increased surface activity. The fabrication of zeolites is performed in a closed system in which the reaction between the initial components leads to nucleation and further growth. Under controlled conditions, one can achieve a defined crystal size as required for the nutrient transfer. An increase in the number of nuclei leads to a decrease in crystal size, and vice versa. This is a complex process that takes place under high-temperature hydrothermal conditions. The process initiates with an alumina–silicate hydrogel that originates from the combined action of

mineralizing and structure-directing agents (SDAs), which has an arrangement of AlO_4^- and SiO_4^- around the charged template species.

The following parameters are interlinked with the formation of zeolites: (i) structure-directing agents or organic additives; (ii) type of precursor and synthesis suspension; (iii) initial silicon and aluminium source; and (iv) synthesis conditions (temperature, pressure, time, etc.); and (v) heating methods (sonication, microwave, conventional). Herein, the focus of synthesis is based on the application of zeolites as a carrier molecule with particle size in the nanometer range (1–1000 nm) and a defined pore structure, based on the presence of micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) [60].

4.1. Microporous Zeolites

Microporous zeolites are broadly used in industry as heterogeneous catalysts and solid acid catalysts in the fields of oil refining and petro-chemistry [61]. The micropore diameter is typically less than 2 nm. The synthesis of such zeolites is basically carried out by the conventional hydrothermal route, whereby alumina–silicate gel is given in the hydrothermal treatment at 60–200 °C for 1–20 days [62]. Lind type A (LTA) zeolites with micropores are synthesized at room temperature over 3 days. The process was further optimized in which the initial gel was heated at 35–65 °C to yield crystals of 30–400 nm in size [63]. FAU-type zeolites were fabricated by Huang et al. through a three-step process, which included aging at room temperature for 24 h, followed by crystallization at 38 °C for 24 h and 60 °C for 48 h. Nano-zeolites of around 30–110 nm in size were produced by varying water ratios [64]. Nucleation at low temperature followed by crystallization at high temperature was used to synthesize microporous zeolite Y of 120–200 nm in size.

Lind NaA-type zeolites were prepared using pure source material, as proposed by Majeed et al. [65], including three solutions: seeding gel, feedstock gel, and overall gel. Optimization in such a process required mixing of both solution A (silica) and solution B (alumina), followed by heating overnight at 100 °C and calcination at 500 °C for 3 h. The successfully prepared zeolites achieved a crystallinity of 97.6%, the Si/Al ratio being 1.03, the surface area of 581.21 m²/g, the pore size of 0.45 nm, and an average particles diameter of 74 nm. A detailed study of ambient conditions and slow nucleation kinetics during the formation FAU-type zeolites with micropores [66] was conducted by Valtchev et al. They explained the complete nucleation and crystallization stages that directed the formation of 100–300 nm of spherical aggregates which were further built by 10–20 nm of crystals, providing new insights into zeolite formation at room temperature. EDI-type microporous material was synthesized using tetramethyl ammonium cations as a template and a copper amine complex as a co-template [67].

The influence of various parameters on the size and the degree of crystallinity was investigated. It was observed that the single addition of copper cations or ammonia leads to the formation of FAU zeolites, whereas a combination of both materials generated EDI-type porous crystals. The key step was the addition of copper $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complexes during the aging period, which promoted crystallization and stabilization of the sol–gel matrix even at high temperatures. Application of metal–amine complexes in the synthesis opens up the possibility of achieving new shapes, such as square planar or linear, and they also carry a high positive charge for anionic silicate interaction.

Despite numerous applications, their relatively small and singularly sized micropores often limit the mass transport to and from the active sites, thereby restricting the applicability of these zeolites. The dimensions cause them to suffer from significant diffusion limitations [68]. The microporous network makes the zeolite susceptible to coking, leading to rapid deactivation, low accessibility for reactants, and undesired by-products due to side reactions [69,70]. The modifications in the zeolite structure are needed to generate enhanced pores so that molecules can easily diffuse in and out through the active channel.

4.2. Hierarchical Zeolites

Zeolites with two levels of porosity, mesopore (>2–50 nm) and macropore (>50 nm), are termed hierarchically structured zeolites. Possible strategies explored to fabricate such zeolites include generating intra-crystalline mesopores inside microporous zeolite structures and introducing nano-zeolites into interstitial spaces. Bottom-up (hard templating and soft templating) and top-down (desilication and dealumination) approaches have been employed to generate macropores; their pros and cons are described in Figure 4.

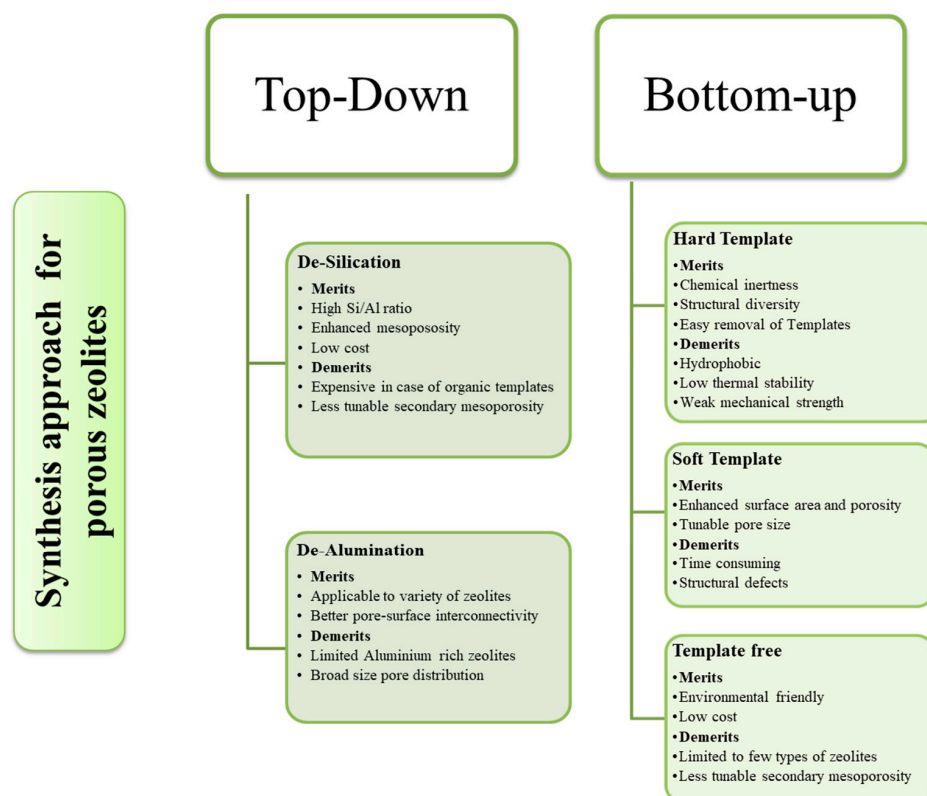


Figure 4. Advantages and disadvantages of bottom-up and top-down strategies for the synthesis of porous zeolites.

The synthesis methodology plays a crucial role in the formation of hierarchical zeolites [71]. Zeolite types BEA, MOR, LTA, CHA, and MFI are synthesized using sustainable raw materials (such as kaolin, diatomite, and coal ash), which results in mesoporous structures having a pore size of 7–50 nm [72]. Facile synthesis methods have been explored, not only reducing the cost of synthesis, but also making the process eco-friendly [73]. Zeolite Beta (ZSM) and zeolite Y (sodalite) were synthesized using cationic surfactants such as tetramethyl ammonium hydroxide (TMAOH), tetra propyl ammonium hydroxide (TPAOH), and cationic polymers such as poly diallyl dimethyl ammonium chloride (PDADMAC) [50]. Pore size analysis of the resulting zeolites revealed their mesoporous structure, with pore sizes ranging from 5–40 nm. The use of surfactants and cationic polymers enhances the porosity, but also increases the cost of production [74]. The use of organic materials makes the process highly controlled as compared with inorganic, but also introduces protons into the mesoporous framework without NH_4NO_3 ion exchange treatment, which is a crucial step while using NaOH [75].

The percentage of aluminium inside the reaction mixture plays a crucial role in determining the pore size of zeolite material, based on commercial zeolite ZSM-5 with Si to Al ratio ranging from 15 to 1000 [76]. When the Si/Al ratio was below 15, very limited mesopore generation was observed, but when the ratio was increased to 200, the formation of macropores was observed. The optimized silicon to aluminium ratio was found to be

50 for maintaining both a pore size of 2–50 nm and the crystallinity of zeolites [77]. Both top-down approaches, i.e., densification and dealumination, have been applied to a wide range of zeolite types, including MFI, MTW, MOR, BEA, FER, IFR, etc., to optimize the novel structures with defined pore sizes [78,79].

Many templates are employed to develop novel zeolite structures, properties with new framework topologies, and diverse chemical compositions. The physicochemical properties of synthesized zeolites are affected by the template used in the method. Numerous fundamental studies have been performed to shed more light on the intimate mechanism of precursor conversion and formation in the presence of structure-directing agent SDA [63]. Tetra-alkyl ammonium cations and several amines are commonly used to obtain zeolite nanocrystals with uniform crystal size, which requires the homogenous distribution of viable nuclei in the system. Tetra alkyl ammonium cations increase the crystalline yield by keeping the basicity high and modifying the textural and morphological features of the crystals formed [68]. A high concentration of SDA in the suspension leads to the formation of transparent precursor mixtures which are used to synthesize various types of zeolites frameworks: (FAU), (MFI type), (SOD), (LTA), and (BEA) [80]. Water-clear suspensions are initiated by the hydrolysis of Al and Si alkoxides, followed by polymerization and condensation reactions, leading to the formation of nanocrystals [29,81–83].

Bottom-up strategies for the production of hierarchical mesoporous/macroporous zeolites include hard and soft templating hydrothermal modifications [84]. Hard templates, usually with rigid structures such as carbon nanotubes, carbon aerogels, and sucrose, are introduced into the precursor gel because they can be easily eliminated after synthesis to generate mesoporosity. Leverages related to the usage of carbon source are: (i) these which are easily dispersed in the synthetic gel of zeolite due to their size in nanometer range [85]; and (ii) restrictions on the growth of zeolites within the void spaces [86]. For different kinds of zeolites (MFI, BEA, LTA, FAU, and LTL), the confined space strategy is generally applicable [87–90]. Certain disadvantages associated with using hard templates are also observed, the first being the phase separation between hydrophobic carbon and hydrophilic gel, which is rectified by steam. The second is the high-temperature combustion of carbon compounds, which results in a loss of precursor, and is a costly process. In general, a hard-templating method provides low yields and limits the porosity generated in the zeolite structure.

To achieve better control over mesopore size and connectivity, soft templates are preferred over hard templates [91]. Soft templating offers the advantages of being diverse and flexible. The soft templating route was initially based on the use of small cations and surfactants which act as SDAs to form both micro- and mesopores in a given sample. However, the yield only gave rise to a mixture of zeolite crystals with amorphous silica, as a result of phase separation. Biological templates such as natural sponges, wood [92], leaves of plants [93], and bacterial threads [94] were also used in the past.

Zeolites synthesized by these methods have a high surface area, tunable pore size and high thermal stability, etc., and are excellent candidates to be used in agronomy for the delivery of pesticides, insecticides, and fertilizers. Delivery of agrochemical agents with nanocarriers has multiple potential benefits, including improved shelf life, stability, high diffusion rate, less exposure of agrochemicals to end-users, enhanced site-specific uptake, and high solubility. They not only facilitate the slow and prolonged release, but also maintain good soil health necessary for plant growth. The templating route is generally considered costly; however, it leads to the partial collapse of structure and requires post-synthesis treatment, but aids in achieving better physicochemical properties of the desired shape, size, and porosity with a low degree of agglomeration. The challenges in this process still need to be looked at more carefully for its applications in industry.

Efforts are continuing to develop smaller sizes of zeolite nanoparticles, with different strategies for microporous zeolites, mesoporous zeolites, and macroporous zeolites. The research findings related to zeolite type, synthesis methodology, particle size, and porosity are summarized in Table 1.

Table 1. Synthesis methodologies adopted for micro-, meso- and macroporous zeolites and their findings.

Zeolite Type	Synthesis Methodology	Particle Size	Porosity	Research Findings	Reference
Microporous zeolites					
Zeolite Beta	OSDA (organic structure directing agent) free synthesis.	Size: >100 nm,	Micro porous volume: 0.16–0.23 cm ³ g ^{−1}	Seed-assisted synthesis	[95]
ZSM-5, ZSM-8	Hydrothermal synthesis	Size: >50 nm,	Microporous, pore diameter: 6 Å	High-temperature hydrothermal synthesis (80–240 °C) with varying ratio of precursors (Si/Al) used	[96]
FAU	Organic template-free room temperature synthesis	40–50 nm,	Microporous, pore diameter: 0.74 nm	Crystallization time up to 38 days, where 100–300 nm aggregated results into formation of 40–50 nm crystals	[70]
EMT	Organic template-free homogenous suspension	6–15 nm, microporous, pore volume: 0.28–0.85 cm ³ g ^{−1}	Microporous, pore size: 0.2–0.45 nm	Tuning of precursor solutions with crystallization under mild hydrothermal conditions	[97]
Zeolite beta, ZSM-5	Sustainable synthesis	50–100 nm,	Microporous, pore volume: 0.21 cm ³ g ^{−1}	Reduced cost of production, high yields of zeolites, and reduction in reaction pressure	[98]
FAU(Y)- Type	Autoclaved synthesis	20–30 nm,	Microporous, pore diameter: 0.74 nm	Tetra-methyl ammonium hydroxide (TMAOH) and tetra-methyl ammonium bromide (TMABr) were employed as organic templates	[68]
Mesoporous zeolites					
BEA, MOR, CHA, MFI-type, ZSM-5, ZSM-34, ECR-1	Green synthesis	50–100 nm	Mesoporous, pore size (7–50 nm)	Sustainable raw materials (such as kaolin, diatomite, coal ash, etc.) used. Introducing continuous flow synthesis route	[65]
Zeolite-A (LTA, SOD-type)	Sol-gel system	200–600 nm,	Mesoporous zeolites	Optimization of synthesis parameters including choice of reactants, Si/Al ratio and crystallization time	[66]
Na-A zeolite	Sol-gel method	75 nm,	Mesoporous, pore size: 2.8 nm	High surface area and pore volume achieved	[69]
Zeolite Beta	Dense gel steam-assisted conversion	20–40 nm,	Mesoporous, pore diameter: 13 nm	Mesopores size of 13 nm formed using Tetra ethyl ammonium hydroxide (TEAOH). Reduced time of synthesis	[99]
Beta-H, ZSM-5-H	Autoclave crystallization	Beta H: 200–400 nm, ZSM-5-H: 0.3–1 µm,	Mesoporous, pore size: 5–40 nm	Organic cations tetra propyl ammonium hydroxide (TPAOH) and cationic polymer poly-diallyl dimethyl ammonium chloride (PDADMAC) were employed	[100]
MFI type	Steam-assisted crystallization-aggregation method	0.5–3 µm,	Mesoporous, pore size: 11–15 nm	Zeolite with Si/Al ratio-5 to 20 was synthesized with dual porosity by using TPAOH	[101]
Meso-Z5	Self-assisted seed induction method	400 nm,	Mesoporous, pore size: 10–40 nm	Silicalite-1 seed of size 200 nm was used into OSDA free precursor gel	[102]
Zeolite Y (Sodalite type)	Hydrothermal synthesis	1–3 µm,	Mesoporous, pore size: 5–15 nm	Tetramethyl ammonium hydroxide (TMAOH) and cetyl trimethyl ammonium bromide (CTAB) were used as cationic surfactants	[103]

Table 1. Cont.

Zeolite Type	Synthesis Methodology	Particle Size	Porosity	Research Findings	Reference
Macroporous zeolites					
SAPO-34 (CHA-type),	Hydrothermal synthesis	5–10 μm ,	Macro-porous, pore size: 100 nm	Hydrothermal synthesis via in situ growth etching with excess hydrofluoric acid. Zeolite formed with excellent catalytic properties against methanol to olefin (MTO) conversion	[104]
ZSM-5, MFI Type	Organic template Hydrothermal synthesis	290–680 nm,	macro porous, pore diameter: 137–300 nm	Mesoporous silica nanoparticle as sacrificial template along with TPAOH (tetra propyl ammonium hydroxide)	[105]
TS-1 zeolite (MFI type)	Steam assisted crystallization (Dry gel conversion)	TS-1: 1.5–2 μm ,	Macro-porous, pore size: 100 nm	Mesoporous Ti-SiO ₂ nanoparticles were used as templates along with TPAOH (tetra propyl ammonium hydroxide)	[106]
ZSM-5	Alkaline-media erosion method (A-ZSM-5) Gel-casting method (G-ZSM-5)	150–200 nm	Macroporous, Pore size: 2–100 nm	Organic monomer acrylamide along with cross-linker N-methylene bis-acrylamide (NBAM) were used for gel casting. Zeolites with excellent catalytic properties and 1,3,5-triisopropyl benzene and n-hexadecane were synthesized	[49]

Figure 5 summarizes the relationship between particle size and pore size in types of porous particles from Table 1: micro-, meso-, and microporous. Regardless of the overall diameter of the particle, they are categorized into these subtypes depending upon the size of pores formed during the synthesis methodology adopted. In general, there is a trend of larger sized particles having larger pore size, and vice versa, which may seem obvious; however, it is an important observation in determining synthetic strategies for a given application. The crystal size can range from 10 to 1000 nm. Hierarchical porous zeolites with meso- (2–50 nm) and macropores (>50 nm) require crystallization with the use of surfactants, organic cations, and templates to control the size of particles, as well as the pores formed. The presence of large pores will enhance the surface area; thus, the adsorption capability of zeolite will increase. The higher surface area will provide higher fertilizer loading capability. The pore size and particle size play important roles in determining the surface area and structure of the nano-zeolite formed. Relationships among the surface area, pore size and particle size are depicted in Figure 5. However, smaller pores are preferred when they are used as carriers because the solvent will pass through these pores rapidly, which will not facilitate the slow release of loaded molecules. The reduced size of nano-zeolites with meso- and macropores through chemical methods enhances their surface/mass ratio in order to allow the increased absorption of nutrients by roots.

Methodologies including hydrothermal synthesis with the use of inorganic structure directing agents are preferred and most common because they do not require any high-temperature removal of additive agents leading to disruptions of the zeolite framework. Top-down approaches such as dealumination and desilication were also proven to be effective, because they lead to the generation of mesopores [54]. Synthesis methods such as autoclave crystallization, hydrothermal crystallization, and sol-gel lower the ageing time, are cost-effective, and are environmentally friendly. However, there are still considerable challenges on the synthesis aspect to achieve controllable molecular dimensions, crystallinity, and high adsorption capability, along with special attention towards how nucleation growth occurs and kinetics are studied [107].

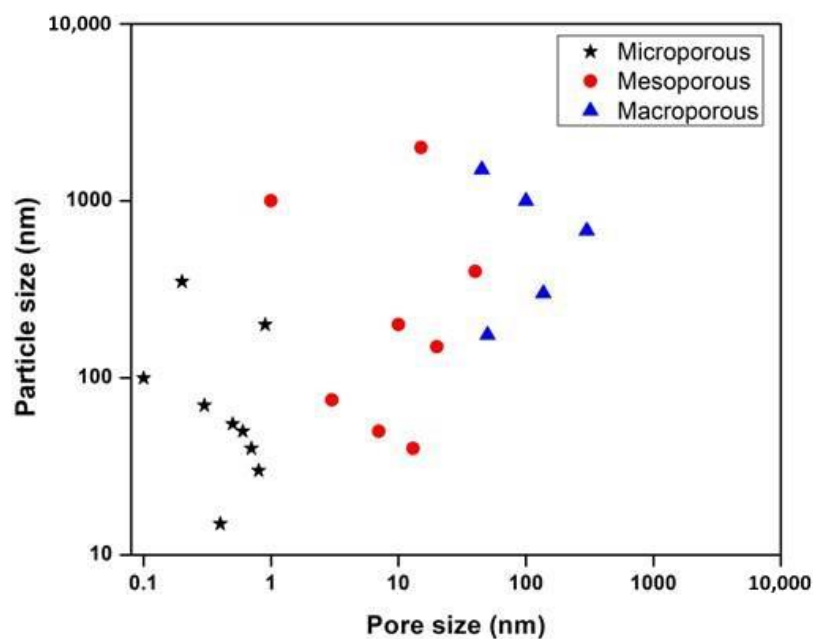


Figure 5. Plot showing different types of zeolites from Table 1, i.e., micro, meso-, and macroporous in relation to particle size and ratio of pore size and porosity.

5. Application of Nano-Zeolites as Fertilizer Carrier

To maintain an adequate level of nutrients in the soil and to keep water resources clean, applications of additives such as zeolites to the soil are of great benefit [108]. Application of the zeolites can be achieved through soil or foliar treatment, whereupon properties such as surface chemistry, size, and concentration play crucial roles in determining the toxicity and other probable changes, as depicted in Figure 6. They are either administered by roots or by foliar spray into the plants. Depending on the application, the zeolites are synthesized, and based on their composition, they are applied in agriculture. The morphology and surface of a particle play a crucial role in determining their biocompatibility. The use of biopolymer-based coatings can improve the uptake, and retention times are also focused [109]; zeolites have historically been used to boost agricultural efficiency [16]. They are used as natural inorganic soil conditioners to improve the physical and chemical properties of soil, such as maintaining infiltration rate, water-holding capacity, cation exchange capacity [110], and hydraulic conductivity [62]. It has also been reported that soil amendments using zeolite materials improves the water retention capability, which can reduce water usage in agricultural activities [14].

Zeolites were used in Japan and the USA 300 years ago for various purposes, including soil conditioning [111]. Incorporating zeolites into soil improves the nutrient-retaining capacity by influencing the physical, chemical, and biological properties that control the nutrient dynamics in soil. For example, because of the high cationic exchange properties of zeolites, they exhibit increased NH_4^+ sorption selectivity due to electrostatic attraction between negatively charged sites of the zeolite structure and positively charged NH_4^+ . It has been reported that the cation exchange capacity of natural zeolites is 2–3 times higher than most of the minerals [112]. Researchers have also observed that zeolites, with their specific selectivity for ammonium phosphorous, potassium, zinc, sulfate, etc., can take up this specific cation from farmyard manure, composts, or nutrient-bearing fertilizers, thereby reducing losses of nitrogen to the environment [13,113–115]. The retention capability depends upon various factors, including the structure of the zeolite, Si/Al ratio, contact time, temperature, pore size, and concentration of other ions in the soil.

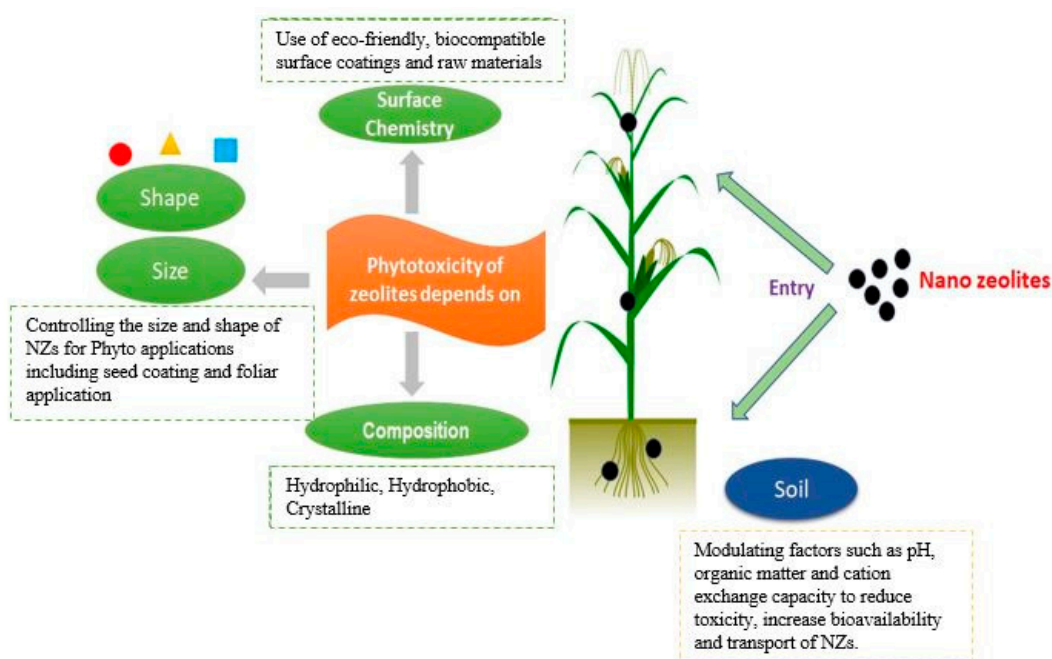


Figure 6. Introduction of nano-zeolites and their potential effects.

Zeolites are reported to be used as slow-releasing carriers of fertilizers, insecticides, and other additives [116,117], which act as growth stimulators for improved fertility and biological activity of the soil, as depicted in Figure 7. These active ingredients are easily loaded into porous zeolites just by mixing to bring out the targeted effects. Del Pino et al. [118] demonstrated the controlled release of P and K from phillipsite zeolite, which follows first-order release kinetics. A chemical reactor at a constant flow was employed, which provides favorable conditions to evaluate the nutrient supply capacity of slow-release fertilizer (SRF), ensuring adequate supply to the plants. The majority of research has been targeted toward naturally occurring clinoptilolite zeolites, due to their applications as a solid medium as a fertilizer material. Clinoptilolite has a theoretical cation exchange capacity (CEC) value of 2.16 cmol/kg for NH_4^+ [119]. Clinoptilolite increases the nitrogen use efficiency by reducing ammonia volatilization and increasing the exchange of NH_4^+ and NO_3^- [120]. The small pores in zeolite crystals facilitate the adsorption of ammonium cations, but deny access to nitrifying microorganisms [121].

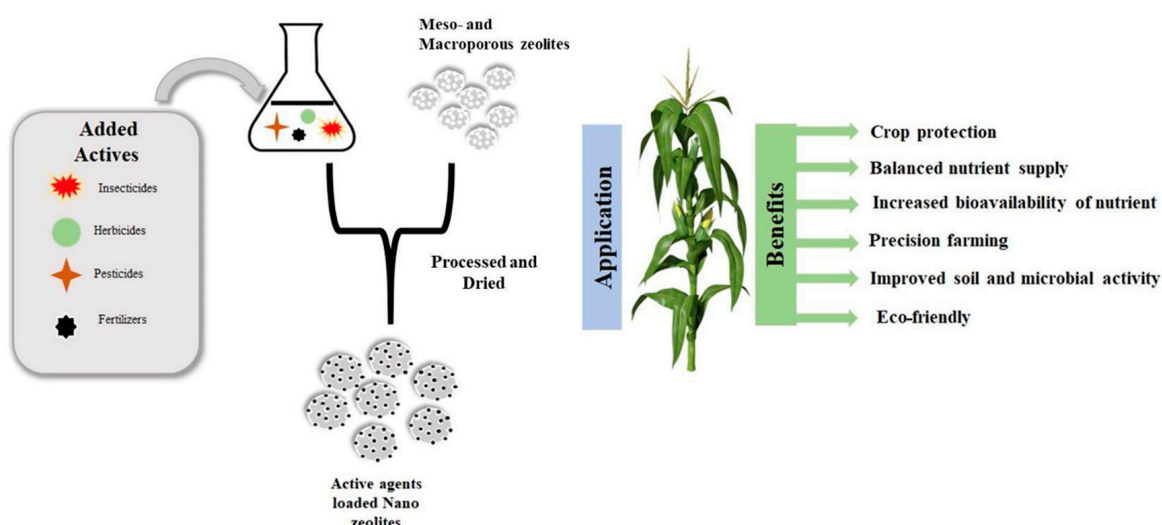


Figure 7. Nano-zeolites as carriers for the slow and targeted release of compounds.

The use of water-soluble fertilizers leads to groundwater contamination, which can be resolved using surfactant-modified fertilizer [13]. Surfactant addition increases the anionic sorption capacity, which aids in the removal of cations and organic compounds [122–124]. Modifications of zeolites by surfactants such as hexadecyl trimethyl ammonium bromide (HDTMA-Br) and octadecyl trimethyl ammonium bromide (ODTMA-Br) have been reported to remove the chromates and iodides from the solutions [125]. The adsorption capacity of zeolites primarily depends upon mass, particle size (smaller size; more surface area), contact time (directly proportional to the amount adsorbed), temperature, and the initial amount of cations in the solution [126]. Modifications with strong acids can increase the adsorption capacity of zeolites. Omar et al. [127] demonstrated significant improvements in soil-exchangeable ammonium retention by 40% in zeolite-treated soil. The urease activity was also increased by zeolite application, which lowered the nutrient release from fertilizer [128]. Surfactant-modified zeolite (SMZ) turned out to be an efficient transporter of sulfate with a loading capacity of 15 and 25 mmol/kg and instant release capacity. Column leaching testing confirmed that the sulfate release reduced 5–7-fold when SMZ was employed as compared with normal zeolites [13].

Naturally available zeolites, due to their structure and properties (i.e., inert and non-toxic), can be used as slow-release carriers of fertilizers. The physical and chemical properties of zeolites can be exploited for applications as carriers for nutrient delivery [129]. Their efficiency as carriers of nutrients has been verified using nitrogen, phosphorus, and potassium compounds [130]. Zeolites enhance the action of compounds such as slow-release fertilizers, both in horticultural and extensive crops. The primary applications of zeolites in agriculture are nutrient loading, storage, and slow release. The applications of natural and synthetic zeolites as carriers of fertilizers are summarized in Table 2. Various types of naturally occurring zeolite, such as phillipsite and clinoptilolite, are employed for delivering macro- and micronutrients to crops [131]. Yuvaraj and Subramaniann [132] reported that nano-zeolite adsorbed more Zn, and they also observed that Zn was released from ZnSO_4 for up to 200 h, and that from nano-zeolite was for up to 800 h. ZSM-5 zeolite traps the triazine group of herbicides in the intra-crystalline void space and promotes their slow-release, as shown in Figure 8. The SEM micrographs show the bare zeolite synthesized along with the zinc-loaded zeolites and the release pattern of zinc from nano-zeolites as compared with the conventional source of zinc sulphate. The release from nano-zeolites is prolonged up to 1176 h.

These porous structures have a high adsorption capacity to accumulate N, P, K, and S nutrients from the precursor solutions. They not only carry the nutrients, but also facilitate prolonged release as compared with the bare nutrients provided to the plants. Enhanced micronutrient use efficiency with zeolite supplementation is also reported in the literature [22,27]. The better availability of the nutrients in soil with the application of zeolites will ultimately facilitate enhanced nutrient availability in plants.

Both synthetic and naturally available zeolites can be used as carriers for the transport of macro- and micronutrients. Evidently, their capability as compared with the commercially available fertilizer to enhance nutrient uptake efficiency is enhanced when zeolite loaded with ammonia and potassium showed increased growth in treated plants and enhanced soil quality [118].

Table 2. Zeolites as carriers of micro- and macronutrients.

Type of Zeolite	Procurement Method		Important Parameters and Nutrient Loading	Research Findings	Ref.
Tenerife phillipsite	Naturally available zeolite		Phosphorous (P) and potassium (K) were loaded from KH_2PO_4 and K_2HPO_4	Three forms of available nutrients: KH_2PO_4 crystals covering the surface of zeolites, some filled up in the zeolite pores, and a very low fraction of exchangeable K and precipitated forms of P	[121]
Surfactant-modified zeolite (SMZ)	Naturally available with 74% clinoptilolite, 12% feldspar and 12% quartz	Surfactant-modified (HDTMA)	Size: 0.42–0.83 mm, sulphate	Zeolite modified to 150–200% ECEC (external cation exchange capacity) retained 70–80% of loaded sulphate as compared with water-soluble sulphate. Column leaching tests confirmed that sulphate release rate was reduced 5–7-fold using SMZ	[13]
				Zeolite modified with cationic surfactant, able to sorb up to 80 mmol kg^{-1} of nitrate. Column leaching test showed a decrease of 95% in the effluent nitrate concentration was achieved	[116]
Natural zeolite (Clinoptilolite)		Ball-milling	Size: 90–110 nm, zinc from ZnSO_4	Release study revealed that Zn from nano-zeolite extends up to 1176 h as compared with Zn release from ZnSO_4 exists up to 216 h.	[133]
Clinoptilolite	Naturally available		Size: 50 μm , 200 μm Ammonium chloride	Molecular dynamics simulations were adopted to confirm the diffusion of ions through zeolites. Smaller particles of 50 μm release fertilizer at slower rate as compared with 200 μm particles	[117]
Zeolite–chitosan fertilizer		Chemically derived using impregnation method	Sodium nitrate (NaNO_3) as nitrogen source.	Slow release of nitrogen achieved, by zeolite: chitosan (1:1), whereas the fastest was shown in case of zeolite alone as a fertilizer	[118]
Natural zeolite	Naturally available (mordenite and clinoptilolite)		Size: 1–2 mm, ammonium sulphate $((\text{NH}_4)_2\text{SO}_4)$ and potassium chloride (KCL)	As compared with the commercially available fertilizer, zeolite-loaded ammonia and potassium showed increase growth in treated plants and enhanced soil quality	[134]
Natural zeolite	Naturally available (Shangdong, China)		N fertilizer sources: ammonium chloride and mono ammonium orthophosphate	Zeolite as slow-release fertilizer (SRF) increases the spinach plant yield as compared with conventional nitrogen fertilizer	[135]

Table 2. Cont.

Type of Zeolite	Procurement Method		Important Parameters and Nutrient Loading	Research Findings	Ref.
Zeolite-A	Naturally available	Surfactant (HDTMA-Br) modified zeolite (SMZ)	KH_2PO_4 was used as phosphate (PO_4^{3-}) fertilizer	Surfactant-modified zeolite shows increased loading of P by factor of 4.9 along with the slow release of P	[136]
Natural zeolite	Naturally available (Handu Co. Korea)		Size: 1–2 mm, ammonium sulphate $((\text{NH}_4)_2\text{SO}_4)$ and potassium chloride (KCL)	Treated plants with zeolites show high yield as well as increased nutrient availability for sustained development	[137]

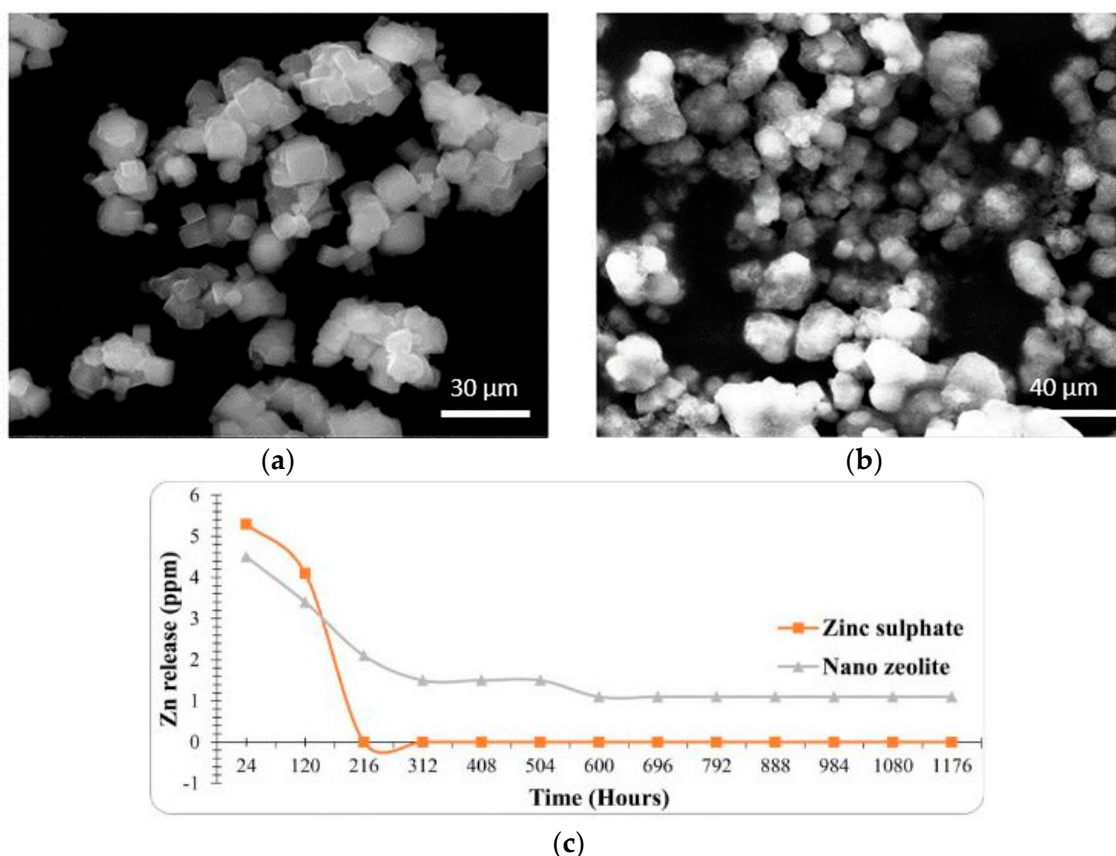


Figure 8. Reproduced from [133]: (a) Nano-zeolite; (b) zinc-loaded Nano-zeolites; (c) release study of zinc from nano-zeolite in comparison to zinc sulfate.

6. Toxicity of Zeolites

Zeolite toxicity is an important consideration when it comes to the application perspective. As compared with mammalian toxicity, coating plants with particle films are not phytotoxic [138]. In seed-coating, zeolites are mainly washed off by rain showers [139], the sodium form of some zeolites inhibits the growth of some plant species [140], and their ion exchangeability may adsorb some micro essential elements such as zinc and copper ions. Even some macro-elements such as bromine and chlorine are not taken up by plants due to their low affinity with zeolites [119].

6.1. Phytotoxicity

The toxicity issue in plants is due to the elemental composition of zeolites. Aluminium is generally considered toxic to plants; it inhibits root growth [141], induces oxidative stress [142], disturbance of cytoplasmic Ca^{2+} [143], and induces callose (1, 3- β -D-glucan) formation [144]. Silicon, on the other hand, has no toxic effect, even at higher concentrations; thus, to minimize all these issues from the application perspective, zeolites with a high Si/Al ratio are considered [145]. Dealumination is also considered one effective method to reduce aluminium content in synthesized zeolites. Various routes can be employed for extracting aluminium from zeolites, mainly classified into two categories: one utilizing chemical agents, and the other hydrothermal treatment [146]. Withdrawal of aluminium atoms produces vacancies and a partial fall-out of zeolite structure. Depending on the dealumination treatment, severe changes also occur in the properties of zeolites [147]. It was also reported that the thermo-stability of the product gradually decreases after dealumination treatment higher than 65%. Hydrolysis of Al–O–Si bonds is initiated in steam, and aluminium atoms are removed from the structure, creating vacancies. A part of the vacancy is filled by silicon species coming from amorphous material, while others grow and create mesopores [148], thereby reducing the toxic effects due to aluminium content.

6.2. Cytotoxicity

The biological activity and mammalian cytotoxicity have been evaluated by various studies [149,150]. The first study on cytotoxic effects of the mineral fiber zeolite erionite revealed that, due to the presence of zeolites, the patients were diagnosed with chronic fibrous pleuritis. A similar assessment was carried out by Suzuki [151], whereby the preliminary studies indicated that both erionite and mordenite can cause fibrosis and mesothelioma in mice lungs. Different types of zeolites, including MTT, rod-shaped MFI-2, spherical MF-1, and FAU, have been studied for toxicity issues because of their structure [151]. The concentration of zeolites is also an important parameter in determining toxicity; in one trial, the dose value was kept between 5 and 50 $\mu\text{g mL}^{-1}$ in a monocyte–macrophage cell line (J774); zeolites with small aspect ratios, i.e., spheroid forms, exhibited low-level cytotoxicity even at high concentrations, but fibrous zeolites such as MTT and TON were toxic even at lower concentrations [152]. The surface reactivity of these negatively charged zeolites is one of the major issues in the generation of reactive oxygen species (ROS), which contributes to toxicity. Fubini et al. explored the surface reactivity of these zeolites and their influence on OH radical generation. The samples were placed in the following order for their ROS generation ability: FAU < MTT < CRIS and TON < MFI-1. This issue can be overcome by coating the surfaces of zeolites, making them more biocompatible [149]. Selecting zeolites with a defined morphology, such as spherical-shaped or rod-shaped, will decrease their toxic effects due to the structure of the cells; coating them with different polymers does not have any effects on the porosity, except for stabilizing their surface reactivity. Studies have also proven that un-functionalized and calcined material shows less cytotoxicity [152].

7. Challenges and Future Perspectives

In a world of growing urbanization and an ever-increasing population, in which resources are scarce, there is little alternative but to optimize agricultural productivity. Considerable research has been carried out globally to exploit the capability of zeolites as media for the transport of fertilizers. The huge potential applicability of these zeolites also comes with certain challenges which need consideration to generate improved, cost-effective, and feasible versions of zeolite. Improving the synthesis methods of these zeolites is a major challenge, because there are only 232 types of zeolite that can be synthesized; fundamental knowledge of their properties is yet to be established [150]. To understand the synthesis approach, the nucleation and crystallization of zeolites should be better understood. The use of SDAs also makes the synthesis approach quite expensive, which needs to be reconsidered. Better knowledge of variation in the acidic properties, assessment of the stability of hierarchical porosity, and enhanced focus on the measurement of transport

properties are some of the studies which need to be carried out for large-scale applications and syntheses of zeolites [151]. For zeolites to be employed as carrier structures, their loading capability and the release profile of the loaded material with respect to time need to be managed. The pore sizes of zeolites are usually large, which allows the material to be released rapidly; therefore, the textural properties of zeolites need to be modified to obtain a controlled release profile [18]. The distribution of naturally occurring zeolite sources is also limited, which increases the price and gap between supply and demand [35].

Zeolites have numerous applications in agriculture, particularly in soil management, water retention, and heavy metal pollution removal. Properties such as the ion exchange capacity and adsorption are pertinent for agronomy. The application of zeolites enhances nutrient retention in soil and assists in the slow and prolonged release of nutrients. They are also employed as carriers of nutrients or media for free nutrients to promote nutrient use efficiency. Increasing public interest in the utilization of porous nano-zeolites in agriculture has partially been due to the unfavorable effects of chemical fertilizers leading to ground-water contamination, although zeolites are non-toxic and safe for human consumption. The positive impacts of zeolites are increased crop productivity and growth, and reduced greenhouse gas emissions and energy involvement. Further studies are needed to optimize the synthesis of hierarchical zeolites, their cost-effectiveness, and their long-term impacts on soil health and agriculture.

8. Conclusions

A multitude of engineered nano-zeolites have promising applications in the field of agriculture as nutrient delivery molecules and soil conditioners. However, there are a lot of stones unturned towards the exploitation of their full potential due to physiochemical properties which will revolutionize the field of agronomy and for the welfare of global food security. Nano-zeolites are the best candidates for increasing crop yield and reducing agriculture inputs costs. The use of zeolites in increasing plant growth in many research studies has been demonstrated, and their usage is also expected to reduce urea N-fertilization to one-half or one-third of current amounts. There is a need to examine the synthesis approach to prepare nano-zeolites that are eco-friendly, cost-effective, and straightforward. Use of inorganic structure directing agents (SDAs) in hydrothermal treatment is the best applied approach for achieving homogenous nano-sized zeolites. Their application as a carrier molecule will solve issues associated with contemporary conventional techniques, and may confer enhanced agri-potential by preserving the physiological fitness of plants and soil. Their ion exchange properties and adsorption capabilities can be fully utilized in agronomy. Comprehensive tools need to be developed for the assessment of nano-zeolites and their framework for improving knowledge on toxicity and risk assessments for sustainable food chains and ecosystem functioning.

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