

REVIEW PAPER

Zeolites synthesized from agro-industrial residues applied in agriculture: A review and future prospects

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Abstract

Zeolites have been widely applied as catalysts, wastewater treatment agents, gas adsorbents and fertilizers, among others. However, the use of natural zeolites or those synthesized from oversaturated commercial solutions are more explored commercially than the zeolites synthesized from residues. Therefore, the aim of this review is to highlight the importance of zeolites synthesized from agro-industrial residues and their use in agriculture. This review has been divided into three different sections, that is, zeolites, agriculture applications, synthesis of zeolites from residues and their application in plant growth. In the first section, the definition, types and the critical properties of zeolites are explained. The second section gives a brief review of the application of zeolites in agriculture. Finally, the synthesis of zeolites from residues, such as coal ash, rice husk ash and sugarcane ash, with special attention to renewable sources is presented. The optimization of the synthesis of zeolites from residues with the incorporation of specific nutrients necessary for the cultivation of soybeans, corn and sugarcane (considered the most significant crops in Brazilian agriculture in terms of the planted area) can significantly contribute to the concept of circular economy at the industries and the fulfilment of sustainable development objectives, especially, the number 12 (SDO—12—Responsible consumption and production).

KEYWORDS

agriculture, agro-industrial residues, zeolites

1 | INTRODUCTION

Zeolites are widely used as ion exchangers for water purification (Jedla et al., 2022; Khadem et al., 2022), catalysts (Clemente et al., 2019; Gao et al., 2023; Gonzalez Martinez, 2020), detergents formulation (Koohsaryan et al., 2020; Yusriadi et al., 2020), nuclear waste entrapment

(Escamilla-Pérez et al., 2023; Li et al., 2022; Murukutti & Jena, 2022), building materials (Kaplan et al., 2021; Lehner & Hrabová, 2023; Molinari et al., 2019), gas separation and purification (Cho et al., 2023; Qi et al., 2023; Zhang et al., 2023), among others. These materials can be found in nature or be synthesized by aluminium and silicon sources by alkaline activation.

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According to the National Mineral Information Center – US Geological Survey (2023), around 3 million tons of natural zeolites were obtained around the world from 2016. China, South Korea, Japan, Jordan, Turkey, Slovakia and the United States were the countries that most commercialized these materials.

Natural zeolites are obtained by a mining process, which can cause environmental problems. Furthermore, these products take a long time to form in nature, are not standardized and may contain impurities, which limit their application (Bingre et al., 2018). On the other hand, obtaining synthetic zeolites from aluminosilicate solutions requires large amounts of chemical reagents, which are often expensive and produced through polluting processes. Therefore, the use of residues with a significant amount of silicon and/or aluminium, which are usually discarded by industrial processes, can be a sustainable way to produce zeolites. It has already been proven that it is possible to synthesize zeolites from agro-industrial residues (Hermassi et al., 2020; Inácio, 2016; Izidoro et al., 2013; Ybañez et al., 2022).

On the other hand, the world's population, and consequently, the demand for food, increase every year, as well as solid wastes from industries and agribusiness. It is important to notice that nowadays, the approach to sustainable agriculture cannot be separated from the use of sustainable products (Cataldo et al., 2021). Therefore, the aim of this review is to highlight the importance of zeolites synthesized from agro-industrial residues and their application in agriculture. A review of the application of zeolites (both natural and synthetic) in agriculture was carried out to study and explore the possibilities of employing the zeolites from low-cost precursors (residues) as fertilizers posteriorly.

2 | SUMMARY OF SCIENTOMETRIC ANALYSIS

In order to understand the relation between the presented themes in this review, scientific data provided important insights into zeolites in agriculture, among other areas. The scientific findings related to the terms 'zeolite' and 'agriculture' from 2013 to 2022 using the Scopus website showed that the total number of articles shared in the database is 436. Figure 1 shows the number of articles by year. In general, publications are constantly growing each year, reaching a peak in 2022. The total publications for 2023 are still uncertain, as the year is not over yet.

According to the analysed data, China, India, Indonesia, the United States, Italy, Iran and Japan are interested in this topic. Brazil occupies the 9th position (Figure 2).

Data obtained from the Scopus website were analysed using the VOS viewing tool. According to Saravanan et al. (2023) maps are created based on text data to identify related events of words read on the database websites. Figure 3 shows the map based on bibliographic data. The minimum number of repetitions considered was five.

According to Figure 3, the main related terms are: fertilizers, soil, nitrogen, ammonia and agricultural wastes, among others. Also, it was found that the main zeolite applied as a slow-release fertilizer so far is clinoptilolite, which is a natural zeolite, whereas the main industrial residue used for the synthesis of zeolites is fly ash from coal. It is believed that applied research related to the synthesis of zeolites and their application in agriculture will continuously grow in the future because of their high efficiency as slow-release fertilizer, and according to Xie and Su (2020), because zeolites have unique properties, and can also be used in other emerging applications, such as:

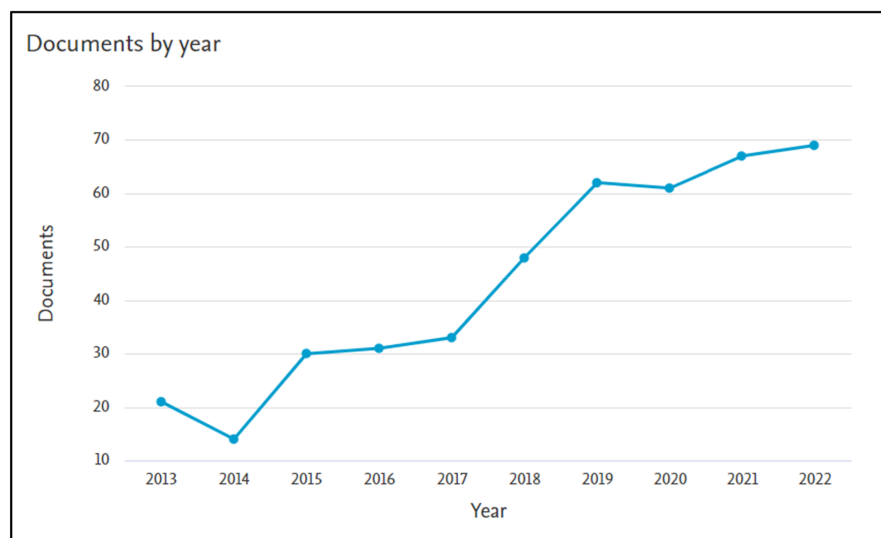


FIGURE 1 Publications with zeolite/agriculture in titles, abstracts and keywords collected by the Scopus website on 21 August, 2023.

aluminium atom. This charge is balanced by alkaline or alkaline earth metal cations, called compensating, interstitial or exchangeable cations (usually Na^+ , K^+ and Ca^{2+}) that are free to move in the lattice channels and can be exchanged for other cations in solution. The manner in which the tetrahedrons are connected forms channels and cavities that can be occupied by both water molecules and charge-compensating cations (Breck, 1973; Giannetto et al., 1990).

Zeolites are considered microporous materials because of their pore diameters being smaller than 2 nm (Rouquerol et al., 1994). Because they have pores with specific dimensions, they can also be defined as molecular sieves. Therefore, what gives the variety of existing zeolites is the way in which the tetrahedrons are united, which results in different pore sizes, associated with the possible substitution of silicon by several other elements, and the type of ion present in the pores.

The pore opening size is defined by the number of T atoms in the ring (Figure 4), and the zeolites can be classified according to the number of central atoms (T) that form the cavity, which results in different pore diameters, given in Angstrom (Table 1).

3.2 | Types of zeolites

Zeolites can be found in nature, and naturally formed in the earth's crust under hydrothermal and geological conditions (Bingre et al., 2018). They can be also synthesized in laboratories or produced industrially on a large scale from sources of silicon and aluminium through hydrothermal reaction. Around 40 naturally occurring zeolite frameworks are known, and more than 10,000 patents related to the synthesis of these materials have been published until now. Each new zeolite framework that is obtained is examined by the International Zeolite Association Structure Commission (IZA-SC, 2023).

The main commercial applications for natural zeolites are soil conditioners and growth media, animal feed, wastewater treatment and pet litter, while for synthetic zeolites are molecular sieves, catalysts and detergents (National Mineral Information Center – US Geological Survey, 2023).

Different types of zeolites (Figure 5), with different frameworks, can be synthesized by varying the composition of the used saturated solutions, and the experimental conditions such as synthesis temperature and pressure, agitation time, hydrothermal reaction time, Si/Al ratio, etc. The combination of these factors resulted in the synthesis of several types of zeolites from their discovery in 1756 to today (Giannetto et al., 1990).

The zeolite nomenclature follows the rules established by an IUPAC Commission on Zeolite Nomenclature. The framework type codes consist of three capital letters generally derived from the names of the type materials. However, a material can also be described using the IUPAC crystal chemical formula (Baerlocher et al., 2007).

3.3 | Properties

Zeolites have pore sizes between 2 and 20 Å, and cavities diameter between 6 and 12 Å. This type of microporous structure makes these materials have an extremely

TABLE 1 Classification of zeolites according to the pore size.

Zeolite	Number of 'T' atoms	Pore diameter (Å)
Small pore	8	$3 < \theta < 5$
Median Pore	10	$5 < \theta < 6$
Large pore	12	$6 < \theta < 9$
Extra-large pore	>12	>9

Source: Giannetto et al. (1990).

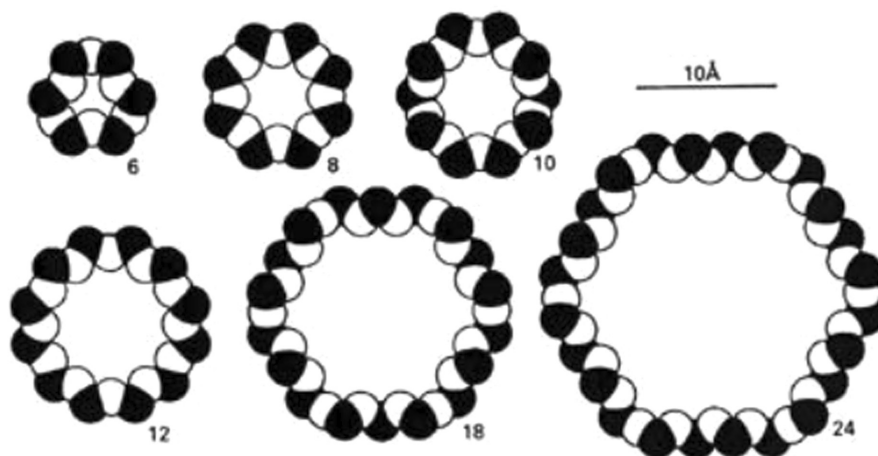


FIGURE 4 Number of central atoms which forms the pore opening of zeolites and their respective pore sizes (Giannetto et al., 1990).

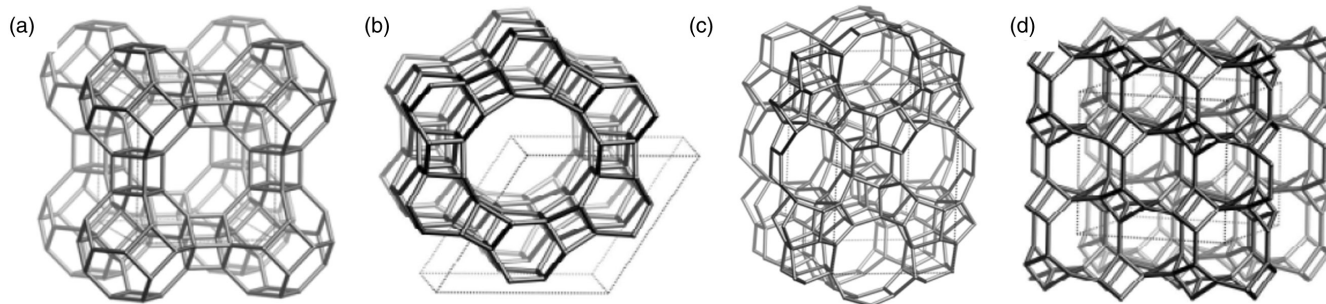


FIGURE 5 Examples of framework types of zeolites: (a) Cubic (LTA - Example: zeolite A); (b) Hexagonal (AFI—Example: zeolite AIPO-5); (c) Orthorhombic (MFI—Example: zeolite ZSM-5); (d) Monoclinic (AFN—Example: AIPO-14). *Source:* International Zeolite Association—IZA (2023).

large internal surface in relation to their external surface (Giannetto et al., 1990). Thus, zeolites can distinguish molecules because of their geometry and pore dimensions and be applied as molecular sieves and gas adsorbents (Cho et al., 2023).

The cation exchange capacity of a zeolite is related to its Si/Al ratio, since for each Si that has been replaced by Al, a negative charge is generated, which is compensated by a cation, as previously mentioned. This characteristic is responsible, for example, for the application in adsorption processes (Milojević-Rakić & Bajuk-Bogdanović, 2023). Both the selectivity for cations and the porosity of zeolites make them be applied as slow-release fertilizers (Bindra et al., 2023; Fan et al., 2023; Sharma et al., 2022).

The high thermal stability of zeolites (from 600 to 1100°C, in the function of the structural and compositional characteristics), physical and chemical stability, and the voids with active sites within the structure enable their application as catalysts. Because of these characteristics, zeolites are used in catalytic cracking in the petrochemical industry (Alaithan, 2022; Liu et al., 2023; Zhang, Bin Samsudin, et al., 2022; Zhang, Li, et al., 2022).

In summary, zeolites have three main properties that are of interest for agricultural applications: high cation exchange capacity, high adsorption capacity and water-holding capacity in the free channels both in soil and pots (Cataldo et al., 2021; Hedström, 2001).

As explained before, zeolites have a wide range of industrial applications, however, the use of natural zeolites or those synthesized from oversaturated commercial solutions are more explored commercially than the zeolites synthesized from residues, which can significantly contribute to the concept of circular economy at the industries, as well as the environment. In addition, the application of friendly-nature materials in agriculture contributes to the fulfilment of the sustainable development goals (SDGs).

4 | ZEOLITES IN AGRICULTURE APPLICATIONS

Food production, which is important for Brazil's economy, requires increased and efficient crop productivity. Thus, the agricultural sector has several challenges, whether related to the weather conditions or the production of efficient fertilizers.

Fertilizers are products that have nutrients in their chemical composition and are applied to the soil or to the surface of the plant to increase its productivity or performance. The main nutrients, known as primary macronutrients, are nitrogen, phosphorus and potassium (NPK). The secondary macronutrients are Ca, Mg and S. In addition, other elements such as Mn, Mo, Zn, Ni, Co, Fe, B and Cu, make up the so-called micronutrients and can be applied depending on the type of plantation.

The excessive use of fertilizers, incompatible with the absorption rate by the plants, makes the fertilizer application process less efficient. According to Cataldo et al. (2021), the excessive use of nitrogen fertilizer, for example, has negative results in agricultural ecosystems because of the nitrogen losses through nitrogen dioxide soil leaching and ammonia volatilization. Usually, the extra fertilizer is washed off and leads to high concentrations of potassium, nitrogen and phosphorus in surface water bodies (eutrophication) or groundwater nitrates (Cataldo et al., 2021).

Ergo, it is necessary to apply slow-release fertilizers (SRFs), such as zeolites, capable of providing nutrients to plants according to their need and absorption rate. Also, zeolitic minerals can be considered very stable in the soil environment (Fansuri et al., 2008).

Besides slow-release fertilizers, Cataldo et al. (2021) explained that zeolites can be also applied in agriculture as carriers of herbicides, fungicides and pesticides (Barbosa et al., 2018), soil conditioners (Yasuda et al., 1998), heavy metals sequestration (Kumar et al., 2007), water

adsorption (Xiubin & Zhanbin, 2001), reducing of undesirable odours caused by H_2S and NH_3 emission in animal husbandry (Kithome et al., 1999), antifungal activity (Rumbos et al., 2016), photosynthesis enhancement by the adsorption of carbon dioxide molecules and their gradual release (Montanari & Busca, 2008), heat stress (Ainsworth & Rogers, 2007), aquaculture (Asgharimoghadam et al., 2012) and animal feed additive (Shurson et al., 1984).

Also, according to Auerbach et al. (2003) zeolites can act as water moderators because they can adsorb up to 55% of their weight in water and release it slowly, according to the needs of the plant. This property can prevent root rot and moderate drought cycles.

It is important to note that once zeolite-based-fertilizer has been consumed, the zeolite will remain in the soil and behave like a soil conditioner, where nutrients can be exchanged into zeolite structure when they are in excess and are released when they are deficient in the soil, to maintain the equilibrium concentrations (reversible skilfulness). Also, when the nutrients are into the zeolite structure, they are out of the reach of bacteria, so they will not be lost to leaching or vaporization processes (Elliot, 2006).

Turning gaze to the plant world, nitrogen, phosphorus and potassium are the three nutrient elements consumed the most in the world. According to Elliot (2006), there are three mechanisms through which zeolites can facilitate the slow or controlled release of these nutrients: (1) nutrient cation exchange; (2) nutrient diffusion; (3) nutrient mobilization.

In the cation exchange mechanism, a zeolite loaded with K^+ , for example, after being applied in the soil, will result in the exchange of K^+ from the zeolite to water in the soil, to maintain an equilibrium concentration. Because plants uptake K^+ from this environment, more potassium is released by the zeolite to maintain this dynamic equilibrium between the soil and the zeolite, in a controlled release process. Other ions from soil, such as Ca^{2+} can be exchanged into zeolite to maintain charge neutrality. By this mechanism, the efficiency of fertilizer application is improved, and this product lasts longer (Elliot, 2006).

In another mechanism, urea for example can be occluded within the microporous zeolite structure by a physical encapsulation process and can be also leached into the soil by a diffusion process (Elliot, 2006). In the third mechanism, nutrient mobilization occurs when zeolite is physically blended with calcium phosphate to act as a controlled-release phosphate fertilizer (Elliot, 2006).

Therefore, research that used zeolites as slow-release fertilizers, soil amendments and other agricultural applications is described below.

Zeolite analcime was synthesized from coal fly ash by Fansuri et al. (2008). The K-zeolite was prepared from the Na-zeolite by ion exchange using a KNO_3 solution. The

product was applied to canola, spinach and wheat crops (Fansuri et al., 2008).

Hermassi et al. (2020) synthesized zeolites merlinoite and type W-rich zeolitic products from coal ash to remove phosphate from wastewater. This research showed that the phosphate loaded sorbent is appropriate for its use as a synthetic slow-release fertilizer.

Li et al. (2014) evaluated the potential of zeolite merlinoite synthesized from Chinese coal fly ashes as fertilizer. The synthetic material is proved to be an efficient slow-release K-fertilizer for plant growth, indicating that it can be widely used for high-nutrient demanding crops growing in nutrient-limited soils (Li et al., 2014).

Simão et al. (2021) did a review showing that zeolites clinoptilolite, type A, Na-P, philipsite, merlinoite, K-G and F type are the main types of zeolites applied as NPK nutrients (Simao et al., 2021). Also, Jarosz et al. (2022) did a very interesting review about the use of zeolites as an addition to fertilizers. They concluded that the results are promising and show a beneficial effect of zeolites on the soil environment and agricultural productivity.

Bhardwaj et al. (2012) synthesized clinoptilolite from chemical reactants and modified their surfaces by using solutions of hexadecyltrimethylammonium bromide and dioctadecyldimethylammonium bromide, commonly used as surfactants. The products were applied to remove nitrate and posteriorly to release nitrogen from the aqueous system. Results showed that a slow release of nitrogen is achievable as it releases NO_3^- still after 15–20 days of leaching study.

Cataldo et al. (2021) reviewed the characteristics of natural zeolites and their application in agriculture. It has shown that clinoptilolite was applied to enhance rice grain yield, and the results indicated a positive effect of the mixture of zeolite and fertilizer (Kavoosi, 2007). Natural zeolites were also used together with industrial fertilizers to improve the conditions of maize and radish production (Ahmed et al., 2010).

Aiad et al. (2021) demonstrated that a combination of organic and inorganic amendments, (including zeolites) can reclaim saline soils and improve wheat and maize productivity in an arid region. Results showed that wheat and maize yield increased by 16.0% and 35.0%, respectively under the combination of the treatments, when compared to crops grown on unamended soil, irrigated with lower leaching fraction and planted using conventional methods.

Bonetti et al. (2021) synthesized zeolites type X from coal ash, loaded them with macronutrients such as phosphorus and potassium, and applied them as fertilizers in the cultivation of *Tagetes patula*. Results showed that the leaching of nutrients occurred gradually, being available during the entire period of plant development. Also, the performance of plants cultivated with zeolite fertilizer was

similar or even superior to the cultivation carried out with traditional commercial fertilizer.

Bybordi and Ebrahimian (2013) demonstrated that zeolite application can increase canola growth and production, which may be through increasing N use efficiency and improving soil physical characteristics. Results indicated that N fertilizer increased plant height, silique number per plant, seed number per silique, 1000-seed weight and seed yield.

Chen et al. (2017) conducted a 2-year field experiment using a strip-plot design to evaluate the impact of natural zeolite amendment on yield performance, quality characteristics and nitrogen use efficiency of paddy rice. They concluded that soil chemical properties, yield performance, N uptake and N use efficiency were significantly enhanced by clinoptilolite zeolite amendment.

Z-ion substrate based on clinoptilolite zeolite was used as a nutrient carrier for maize crops. Results showed that the substrate seems to be an efficient means for fertilizer application of degraded or marginal soils increasing the above-ground biomass of maize (Chomczyńska & Zdeb, 2019).

Natural zeolite was recently used to test the effects of the co-addition of compost, zeolite and ammonium-based fertilizer on the above-ground fresh weight (AFW) of lettuce (*Lactuca sativa* L.), leaf nutrients and soil fertility. Results showed that the response of lettuce yield to chemical fertilizer application and zeolite application is soil type-dependent, whereas compost application significantly improved AFW in both soil types. Zeolite substantially increased the availability of P, K and Na in soil and plants, whereas the concentrations of DTPA-extractable micronutrients and leaf macronutrients were largely unaffected (Kavvadias et al., 2023).

Castronuovo et al. (2023) applied a combination of zeolite synthesized from fly ash and a type of biostimulant to improve water storage and improve spinach cultivation. Using the biostimulant and zeolite resulted in a change in the soil water content, quantified by a 10% increase, highlighting the positive role of allowing good water uptake equal to 6% by the spinach plant for the soil texture considered in this trial.

Dastbaz et al. (2023) investigated the effect of different levels of clinoptilolite zeolite and nitrogen fertilizer on the efficiency of nitrogen use, growth and yield of maize (*Zea mays* L.) in field conditions. Results showed that after the application of 10 and 15-ton zeolite ha⁻¹, the soil cation exchange capacity as well as the soil total nitrogen concentration, the leaf nitrogen concentration, leaf area index, cob length, grain yield and nitrogen use efficiency, increased significantly.

Prisa (2023) reviewed the application of zeolites in the environment and in agriculture. The author highlighted the application of these materials particularly in difficult

climatic situations, and in and its importance in soil management.

Girijaveni et al. (2021) highlighted the importance of the use of zeolites for greater control of both water and nutrient content in the soil since these two aspects are the most important factors for crop productivity and agricultural sustainability. The authors emphasize that water has become very scarce and the cost of chemical fertilizers is increasing each day.

According to the studies reviewed above, most nutrients incorporated into zeolites and applied in agriculture are macronutrients (NPK). Therefore, it was possible to note during this review that there is a lack of studies aimed at synthesizing zeolites with specific nutrients, mainly the micronutrients, required in many plants and specific to individual crops.

5 | APPLICATION OF ZEOLITES FROM RESIDUES IN PLANT GROWTH

Studies have verified that zeolites produced using low-cost precursors (residues), such as coal fly ash, rice husk ash and sugarcane ash, exhibited potential as a controlled-release fertilizer (Bonetti et al., 2021; Estevam et al., 2021; Hermassi et al., 2020; Inácio, 2016). Mallapur and Oubagaranadin (2017) presented a complete review of zeolite synthesis by using different types of residues. Also, Cao et al. (2023) review the recent advances in the synthesis and potential applications of zeolite materials using industrial solid waste and biomass ash.

Synthesis of zeolites can be done with the pretreatment of waste to remove impurities (Panitchakarn et al., 2014), with external aluminium source addition and fusion step (Izidoro et al., 2013; Petrov & Michalev, 2012; Wang et al., 2008), or with the Si and Al solution extracted from the waste (Ye et al., 2008). The most common method of synthesizing zeolite from residues is the classical alkaline conversion in one step by using a sodium hydroxide solution (Izidoro et al., 2012). This method results in a zeolitic material that contains between 20% and 75% of zeolite, depending on the activation reaction conditions and the quantity of unconverted waste. However, because the zeolitic material is a mixture of zeolites and unconverted waste, this material cannot replace pure zeolite in all applications. Because of this restriction, a two-step activation method involving a fusion step followed by conventional hydrothermal treatment (also known as indirect conversion) was developed to improve the conversion of residues to obtain high-purity zeolites (Izidoro et al., 2013; Kazemian et al., 2010; Zhang, Bin Samsudin, et al., 2022; Zhang, Li, et al., 2022). The formation of a particular

zeolite depends strongly on the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the starting or intermediate materials (Barrer, 1982). Other experimental conditions such as temperature, pressure, concentration of alkaline reagent, reaction time and solution/fly ash ratio also affect the type of zeolite to be obtained (Umaña Peña, 2002).

A method of preparing zeolites as fertilizers is using the occlusion process. The occlusion process consists of subjecting the mixture of zeolite and salt to thermal treatment causing the melting of the salt. Depending on the pore diameter of zeolite, the incorporated salt can be stabilized through geometric adjustment and/or electrostatic interaction with the zeolite. The most common salt used in this process is ammonium nitrate, as it is one of the most used in the fertilizer industry (Carvalho et al., 2003).

Potassium zeolite synthesized using KOH also has been shown to be particularly interesting as a fertilizer. Some research has focused on the evaluation of the effects of zeolite synthesized from residues on plant growth (Flores et al., 2021).

5.1 | Coal fly ash

Zeolites 4A was synthesized from fly ash from brown coal and was enriched with ammonium nitrate for slow-release nutrients. The enrichment of the zeolite synthesized and occluded with nitrogenous salt in a ratio of 1:2 (zeolite: NH_4NO_3) presented a 21.1% incorporation of the salt, while the commercial zeolite was 19.8%. The slow release of nutrients, in particular ammonium, was observed in leaching tests in static and dynamic systems, with measurable concentrations in relatively long times (from 100 to 1000 h) suggesting their potential use as fertilizer matrix for controlled release of nutrients (Inácio, 2016).

Ca-bearing K-zeolite synthesized from fly ash (FA) by hydrothermal conversion was used to recover phosphate from urban and effluents. Several synthesis conditions (temperature, KOH solution/FA ratio, KOH concentration and activation time) were applied to two FA samples with similar glass content, but different content of crystalline phases. Merlinoite and W-rich zeolitic products synthesized were found to have sorption properties for [phosphate removal](#). The loaded zeolites are considered a by-product rich in essential nutrients such K and P with a potential use as slow-release fertilizer (Hermassi et al., 2020).

Zeolites of type X, Na-P1 and A synthesized from fly ash by different methods and scales showed different performances in terms of the adsorption capacity of PO_4 and K present in synthetic solutions and industrial effluents. The zeolites modified with calcium chloride resulted in an increase in the adsorption capacity of nutrients. The best performing zeolite was type X produced on a pilot scale

by the hydrothermal process. The release of nutrients from modified zeolites X occurred slowly and gradually, which drives the use of this material as fertilizer (Bonetti et al., 2021).

The mineralogical and chemical analysis confirmed the obtaining of Merlinoite zeolites from coal fly ash by the classic hydrothermal method with a $\text{SiO}_2/\text{K}_2\text{O}$ ratio between 1.41 and 3.46 and K_2O content above 17%, and CEC of 171.57–346.63 cmol kg^{-1} . The synthesized zeolites have low solubility in water (0.89%–3.23%) and in citric acid (14.22%–18.57%). Considering the average release rate of the nutrient, compared to data of average absorption of K by different crops, zeolites have great potential to supply it for longer periods of time for direct application via soil (Estevam et al., 2021).

Potassium zeolites were synthesized from coal fly ash and applied as a source of potassium and nitrogen supplementary in oat cultivation. Two synthesized materials were identified as zeolite W and zeolite chabazite with traces of zeolite W. Both products could be successfully applied as fertilizer for oat plants (Ferret, 2004).

Zeolite merlinoite was synthesized using coal fly ashes by KOH direct conversion method. These fly ashes were collected from two pulverized-coal combustion power plants in Xinjiang, Northwest China. The synthesis results were influenced by the fly ash characteristics and different synthesis conditions (KOH solution concentrations, activation temperature, time and KOH/fly ash ratio). A high-quality merlinoite-rich product was reached with optimal activation conditions (KOH concentration of 5 mol L^{-1} , activation temperature of 150°C, activation time of 8 h and KOH/fly ash ratio of 2 L kg^{-1}) and presented cation exchange capacity of 160 cmol kg^{-1} . The synthetic merlinoite has proved to be an efficient slow-release K-fertilizer for sunflower, a high-nutrient demanding crop growing in nutrient-limited soils (Li et al., 2014).

Coal fly ash was used to synthesize zeolitic material through the alkaline hydrothermal treatment. Experimental tests were performed using the ratio volume of solution/mass of coal fly ash constant at 6 mL mg^{-1} , varying the concentration of potassium hydroxide between 3 and 5 mol L^{-1} , temperature between 100 and 150°C, and reaction time between 24 and 72 h. The zeolitic material obtained in the synthesis conditions at 150°C, 5 mol L^{-1} KOH solution and 24 h time of reaction was identified as zeolite merlinoite and it was chosen for application to soil as a potassium fertilizer for the cultivation of wheat crops. It was found that the zeolite merlinoite obtained from the coal fly ash can be used as a fertilizer, that liberates K with a similar performance to commercial fertilizer KCl in wheat growth (Flores et al., 2017).

A silty loam soil was amended with different percentages (1%, 2%, 5% and 10%) of zeolite sodalite synthesized

from coal fly ash. The effects of the synthetic mineral addition on the hydrophysical properties of the soil and sunflower growth were evaluated. The results indicated that zeolite addition increases the water retention capacity of soil and decreases the drainage capacity. The treatments with high concentrations of synthetic zeolite (5% and 10%) drastically reduce sunflower growth while a concentration of zeolite between 1 and 2% caused a slight decrease in growth (Belviso et al., 2022).

Zeolite A (ZA) was synthesized from coal fly ash using an alkali fusion-hydrothermal method. By changing the hydrothermal temperature and time, ZA with a maximum cation exchange capacity of 237.3 mmol/100g was obtained. ZA impregnated with urea at a mass ratio of 5:1 exhibited a slow release of urea and can promote the growth of the maize seedling (Fan et al., 2023).

Zeolites synthesized from coal fly ash are the most studied, however, the products usually have toxic heavy metals in their chemical composition, which can contaminate the crop. So, renewable starting materials are preferred for agriculture applications.

5.2 | Rice husk ash

The conversion of rice husk with aluminium foil (houses and restaurants wastes) into nanozeolite (NZ) particles has been performed by using zeolitization and calcination processes at different temperatures (200, 300, 400, 500, 600, 700, 800, 900 and 1000°C). The synthesized NZ at 1000°C was heulandite-type zeolite with calcium and potassium as the major single extra-framework cations. Results showed that nitrogen-fixing bacterial and phosphorus-solubilizing bacterial cells were adsorbed on NZ particles. So, NZ particles are considered as a microorganism carrier material which can be used as safety fertilizer and eco-friendly for both soils and plants particularly in arid and semi-arid zones (Hassan et al., 2017).

Rice husk ash (RHA) was used to synthesize potassium zeolites by using commercial KOH and public supply water to approach industrial conditions. The synthesized materials were identified as Chabazite-K and Merlinoite zeolites. The optimum conditions for synthesis were: 5 mol L⁻¹ KOH solution, 2 mL g⁻¹ solution:RHA ratio, 8 h of reaction time and 125°C of temperature reaction. Results showed that these materials can be potentially used as a potassium fertilizer (Flores et al., 2021).

5.3 | Sugarcane ash

Clinoptilolite nanozeolite was prepared using silica derived from sugarcane bagasse ash. The unmodified

nanozeolite (SNZ) and the nanozeolite modified by the surfactant cetyltrimethylammonium bromide (SMSNZ) were evaluated as carriers of nutrients. Nutrient loading resulted in a 9.62% N and 17.01% K₂O content for SNZ and a 13.35% P₂O₅ and 16.26% K₂O content for SMSNZ, which were relatively higher compared to commercial natural zeolite. The chemical characterization confirmed the successful loading of N, K and PK to synthesize nanozeolites from sugarcane bagasse ash and its potential as a controlled-release fertilizer (Ybañez et al., 2022).

6 | CHALLENGES AND PERSPECTIVES

1. Zeolites have many applications because of their thermal stability, shape and cation selectivity, microporosity, gas adsorption capacity, high degree of hydration, low density and electrical conductivity, among other characteristics.
2. Zeolite commercialization can increase and be more competitive when synthesized by solid wastes, not only because the raw materials are usually cheap and abundant, which able the production costs to be reduced, but also because it has a sustainability appeal, increasingly required in today's world. Furthermore, there are a lot of environmental impacts related to the large-scale disposal of solid wastes in dams, ash ponds and others. Ergo, the environment requires rapid action to minimize industrial waste disposal.
3. Zeolites synthesized from residues may present high purity and several applications, however, some aspects such as the reduction of synthesis costs aiming at industrial scale production, operational optimization and sustainable applications, among other aspects, have not been fully elucidated so far.
4. Zeolites synthesized from coal fly ash are the most studied, however, the products usually have toxic heavy metals in their chemical composition, which can contaminate the crop. So, renewable starting materials are preferred for agriculture applications.
5. Although several methodologies of zeolites have been proposed until now, sodalite and type A zeolites, or a mixture of types of zeolites remain the most common because of their stability during the synthesis, however, other types of zeolites, with different pore sizes e functionalities, containing specific micronutrients for slow release in agriculture should be studied.
6. Zeolites as slow-release fertilizers have improved efficiency when compared to traditional fertilizers because they can avoid the leaching of nutrients into the environment besides increasing productivity. Zeolites can also retain nutrients in the soil, and increase

water-holding capacity and organic content, besides improving aeration.

7. There is a lack of studies aimed at synthesizing zeolites with specific nutrients (mainly the micronutrients), required by many crops. Undoubtedly, it is necessary to investigate the long-term soil environmental effects of zeolites, as well.
8. Clinoptilolite is the most applied zeolite in agriculture until now, although natural zeolites are obtained by a mining process, take a long time to form in nature and are not standardized, which can limit their application.
9. It would be interesting to delve deeper into the economic aspect regarding the extraction of various world deposits (transport of clinoptilolite from the mineral deposit to the application area) in terms of corporate sustainability and carbon footprint.
10. Studies on zeolites as slow-release fertilizers are normally limited to nutrients in cationic forms, while for anionic nutrients the loading on unmodified zeolite materials is not efficient. Also, it was not found any ecotoxicological study after the application of zeolites as a slow-release fertilizer.
11. Soil conditioner and controlled release fertilizer markets may consume a high volume of solid wastes in Brazil, and the products may have a sufficient value to overcome the transportation costs, besides a significant potential to be exported.
12. Agricultural techniques must update and become more efficient to keep up with the increase in global food demand, and the use of solid-waste-based zeolites can contribute to new environmental challenges.
13. It is possible to conclude that nature-friendly zeolites can be synthesized from agro-industrial residues and can be also functionalized to uptake and release specific nutrients, to be applied later as slow-release fertilizers, giving higher productivity to the crops, especially corn, soybeans, rice and sugarcane plantations, which are agribusiness products particularly important for Brazil.

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CONFLICT OF INTEREST STATEMENT

None.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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