Brazilian sedimentary zeolite use in agriculture

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This report describes the characterization and application of the Brazilian zeolitic sedimentary rocks as a slow plant-nutrient fertilizer and soil conditioner. The characterization of the head samples showed that it is composed of the zeolite stilbite intertwined with a smectic clay mineral, mixed with quartz. A low-cost quartz separation gravitational technique was used to concentrate the mineral. An enrichment of concentrated natural zeolite was carried out by adding KNO3, K2HPO4 and H3PO4 + apatite. These materials were tested with Rangpur lime rootstock and other with four successive crops grown on the same substrate: lettuce, tomato, rice, and Andropogon grass. The results indicated that N, P and K enriched zeolite was an adequate slow-release source of nutrients to plants increasing 20% of crop production and also improving products quality. Other greenhouse and field experiments with concentrated zeolite applied with urea showed 8% of reduction on losses of ammonia volatilization and improving 5% the corn dry matter yield. Concentrated zeolite used as a sand soil amendment also increased at least 10% of soil water retention and 15% of available water capacity.

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1. Introduction

The use of minerals for agricultural purposes is becoming widespread [1], and zeolitic concentrates have a special niche in this category. Zeolite minerals are crystalline hydrated aluminosilicates of alkali or alkaline-earth metals, structured in three-dimensional rigid crystalline network, formed by the tetrahedral AlO4 and SiO4, which come together to compose a system of canals, cavities and pores [2].

The worldwide number of identified natural zeolitic concentrates demonstrates both their great variety and the present-day interest on their potential applications in the industry and the agriculture [3]. These minerals have three main properties, which are of great interest for agricultural purposes: high cation exchange capacity, high water holding capacity in the free channels, and high adsorption capacity [4]. In Brazil, according to Rezende and Angelica [5] there are three regions with sedimentary zeolite: (1) Corda Formation in the Parnaiba Basin, at North of Tocantins State and South of Maranhao State; (2) Adamantina Formation of the Paraná River Basin, at Sao Paulo State; and (3) Botucatu Formation of the Paraná River Basin at Mato Grosso do Sul State. The depth of this sediment varies widely, reaching 30 m deep in some points and due to the different formations the stilbite concentration varies with sampling site [6,5]. Nevertheless none of these deposits produces zeolites for commercialization. The largest zeolite reservoirs are found in the Parnaiba river valley [6], where the stilbite form of the heulandite group dominates reaching approximately 50% of sediment [7].

While literature shows that zeolites are useful for increasing nutrient use efficiency in a range of crops, few information exists on the use of the Brazilian occurrence spece of zeolite–stilbite, on agricultural systems on acid soils. The objective of this report was to characterize and test the application of the Brazilian zeolitic sedimentary rock as slow release fertilizer and soil conditioner.

2. Case studies of agricultural stilbite use

2.1. Stilbite sampling, characterization and enrichment

An expedition was organized to sampling the zeolite raw material in the basin of the Parnaiba River, reported by Rezende and Angelica [6] as the greatest and surface sedimentary zeolite deposit in Brazil. The samples were collected near the city of Imperatriz, Maranhao State (5° 49′ 44″ south and 47° 21′ 27″ west).

Characterization analyses carried out by Monte et al. [7] demonstrate that the zeolitic sediment and quartz were the major components of the head samples. The head sample contained zeolite stilbite mixed with smectic clay deposits. A characterization with
TEM micrograph showed the presence of stilbite (ideal formula, (Na,K)Ca$_2$[Al$_2$Si$_3$O$_{10}$]·$4$H$_2$O) as one of the main mineral components [7] intertwined with smectic clay. Chemical composition (weight fractions of main components) showed: $\text{SiO}_2$ 64.7; $\text{Al}_2\text{O}_3$ 12.7; $\text{Na}_2\text{O}$ 0.8; $\text{K}_2\text{O}$ 0.97; $\text{CaO}$ 3.1; $\text{MgO}$ 1.5; $\text{Fe}_2\text{O}_3$ 3.3; $\text{P}_2\text{O}_5$ 0.12; $\text{TiO}_2$ 0.60; and $\text{BaO}$ 0.12. Raw material content was 470 g kg$^{-1}$ of stilbite. This report also showed that microproporous volume was 0.0057 cm$^3$ g$^{-1}$; microporous area 12.09 m$^2$ g$^{-1}$ and surface area (BET) 9.71 m$^2$ g$^{-1}$. Fig. 1 shows the scanning electron micrograph (A) on a scale of 30 μm and energy dispersive X-ray (B) of stilbite [8].

The material was crushed and part of it was concentrated, separating contaminants (quartz and iron oxides and hydroxides) from zeolite by means of gravitational concentration, using the Humphrey spiral, resulting in material with 650 g kg$^{-1}$ of stilbite. All fractions were analysed by X-ray diffraction. The mineral was classified by sieving followed by Tyler-series grain size selection from 295 to 37 μm.

As described by Monte et al. [7] concentrated zeolite (Z) was dispersed into solution containing 0.5 mol L$^{-1}$ in a 1:10 weight:volume proportion for saturating the negative charges with the cation. The suspensions were stirred for 24 h at room temperature, centrifuged, filtered and dried at 100°C. The homoionic material was dispersed again into solutions containing $\text{H}_3\text{PO}_4$ 1.0 mol L$^{-1}$ (ZP), $\text{KNO}_3$ 0.5 mol L$^{-1}$ (ZNK) or $\text{K}_2\text{HPO}_4$ 1.0 mol L$^{-1}$ (ZPK) in a 1:40 weight proportion, and were stirred for 24 h at room temperature, centrifuged, filtered and dried at 100°C. Zeolite enriched with $\text{H}_3\text{PO}_4$ was also mixed with phosphate rock (apatite – 340 g kg$^{-1}$ of $\text{P}_2\text{O}_5$), in a 1:10 (m m$^{-1}$) weight proportion. Concentration of N, P and K were analyzed at saturated substrate paste extract and presented: N and K at ZNK treatment were 21,180 and 2,021, 4,042, and 8,084 mg of K per pot[16]. Tomato fruit and Rangpur lime citrus rootstock production in protecting environment. The supply of 6.4 g of enriched zeolite significantly increased dry matter production (Fig. 2A), height and stem diameter (Fig. 2B), which were 37.5% higher in relation to the control without zeolite. Leggo [12] also had demonstrated that plants grown in organic substrate with N-$\text{NH}_4$ enriched zeolite increased 19% dry matter production comparing with other without zeolite.

Bernardi et al. [16] carried out another greenhouse experiment with 3 kg pots of an inert substrate with four levels (20, 40, 80 and 160 g per pot) of the same enriched zeolite [7]. Four successive crops were carried out on the same substrate of each pot: lettuce, tomato, rice and Andropogon grass. Results of the sequential extractions indicated that the doses of zeolite enriched necessary to obtain maximum productivity tended to be higher in the last crop than the first. Successive crops of lettuce, tomato, rice and Andropogon grass carried out on the same substrate of each pot indicated that N, P and K enriched zeolite was an adequate slow-release source of nutrients to plants (Fig. 3). Production of total dry matter of aerial biomass of four successive crops followed a descending order: ZP > ZPK > ZNK > Z.

Vegetable growers have been adopting new farming systems, such as protected and hydroponics systems as an alternative to the traditional field system. There is also the possibility of zeoponic system, termed by Mumpton [4] as the plants growth in synthetic soils consisting of zeolites with or without peat or vermiculite. Papers from Bernardi et al. [16–18] indicate the potential of Brazilian stilbite to be use in zeoponic systems.

Results adapted from Bernardi et al. [16,17] shows the response of lettuce (Lactuca sativa) on fresh weight and dry matter yield as a function of the supplying of KNO3-enriched stilbite (Fig. 4A). The maximum yield of lettuce (dry matter and fresh weight) was obtained with zeolite enriched with KNO3 (ZNK) at the range of 90–104.2 g of zeolite per pot, which represents 3.4–4.5 g of KNO3 per pot.

Evaluation of the P and K addition to a zeoponic substrate for growth tomato (Lycopersicon esculentum cv. Finestra) by Bernardi et al. [16,18] showed positive effects on fruit yield and quality and dry matter (DM) yield. The growth substrate had 1,010, 2,021, 4,042, and 8,084 mg of K per pot [16]. Tomato fruit and DM increased with the higher availability of K in the substrate. The higher fruit and DM (786 and 66 g per pot) were obtained with a mean dose of 6.57 g per pot (Fig. 5B). These results confirm that n
nutrients adsorption and release properties of the Brazilian sedimentary zeolite matched those reported for similar commercial zeolite products [7].

2.2.1. Rock phosphate dissolution
Zeolites mixed with phosphate rock, can act as controlled delivery system and renewable source of nutrients for plants. The dynamic equilibrium that occurs between the zeolite and apatite, providing its dissolution and release of P was early discussed by Lai and Eberl [19]. Allen et al. [9] showed that the mixture of clinoptilolite zeolite and phosphate rock from North Carolina, at 5:1 ratio (w/w) was efficient for the intensive cultivation of wheat (Triticum aestivum). Barbarick et al. [10] also found that the combination of zeolite and phosphate rock could be an efficient phosphorus supplier to plants, since the other elements were not limiting. The results of Bernardi et al. [16] (Fig. 6) are consistent with those previously obtained and demonstrated the enhanced availability of phosphate rock when applied in combination with zeolite. Despite the initial lower level of available P observed in the treatment ZP (with phosphate rock) with successive crops there was a lower decreasing in P availability (Fig. 6B) than in the P soluble form (KH₂PO₄) treatment (Fig. 6B). Furthermore P availability from ZP has tended increasing, especially after the first (lettuce) and second (tomato) crops unlike the soluble P source. Also in the third (rice) and fourth (Andropogon grass) crops can still be seen a higher availability of P in the substrate with phosphate rock.

2.2.2. Nitrogen use efficiency
Urea has been the most used N-source in Brazil [20] due to lower cost per unit of N. But N use efficiency of urea may be decreased due to losses from agricultural system. Nitrogen loss by volatilization of ammonia to atmosphere is one of the main factors responsible for low efficiency of urea applied on soil surface. This loss may reach extreme values, close to 80% of N applied [21]. Mulch may increase the amount of N lost by volatilization, especially when urea is applied on soil surface. The N-urea losses can be reduced.
using zeolites as additives in the fertilizers to control the retention and release of NH₄⁺ [2,22].

In a field experiment Bernardi et al. [23] evaluated dry matter yield and nutritional levels of nitrogen of silage corn fertilized with urea + zeolite. Treatments comprised two types of stilbite zeolite (natural and concentrated), four levels of nitrogen (0, 50, 100 and 200 kg ha⁻¹) and four ratios of zeolite (25%, 50% and 100% of N level). Treatments were applied 60 days after planting in the top-dressing fertilization. The use of concentrated (650 g kg⁻¹ of stilbite) or natural (470 g kg⁻¹ of stilbite) zeolite with urea increased, respectively 5.5% and 3.6% the silage corn dry matter production and N leaf concentrations as showed in Fig. 6.

The main action of zeolite in partial reduction on NH₃ loss by volatilization occurs by the control of retention of ammonium ion, formed by urea hydrolysis in the soil, due to zeolite high cation exchange capacity and ammonium retention from soil solution [24,25]. Besides retaining large quantities of ammonium ion, these minerals also interfere in the process of nitrification [24].

There are many reports in literature demonstrating the increased efficiency of N utilization when urea is used together with zeolite. Crespo [26] showed, in a pot experiment with clinoptilolite, an increase around 130% of N use efficiency, extraction and dry matter yield of Brachiaria decumbens. Bouzo et al. [27] increased productivity of sugar cane with utilization of 6 t ha⁻¹ of zeolite in an Oxisol. He et al. [28] and Werneck et al. [29] achieved reductions of losses by ammonia volatilization when urea was applied with clinoptilolite. Pereira et al. [30] showed that a nanocomposite based on urea intercalation into montmorillonite clay showed a slow release behavior for urea dissolution, even in low montmorillonite amounts (20% in weight).

Evaluation of the mixture of urea and zeolite to avoid ammonia volatilization in pot experiment with Italian ryegrass are illustrated in Fig. 7 [31]. Differences were observed in the rate of N–NH₃ volatilization with addition of 20% of zeolite to urea with an 8% decreasing of accumulated volatilized N–NH₃. Results indicated that approximately 21% of applied N was lost as N–NH₃⁺ when there was no addition of zeolite to urea. Addition of 20% zeolite reduced losses to 19.6%. As expected based on previous results, the lowest percentage of loss was obtained from ammonium nitrate N-source which was similar to the control (without N).

2.2.3. Quality of products

Quality is the sum of all features combined to produce a vegetable nutritionally acceptable and desirable as food. The final qual-
ity of an agricultural product is the result of several factors, among these the balanced nutrient supply. The external appearance of vegetables has great importance, since the consumer purchases the product that seems to be more attractive. Sensory analysis can be an appropriate tool to evaluate the quality or external appearance of the vegetables. This technique is used to measure, analyze, interpret, and quickly discerning the physical and chemical properties of food perceived by the five senses [32,33].

Sensory analysis of the appearance can be an adequate tool for evaluate lettuces quality. An ordering sensory test was carried out by Bernardi et al. [17] for comparing the appearance of lettuces grown in substrate with enriched zeolite. Zeolite with P soluble and insoluble sources showed higher yield, and equivalent visual quality comparing with the control. There were significant positive correlation between N level in tissues and the sensory attributes of plant color and size, P levels also were related with plant size.

Fresh tomato fruits are sources of vitamin C (ascorbic acid), hence production practices, including adequate plant potassium fertilization, are important to determine how its contents can be improved. Vitamin C must be ingested in food form because the human body is not able to synthetize it [34]. Significant differences of ascorbic acid content, evaluated according Ashoor et al. [35], in fresh tomato fruit were also found in relation to potassium supply (Fig. 8) by Bernardi et al. [18]. The highest level of ascorbic acid (26 mg 100 g⁻¹) was obtained with 8 g of potassium per pot. These values were consistent with those described in the literature, where the concentrations of ascorbic acid in tomatoes grown under greenhouse conditions ranged from 7 to 23 mg 100 g⁻¹ of fresh fruit [36] and from 17 to 22 mg 100 g⁻¹ in different cultivars under field conditions [37]. Sampaio and Fontes [38] studied yield and chemical composition of tomato due potassium fertilization, and obtained values of 20 mg 100 g⁻¹ with applications of 180 kg ha⁻¹ of K.

2.2.4. Soil conditioner

Sandy soils may have inadequate water retention for supporting plant growth. To improve these soils for agriculture, horticulture or turf grass, zeolite may be applied as a soil amendment. Zeolites applied as soil amendment improves the agricultural potential of these soils by increasing the efficiency of water use by increasing the soil water holding capacity and its availability to plants [39–42].

Evaluation of the Brazilian mineral zeolite as a soil conditioner was undertaken by Bernardi et al. [43] in a sand soil (89.0, 30 and 80 g kg⁻¹ of sand, silt and clay) with the three levels of zeolite (33.3; 66.7 and 100.0 g kg⁻¹) and a control. Samples for the soil water retention were collected with stainless steel cylinders and water retention curve was determined in Richards pressure chamber equipment. Then an equation of soil volumetric water content as a function of matric potential were adjusted with van Genuchten [44] model. As the zeolite concentration was increased there was an increasing in soil water retention at all matric potentials tested. Results from Fig. 9 shows the change of water retention curve with zeolite amendment and the increase on available water capacity increased 10%, 38% and 67%. These results are in agreement with recent results of Ippolito et al. [45] that also showed an improving on water status of a sandy soil with increasing zeolite rate. Easily available water increased 15%, 51% and 111% in relation to the control, respectively with the use of zeolite (Fig. 9B). The increasing in water availability was also reported by Nus and Braun [41]; Xiubin and Zhanbin [42] and Ippolito et al. [45].

3. Conclusions and outlook

The present results indicate that the addition of zeolite–stilbite concentrate zeolite enriched with N, P and K was an adequate slow-release source of nutrients to plants assuring high yields. Zeolite applied with urea improved N use efficiency and when applied with phosphate rock increased the P availability to plants. Increased water retention and available water capacity of a sand soil when use as a soil conditioner.

Despite the high-impurity content, the uses of natural Brazilian zeolitic concentrates in the agriculture present no major obstacle. The decision for the use of these urea amendments must be (i) conditions of use, which may interfere on products efficiency on controlling nutrient use efficiency, and (ii) economical, since it depends on the nutrient prices and mineral prices and availability.

Fig. 8. Concentration of ascorbic acid in fresh tomato fruits due to potassium levels in the substrate. Adapted from Bernardi et al. [16,18].

Fig. 9. Water retention curve (A) and available water capacity (AWC) and easily available water (EAW) (B) according to level of stilbite stilbite. Source: Bernardi et al. [43].
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References