Microporous and Mesoporous Materials 167 (2013) 16–21

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Brazilian sedimentary zeolite use in agriculture

Alberto C. de Campos Bernardi [a,*,1], Patrícia Peronti Anchão Oliviera [a], Marisa B. de Melo Monte [b], Fernando Souza-Barros [c]

[a] Embrapa Pecuária Sudeste, C.P. 339, CEP 13560-970 São Carlos, SP, Brazil
[b] Centro de Tecnologias Minerais – CETEM, Rio de Janeiro, RJ, Brazil
[c] Instituto de Física UFRJ, Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:
Available online 11 July 2012

Dedicated to Prof. Carmine Colella on the occasion of his 70th birthday.

Keywords:
Stilbite
Slow-release fertilizer
N losses
Water retention curve
Available water capacity

ABSTRACT

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 KNO_3, K_2HPO_4 and H_3PO_4 + 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 green house 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.

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 AlO_4 and SiO_4, 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 Parana River Basin, at Sao Paulo State; and (3) Botucatu Formation of the Parana 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 [5,6]. 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 specie 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

---

* Corresponding author.
E-mail address: alberto@cppse.embrapa.br (A.C. de Campos Bernardi).

[1] CNPQ fellow.

1387-1811/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2012.06.051

TEM micrograph showed the presence of stilbite (ideal formula, $(Na,K)Ca_2[Al_5Si_{13}O_{36}]\cdot 14H_2O$) as one of main mineral components [7] intertwined with smetitic clay. Chemical composition (weight fractions of main components) showed: SiO_2 64.7; Al_2O_8 12.7; Na_2O 0.8; K_2O 0.97; CaO 3.1; MgO 1.5; Fe_2O_3 3.3; P_2O_5 0.12; TiO_2 0.60; and BaO 0.12. Raw material content was 470 $g\,kg^{-1}$ of stilbite. This report also showed that microporous 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 decribed 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 H_3PO_4 1.0 $mol\,L^{-1}$ (ZP), KNO_3 0.5 $mol\,L^{-1}$ (ZNK) or K_2HPO_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 H_3PO_4 was also mixed with phosphate rock (apatite – 340 $g\,kg^{-1}$ of P_2O_5), in a 1:10 ($m\,m^{-1}$) weight proportion. Concentration of N, P and K were analized at saturated substrate paste extract and presented: N and K at ZNK treatment were 21,180 and 15,210 $mg\,kg^{-1}$; P and K at ZPK treatment were 11,289 and 41,925 $mg\,kg^{-1}$; and P on ZP mixture, 7,130 $mg\,kg^{-1}$.

2.2. Nutrient use efficiency

Zeolites improve the efficiency of nutrient use by increasing the availability of P from phosphate rocks, and the utilization of NH_4^+–N and NO_3^-–N, reduce losses by leaching of exchangeable cations, especially K^+, and act also as a slow-release fertilizer [9–11]. According to Leggo [12], due to the high affinity of zeolites for nutrients, these minerals may be used in growth media to improve plants yield. Mixtures of zeolite and fertilizers also had positive effects on lettuce [13] and tomato yields [14]. Zeolites improves the efficiency of nutrient use by increasing the availability of P from phosphate rock, the utilization of $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ and reduced losses by leaching of exchangeable cations, especially K^+ [9–12].

In a greenhouse experiment carried out by Bernardi et al. [15] with Rangpur lime (*Citrus limonia* Osbeck) rootstocks cultivated during 93 days in 150 cm^3-dibble tubes containing composted organic substrate of cocopeat and vegetal coal (3:1). Treatments comprised four enrichment types of concentrated natural zeolite: pure concentrated zeolite (Z), zeolite + KNO_3 (ZNK), zeolite + K_2HPO_4 (ZPK) and zeolite + H_3PO_4 + apatite (ZP) prepared as described by Monte et al. (2009). These treatments were also compared with a complete nutrient solution supplying. Fig. 2 illustrates that the supply of nutrients through the mineral zeolite enriched with NPK added to the organic substrate was a viable alternative for 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 steam 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 KNO_3-enriched stilbite (Fig. 4A). The maximum yield of lettuce (dry matter and fresh weight) was obtained with zeolite enriched with KNO_3 (ZNK) at the range of 90–104.2 g of zeolite per pot, which represents 3.4–4.5 g of KNO_3 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*

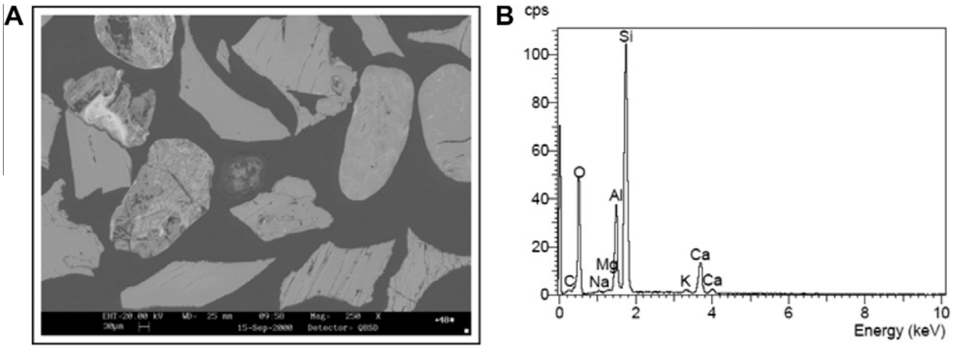

Fig. 1. Stilbite scanning electron microscope – SEM (A) image and energy dispersive X-ray analysis (B). Source: Duarte et al. [8].