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Modified Zeolite-Based Composite as Urea Slow-Release Fertilizer – A Mini Review

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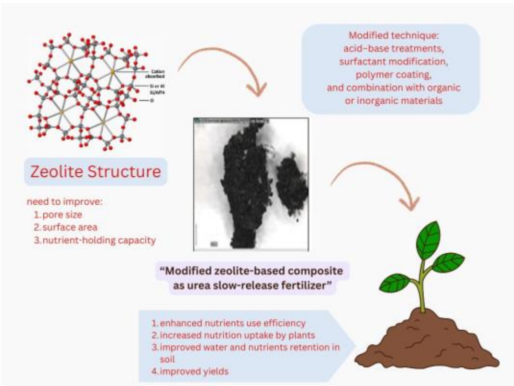
Graphical Abstract



Highlights

- Slow-release fertilizers (SRFs) has gained significant attention in recent years due to their potential to enhance nutrient use efficiency (NUE) and mitigate environmental impacts associated with conventional fertilizers
- Zeolites, crystalline aluminosilicate minerals, are extensively studied for their application in slow-release fertilizer (SRF) formulations due to their unique physicochemical properties.
- The modification of natural zeolite improve pore size, surface area, and nutrient-holding capacity, allowing for a slower and more controlled release of nitrogen.

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ABSTRACT

Urea is the most commonly used nitrogen fertilizer in agriculture due to its high nitrogen content and low cost. However, its efficiency is often below 50% because of nitrogen losses through leaching, volatilization, and surface runoff. To reduce these losses and improve fertilizer efficiency, slow-release fertilizers (SRFs) using modified zeolite-based composites have been developed. Zeolite is a porous aluminosilicate mineral with excellent ion exchange and adsorption properties, making it a good carrier for urea. However, natural zeolite has limitations, such as impurities and low surface area, which can be improved through modification techniques like acid–base treatments (dealumination and desilication), surfactant modification, and

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combination with organic or inorganic materials. These modifications improve pore size, surface area, and nutrient-holding capacity, allowing for a slower and more controlled release of nitrogen. This mini review discusses recent studies on the preparation, characterization, and performance of modified zeolite composites for urea delivery, showing their potential to reduce environmental impact and increase nutrient use efficiency in agriculture.

1. Introduction

Agriculture plays a fundamental role in ensuring global food security, particularly in light of rapid population growth. The global population is expected to reach approximately 9,6 billion by 2050, which will substantially increase the global demand for food [1]. This growing demand, lead to the extensive use of fertilizers to improve soil condition and rapidly increase crop yield. However, the unregulated and excessive application of fertilizers contributes soil degradation and significant nutrient losses through leaching, largely due the high solubility and mobility of conventional fertilizers [2].

Urea is the most commonly used nitrogen fertilizer in agriculture, primarily due to its high nitrogen content (46%) and relatively low production cost [3]. However, its nitrogen use efficiency (NUE) is typically below 50%, as significant losses occur through surface runoff, leaching, and volatilization, resulting in reduced plant uptake and environmental contamination [4]. Under soil conditions urea undergoes rapid hidrolysis fasilitated by the enzyme urease, to form ammonium ions (NH_4^+) [5]. These ions can be directly absorbed by plants further oxidized to nitrate (NO_3^-) through nitrification or lost as ammonia (NH_3) via volatilization, depending on soil pH, temperature, and microbial activity [6]. Plants uptake inorganic form of nitrogen as NH_4^+ and NO_3^- [7]. However, organic forms of nitrogen such as amides and amino acids can be taken up, their contribution to total nitrogen uptake is minimal. The preference for NH_4^+ or NO_3^- uptake varies among plant species and is influenced by soil conditions, including pH, temperature, and moisture levels [8]. Understanding these dynamics is crucial for optimizing nitrogen use efficiency and minimizing environmental impacts associated with nitrogen fertilization.

Slow-release fertilizers (SRFs) has gained significant attention in recent years due to their potential to enhance nutrient use efficiency (NUE) and mitigate environmental impacts associated with conventional fertilizers [9]. Slow-release fertilizer (SRFs) have been specially designed to delay nutrient release in synchrony with the needs of plants for nutrients, consequently enhancing nutrients use efficiency and improving yields [10].

Zeolites, crystalline aluminosilicate minerals, are extensively studied for their application in slow-release fertilizer (SRF) formulations due to their unique physicochemical properties. Their high cation exchange capacity (CEC), thermal stability, and porous structure make them particularly suitable as carriers or matrices for nutrient encapsulation and controlled release [11]. The porous structure of zeolites, characterized by micropores with diameters ranging from 0.3 to 1.0 nm, facilitates the effective incorporaton of essential macro and mironutrients [12]. These nutrients are subsequently released slowly and sustainably to plants, depending upon their affinity to the zeolite. This controlled release mechanism enhances nutrient availability in the soil and improves crop nutrient uptake compared to conventional fertilizers. Furthermore, the high CEC of zeolites, varying between 200 and 300 cmol(+) kg^{-1}, enables them to retain and exchange various cations such as NH_4^+, K^+, and Ca^{2+} [13]. This property is crucial for maintaining nutrient equilibrium in the soil, thereby improving fertilizer efficiency and reducing nutrient losses.

The thermal stability of zeolites, which increases with a higher Si/Al ratio, ensures their structural integrity under varying environmental conditions [14]. This stability is essential for their function as SRF carriers, as it allows for consistent nutrient release over time. In addition to their natural properties, modification of zeolites has been extensively investigated. Techniques such as acid/base treatment [15], ion exchange [16], polymer coating [17], and incorporation with other functional materials have been explored to enhance their adsorption capacity, release kinetics, and chemical compatibility with urea [18]. These modifications improve their capacity to carry and release nutrients, further optimizing their performance in SRF applications.

This review article aims to investigate the development and potential of modified zeolite-based composites as urea slow-release fertilizers. Various approaches have been employed to improve the nutrient retention, release behavior, and environmental stability of zeolites, including surface functionalization, polymer coating, ion exchange, and the formation of hybrid composites with organic or inorganic additives. By focusing on advances over the past few years, this review aims to provide a comprehensive understanding of the mechanisms, materials, and effectiveness of modified zeolite-based composites, and their role in supporting sustainable and efficient fertilizer technologies.

2. Methods Used For Literature Collection

This article review based on the most recent publications published during the last ten years. Numerous literature on modified zeolite-based composite as urea slow-release fertilizer fabrication were gathered from various article database such as Scopus, ScienceDirect, MDPI, ResearchGate, Google Scholar, ACS Publication, Nature, and others. The order of references and themes arranges reviews. The primary goal of this research is to examine the preparation and characterization of modified zeolite-based composite; and their effectiveness on slow-release fertilizer and urea use efficiency.

3. Results and Discussion

3. 1 Modified Zeolite-Based Composite

Zeolite are crystalline aluminosilicates consisting of a three-dimensional framework of SiO_4 tetrahedra, where some silicon atoms are isomorphosly substitued by aluminium, forming AlO_4 units (figure 1) [2] This substitution introduces a net negative charge to the lattice, which is compensated by the presence of exchangeable cations such as alkali metals (e.g., Na^+, K^+), alkaline earth metals (e.g., Ca^{2+}, Mg^{2+}), and occasionally other mono- or multivalent metal ions [19]. Despite its wide applications in slow-release fertilizer, natural zeolite has limitations due to instrinsic structural impurities and non-ideal physicochemical properties. These limitations can be overcome by modifications of the structure of natural zeolite to improve their capacity to carry and release nutrients, further optimizing their performance in SRF applications.

Nurliati, et al. [15] reported the modification of natural zeolite through dealumination and desilication processes using acid-base treatments aiming to tranform the microporous structure to hierarchical pore system. The result demostrated that the crystallinity of the zeolite was preserved following modification. However, a significant increase in the Si/Al ratio was observed, rising from 6.688 in the original Na-zeolite (NaZ) to 11.401 in the modified zeolite (ZA2B), indicating successful framework alteration. Furthermore, the specific surface area increased from 125.4 m^2/g (NaZ) to 168.0 m^2/g (ZA2B), suggesting the formation of mesopores alongside the existing microporous network. This acid-base treatment enhances the potential of zeolite for slow-release fertilizer applications by introducing a mesoporous structure, which facilitates improved nutrient loading and controlled release behavior.

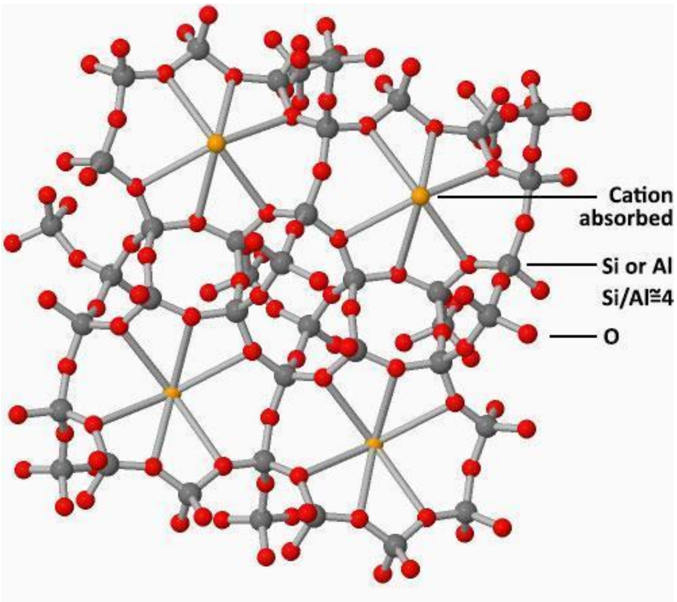

Figure 1. The Tetrahedral Framework of Clinoptiloite [20]

Legese, et al. [9] investigated the preparation and characterization of natural and surfactant-modified zeolite, employing hexadecy trimethyl ammonium bromide (HDTMABr) as the modifying agent. Scanning electron microscopy (SEM) images of the untreated natural zeolite (UNZ) displayed prismatic aggregates of the host zeolite (phillipsite). Surfactant modification and the addition of dopants (nutrients), minor morphological alterations were observed. The SEM analysis also revealed distinct pore channels on the zeolite surface, consistent with the structural features of porous materials (Figure 2).

The specific surface area and porosity of zeolite materials are significantly influenced by surfactant modification. In the case of clinoptilolite, treatment with a surfactant increased the specific surface area from 29 to 140 m^2/g and the total pore volume from 0.1045 to 0.2460 cm^3/g. However, the incorporation of nutrient dopants into both unmodified and surfactant-modified zeolite composites resulted in a reduction in surface area and pore volume. This decrease is attributed to the partial occupation of the pore structure by the introduced nutrients, which limits available pore space. Application of UNZC and SMNZC at the same rate equally affected total nitrogen uptake. Thus, this finding showed that UZNC is a better carrier of cationic nutrients, while SMNZC is preferable for the slow release of NO3 - and available P. In conclusion, both the modified and unmodified support forms showed better performance than conventional fertilizer in delivering nutrients slowly and sustainably [9].

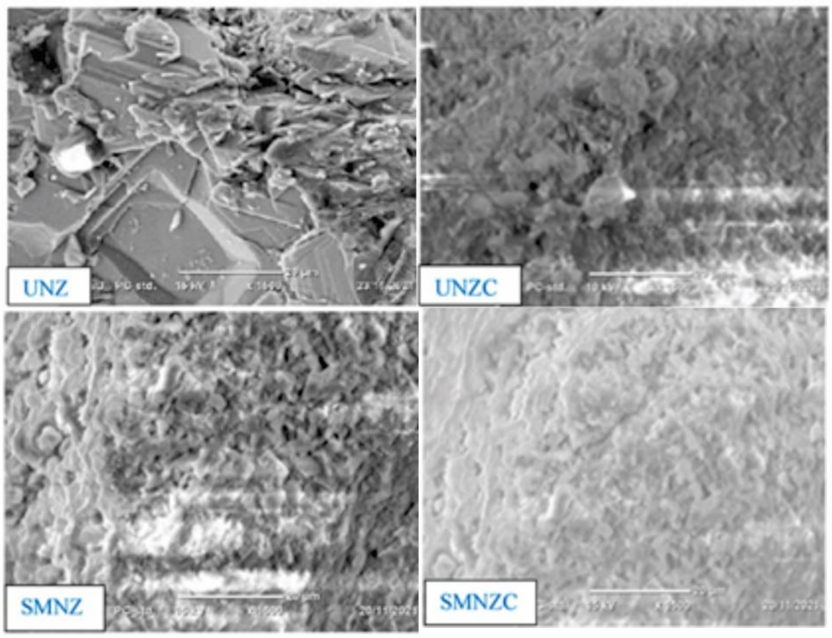

Figure 2. Scanning electron microscopy image of zeolite samples before (UNZ and SMNZ) and after impregnated with nutrients (UNZC and SMNZC) at 20 µm resolution. *UNZ = unmodified natural zeolite, SMNZ = surfactant-modified natural zeolite, UNZC = unmodified natural zeolite based composite fertilizer, SMNZC = surfactant-modified zeolite based composite fertilizer [9].*

Maghsoodi, et al. [21] reported the modification of urea-impregnated zeolite (UZ) as carriers. The result indicated that the urea interacted with the zeolite matrix, contributing to a controlled release profile. Transmission electron microscopy (TEM) images displayed the highly crystalline nature of the zeolite surface (Figure 3a). Many cavities and channels characteristic of the zeolite framework were observed, and the impregnation with urea led to partial occupation and blockage of these porous structures (Figure 3b).

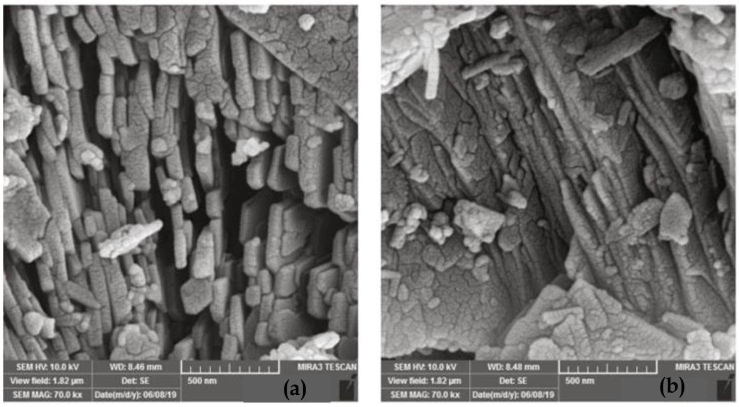

Figure 3. TEM Image of (a) zeolite and (b) urea-impregnated zeolite (UZ) [21]

Utami, et al [22] also investigated the modification of urea-impregnated zeolite by incorporating humic acid, aiming to enhance the interaction and bonding between urea and the zeolite matrix. The results indicated that the final product exhibited good adhesion, with the components well-bonded and no significant separation observed. A slightly whitish coloration, attributed to minor inhomogeneities from localized zeolite agglomeration, was present in small areas of the formulation (Figure 4). The incorporation of humic acid played a crucial role as a binding agent, enhancing the interaction between urea and zeolite within the matrix. This demonstrated the ability to retain ammonium ions effectively. This retention capability contributes to a gradual conversion of ammonium to nitrate, thereby enhancing nitrogen use efficiency. As such, the modified formulation shows promising potential for application in sandy soils, where nutrient leaching is a major concern.

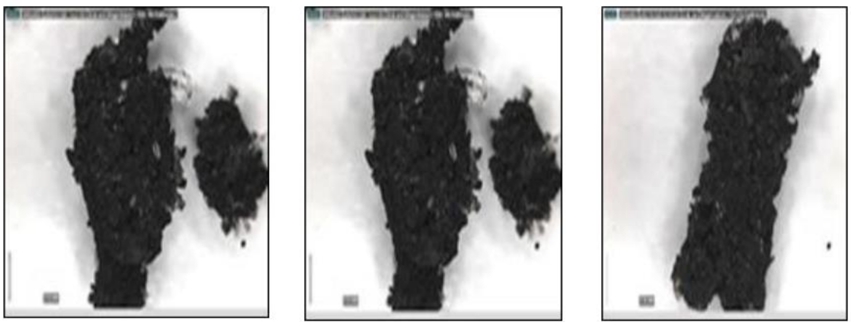

Figure 4. Slow-release Urea Modified Product [22]

Kartini, et al. [23] reported the incorporation of urea into bioplastics using carboxymethyl cellulose (CMC) as the polymer matrix, with zeolite or activated carbon serving as additive fillers. The bioplastics were made by mixing the zeolite or activated carbon suspension with urea into a sodium carboxymethyl cellulose (Na-CMC) gel. The study revealed that the addition of zeolite increased the tensile strength of the bioplastics by about two times. while the addition of glycerol improved the material's flexibility, as indicated by a higher elongation at break. The release of urea from bioplastics was slower for bioplastics with zeolite than with activated carbon, highlighting the potential of zeolite-based composite bioplastics as effective slow-release urea carriers for agricultural applications.

Ishartono et al. [24] also developed a modification of a zeolite-based composite for use as a urea slow-release fertilizer (SRF), utilizing white cement in a zeolite–clay composite cylinder as an encapsulant for urea fertilizer. The study investigated the effect of different zeolite-to-clay ratios on the physical characteristics of the composite cylinder, aiming to optimize its use as an encapsulation matrix for urea granules. Additionally, the incorporation of white cement into the zeolite–clay composite was explored to enhance the mechanical strength and water resistance of the matrix. This improvement is attributed to chemical interactions among white cement and aluminosilicate materials in the zeolite–clay mixture, which occur through hydration and pozzolanic reactions. The resulting composite demonstrated the ability to act as an effective slow-release matrix for urea fertilizer.

Numerous studies have demonstrated that the modification of zeolite-based composites can significantly overcome the inherent limitations of natural zeolite structures, particularly in terms of nutrient adsorption and release capacity. Enhancements through the incorporation of binders such as white cement, clay, or polymeric materials have been shown to improve the mechanical strength, water stability, and controlled-release properties of the composites. Chemical interactions, including hydration and pozzolanic reactions between zeolite and added materials, contribute to the formation of a more effective encapsulation matrix for urea. Consequently, modified zeolite-based composites exhibit great potential as key materials for the development of efficient and environmentally friendly slow-release urea fertilizers.

3. 2 Effectiveness Modified Zeolite-Based Composite as Slow release fertilizer

Zeolite, which are porous aluminosilicates, exhibit high potential as viable candidates for employment in nutrient transportation. Aina et al. [25] investigated the growth response of corn plants (Zea mays L.) to the application of modified zeolite-coated urea as a nitrogen slow-release fertilizer. The study assessed several growth parameters, including corn cob weight (grams), cob length (cm), and kernel weight (grams), measured at harvest. The results indicated that the application of zeolite-coated urea positively influenced corn growth. Specifically, the highest corn cob weight (120.92 grams) and cob length (14.25 cm) were observed with a 10% concentration of zeolite-coated urea. In contrast, the greatest kernel weight (84.31 grams) was achieved with a 30% concentration of the coated fertilizer. These findings suggest that varying concentrations of zeolite-coated urea can differentially enhance specific yield components of corn.

Ahmad, et al. [26] also demonstrated the potential of zeolite impregnated urea formulation as slow-release nitrogen fertilizer in soil incubation. The formulation zeolitic urea rasio (1:1, 2:1, and 3:1) significantly delayed the release of NH4-N up to 14 days. In contrast, conventional urea and formulations with lower zeolite content (ratios of 1:3 and 1:2) released NH_4^+-N more rapidly, peaking by the 7th day of incubation. Flooded condition released NH4-N earlier than non-flooded condition. The release of NO3-N was also delayed by zeolitic urea formulations as compared with urea alone, with peak levels occurring between 28 and 42 days. Among all treatments, the 1:1 zeolitic urea maintained the highest nitrate levels until the end of the experiment. Ammonia volatilization was highest (44% of applied nitrogen) in the urea-only treatment, while the lowest loss (29%) was recorded in the 1:1 zeolitic urea formulation. Flooded conditions showed ammonia volatilization 2 to 3 days earlier than non-flooded condition. Results suggested that zeolitic urea 1:1 can be successfully used as slow-release N fertilizer both under flooded and non-flooded soil conditions.

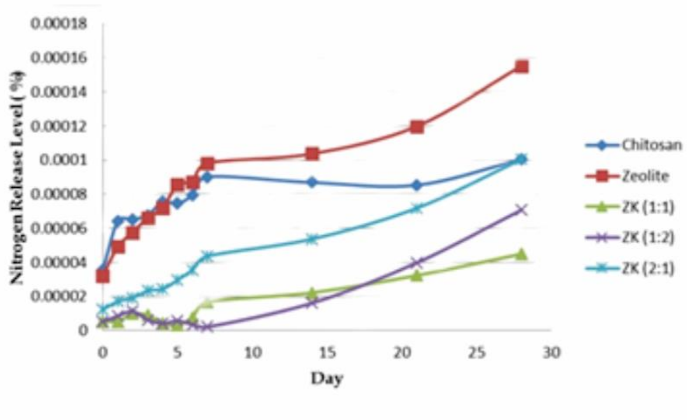

Figure 5. Level of Nitrogen Release of Fertilizers

Zeolite and chitosan are natural polymer materials that have the potential to produce fertilizer slowly because the are hydrophobic and environmentally friendly. Chitosan, a biopolymer obtained from chitin, can function as a physical barrier that modulates the water permeability of the fertilizer matrix, thereby slowing the rate of nutrient diffusion. In a study conducted by Maharani et al. [27] the combination of modified zeolite and chitosan was explored for its effectiveness in regulating nitrogen release. This study showed the slowest nitrogen release rate (Figure 5) is zeolite-chitosan fertilizer with rasio of zeolite and chitosan is 1:1 (% w/w), while the fastest nitrogen release produced by zeolite fertilizer.

Malekian et al. [28] conducted a study to evaluate the effectiveness of natural clinoptilolite (Cp) and its surfactant-modified form (SMZ) in reducing the leaching of ammonium (NH_4^+) and nitrate (NO_3^-) from agricultural soils. Clinoptilolite, a naturally occurring zeolite, possesses a negatively charged framework balanced by exchangeable cations, making it an effective cation exchanger. Modification of Cp with hexadecyltrimethylammonium bromide (HDTMABr) enhanced its external cation exchange capacity (ECEC) by forming a bilayer on the zeolite surface. This modification reversed the surface charge, thereby improving its affinity for anionic species like nitrate. Field studies demonstrated that natural Cp could exchange up to 11 mg/g of NH_4^+, while the surface-modified zeolite (SMZ-Cp) was capable of exchanging as much as 800 mmol/kg of NO_3^-. These findings underscore the potential of both Cp and SMZ-Cp as effective carriers for controlled nitrogen release, contributing to reduced nutrient leaching and improved nitrogen use efficiency in agricultural applications.

Maghsoodi et al. [21] reported that urea exhibited strong interactions with various carrier materials—including humic acid (UH), biochar (UB), zeolite (UZ), and hydroxyapatite (U-HAP)—which effectively regulated its release rate. Compared to uncoated urea, these composite formulations reduced the urea release rate by factors of 4.5, 6.5, 9.0, and 11.5, respectively. Upon application to calcareous paddy soils (Figure 6), cumulative nitrogen release over 20 days revealed that 89.9% (UH), 76.5% (UB), 75.0% (UZ), and 58.1% (U-HAP) of urea had been transformed into ammonium (NH_4^+). These findings highlight the ability of UB, UZ, and U-HAP formulations to provide a more controlled and gradual nutrient release, which could minimize nitrogen losses and enhance nitrogen use efficiency under field conditions.

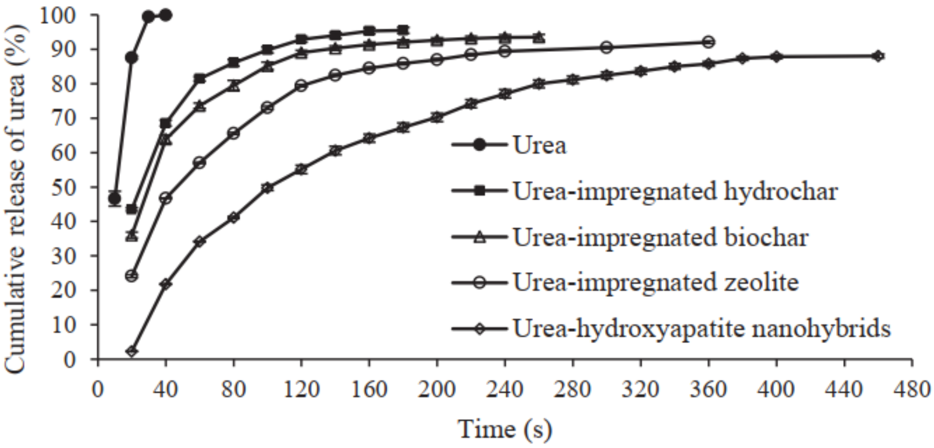

Figure 6. The release behavior of urea with inorganic materials [21]

Khan et al. [29] also demonstrated that the positive impact of natural zeolite–coated fertilizer (NZCF) treatment on lettuce growth (Figure 7) were closely associated with improvements in the soil's chemical, physical, and biological properties. The application of NZCF contributed to a more sustained nutrient release, as evidenced by a reduction in soil pH, elevated levels of total dissolved solids (TDS), enhanced water retention capacity, and improved nutrient bioavailability for plant root uptake.

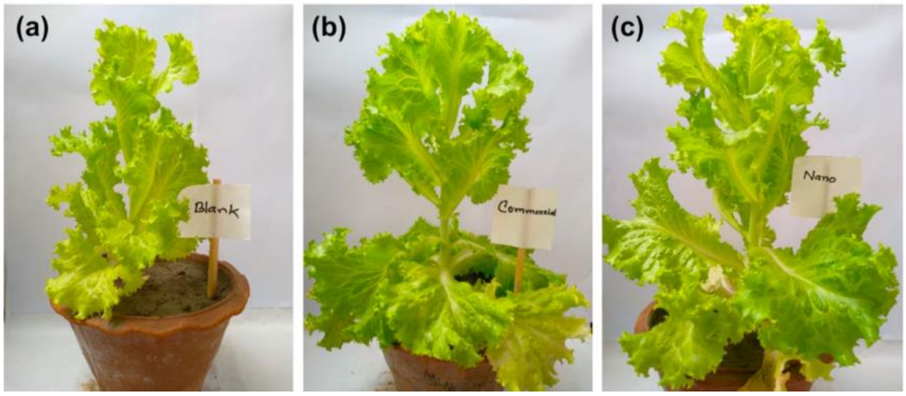

Figure 7. Lettuce plat images: (a) without urea; (b) urea as commercial fertilizer treatment; (c) NZCF treatment [29]

4. Conclusion

Modified zeolite-based composites have shown great potential as effective carriers for urea in slow-release fertilizer (SRF) applications. Natural zeolites, known for their high cation exchange capacity, porous structure, and thermal stability, can be improved through various modification techniques such as acid-base treatment, surfactant treatment, polymer coating composite and the addition of materials like humic acid, chitosan, white cement, etc. These modifications enhance the ability of zeolites to retain and gradually release nitrogen, reduce nutrient losses due to leaching and volatilization, and improve fertilizer efficiency. Studies have shown that modified zeolite composites can increase soil nutrient availability, improve water retention, and support better plant growth compared to conventional fertilizers. Despite their advantages, challenges such as production cost, field performance under varying conditions, and scalability remain. Therefore, further research is needed to optimize formulation, assess long-term impacts, and ensure practical use in sustainable agriculture.

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CRediT Authorship Contribution Statement
The manuscript was written through the contribution of all author. All author have approved the final version of the manuscript. Siti Mahmudha: conceptualization, resources collection, literature review and writing-original draft. Taranipa Marfitania and Muhammad Idris: resources collection and writing-review and editing. Sulwiyatul

Kamariyah Sani, Pina Budiarti Pratiwi, and Eko Pujiyulianto: visualization, writing-editing, and project administration.

Conflicts of Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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