

CHARACTERIZATION OF AN ACIDIC VOLCANIC ROCK MINING RESIDUE AND ASSESSMENT OF ITS NUTRIENT RELEASE POTENTIAL FOR STONEMEAL

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Abstract

The fertilization of soils with application of comminuted acidic volcanic rock is an alternative that can partially or completely replace the use of soluble chemical fertilizers. This technique is called stonemeal. Nutrient extraction studies were conducted in the laboratory to determine the capacity of a rock dust sample from a crushing facility in Nova Prata Municipality, Rio Grande do Sul. The study material was an acidic volcanic rock residue collected in the Extraction Industry Union Quarry, Nova Prata, Rio Grande do Sul, with a particle size range of < 0.6 mm. Chemical, mineralogical, physical and physico-chemical analyzes of the rock dust were performed. Nutrient extraction tests were also carried out in 2% citric acid solution (CA) and in a solution of organic acids from the rhizosphere (OAR) for two temperature levels: 25 °C and 50 °C. The nutrient release studies were performed in duplicate by extraction and subsequently, the concentrations of Ca, Mg, K, Fe, Cu, Mn and Zn were determined. There was a significant variation in results between the two extraction solutions: the 2% CA solution resulted in higher release of Ca and the OAR solution increased the release of K.

Keywords: stonemeal, mineral particles, mining residues.

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Introduction

In Brazil, several researchers have contributed to decrease external dependence on raw materials of chemical fertilizers (Bergmann and Zanetti, 2012) by developing and conducting studies using natural fertilizer consisting of mineral particles. The soluble mineral phases can improve the fertility of the soil and gradually release its nutrients (Amparo, 2003). According to the authors Resende et al. (2002), and Machado et al. (2005), when the components available in the rocks are released, they can meet the crops' needs and maintain the nutrient potential for subsequent crops.

The minerals of volcanic igneous rocks, among which basalt is most common, have in their composition, mainly silicon and aluminum oxides as well as iron, manganese, magnesium, sodium, potassium and calcium oxides (Turner; Verhoogen, 1960). Therefore, the existing chemicals in these rocks that can be released are calcium, magnesium, potassium, iron and phosphorus, plus trace elements in the form of micronutrients. In dissolution of the primary silicates, part of the available elements is released through the use of organic acids, mainly potassium, magnesium, iron, aluminum and silicon oxide. So, if the rate of transformation of the silicates is high, there will usually be a good availability of nutrients (Knapik, 2005).

During the rock weathering process and formation of the soil, there are different reactions that can occur simultaneously, making it difficult to predict how the mineral will dissolve. The increased potential for rock dissolution occurs with the comminution of the rock, facilitating the action of organic acids present in the rhizosphere and allowing nutrients to be absorbed by plants (Harley; Gilkes, 2000).

The authors Li et al. (1997) and Gardner & Parbery (1983), cite citric acid (CA) as the most abundant in the plant rhizosphere. The use of CA in the study of nutrient release aims to simulate the soil/root environment, promoting conditions similar to the natural environment. This organic acid is commonly exuded by plant roots, remaining at high concentrations in the rhizosphere (Song and Huang, 1988). The low molecular weight organic acids act through the formation of complex organic acids, metals, ligand exchange and protonation reactions (Simard et al., 1992). The diluted solutions of these acids, normally in increasing times balanced against the sample, have been used in kinetic studies of the release of K and Mg reserves (Song e Huang, 1988).



The Brazilian legislation regulating the use of organic and mineral fertilizers, and agricultural correctives (MAPA, 2007) approved the official analytical methods of these minerals. These methods describe the procedures for nutrient analysis using a 2% CA extraction solution.

The minimization of environmental impacts caused by the exploitation of acidic volcanic rock deposits, such as changing the landscape, depends upon the reduction and use of the generated waste. In Nova Prata, Rio Grande do Sul, the estimated annual production of mining waste was 52,400 m³ in 2005. However, only a fraction of this waste is used to produce gravel and the rest remains in the quarry without proper disposal (Toscan et al., 2007). The use of acidic volcanic rock dust generated in gravel production is common in the Nova Prata region, but only a gravel mining company sells the rock dust with a particle size < 0.6 mm. The careful study of the fertilizing potential of this rock dust, regarding the nutrient content and release and the economic and market feasibility analysis still needs to be expanded to include the development of sustainability policies in the mining activities.

In light of this context, the aim of this study was to characterize the acidic volcanic rock residue of the mining district of Nova Prata, Rio Grande do Sul, and evaluate, through laboratory simulations, its potential to provide macro and micronutrients that contribute to the positive change of soil fertility.

Experimental

Materials and Reagents

A sample of the residue from the crushing plant floor in the town of Gramado, municipality of Nova Prata, Rio Grande do Sul, was studied. The sample preparation comprised the following procedures: dry sieving in a number 30 ASTM sieve (< 0.6 mm) and drying in an oven for 24 hours at 100 °C. For the sample's cation exchange capacity studies the ammonium sulfate reagent was used. To determine the specific surface area, by adsorption from an aqueous medium, methylene blue was used. Solutions of 2% citric acid (CA) and organic acid from the rhizosphere (OAR) were used for nutrient extraction.

Chemical, mineralogical, elemental, physical and chemico-physical characterization

The chemical and mineralogical composition of the mineral particles was determined by X-ray fluorescence technique and X-ray diffraction.

The elemental sample analysis was determined by ICP-MS technique.

The surface area of the particles was determined by methylene blue adsorption method and expressed in mg^2/g (Van DenHul; Lyklema, 1968; Carter et al., 1986). In this case, a mass of 0.1 g of the sample was added to 0.1 L of methylene blue solutions at different concentrations. The solutions were stirred at 40 rpm at room temperature for an hour and left to stand for 23 hours. After this interval, the solutions' concentrations were determined by UV-visible spectrophotometry at a wavelength of 669 nm and the adsorption capacities were determined in accordance with Langmuir isotherms, as described by Van DenHul; Lyklema (1968).

The cation exchange capacity of the particles was performed by adding 5 g of the sample with 0.05 L of NaCl 1 mol/L activating solution, with stirring at 70 rpm for 24 hours, with the final suspensions vacuum filtered, washed with 0.3 L of deionized water and dried in an oven (100 °C) for 24 hours. Afterwards, an amount of 0.25 g of activated particles were added to 0.1 L of 100 $\text{mgNH}_3\text{-N/L}$ solution and stirred for 2 hours. The ammonia nitrogen concentration was subsequently determined (APHA, 1995) and consequently, the adsorption capacity of the particles, based on the number of milliequivalents (meq) of adsorbed ammonium cations.

Nutrient extraction studies

The analysis of the concentrations of Ca, Fe, K, Mn, Mg, Cu and Zn were made by atomic absorption. The extraction studies were carried out to simulate the acidic soils with CA and OAR. In the case of extraction by CA solution 1 L of 2% CA solution was used with 50g of particles (adapted from The Secretariat of Agricultural Defense [SDA] Normative Instruction N°. 28/2007, Ministry of Agriculture, Livestock and Supply [MAPA], 2007). Additionally, OAR solutions containing acetic acid, 1 mol/L, citric acid, 0.72 mol/L, lactic acid, 0.49 mol/L and



oxalic acid, 0.12 mol/L (Pires, 2003). In this case, 1 liter of the resulting solution was mixed with 250 g of the sample. Both suspensions were stirred (40 rpm) and were evaluated at temperatures of 25 °C and 50 °C for 6 hours as described by Pires (2003).

Results and Discussion

Chemical, mineralogical, elemental, physical and chemico-physical characterization

According to Table 1 it can be observed that the sample contains 59% anorthite, which is a mineral of the plagioclase feldspars class, with 19% Ca in its structure. As it is a calcic plagioclase its weathering resistance is low (Alleoni and Melo, 2009) and, therefore, can release its nutrients more easily to the environment. Also sanidine makes up 15% of the sample, which is a potassium feldspar, with 12.88% K. This mineral has medium resistance to weathering (Alleoni and Melo, 2009). Augite makes up 9% of the sample, an iron-magnesium mineral of the pyroxene group, consisting of 15% Mg, 6% Fe and 21% Ca. The pyroxene minerals are heavily influenced by weathering and because of this, can release nutrients (Ca, Mg, Fe) and/or elements (Fe, Al, Si, Mg, O) and form new minerals (Song and Huang, 1988). It is noted that the quartz/cristobalite phase did not reach 20% mineral content and that the aluminosilicates are predominant. Studies (Kautzmann et al, 2011; Nunes, 2012) showed that rock dust samples from the same region did not provide aluminum to the environment.

Table 1. Semi-quantitative mineralogical characterization by X-ray diffraction.

Mineral phase	Quartz	Anorthite	Sanidine	*Cristobalite	Augite
Chemical formula	SiO ₂	CaAl ₂ Si ₂ O ₈	KAlSi ₃ O ₈	SiO ₂	(Ca, Mg, Al) ₂ (Si,Al) ₂ O ₆
Concentration (%)	10	59	15	6	9

* Polymorphous crystal structure of quartz.

Table 2 shows that the SiO₂ and Al₂O₃ contents correspond to more than 75% of the composition, followed by Fe₂O₃ and CaO. The results also show that the particles studied have 3.56% CaO, 3.31% K₂O and 1.27% MgO. According to Turner and Verhoogen (1960), the presence of these components is common in the aluminosilicates of acidic volcanic rock.

Table 2. Chemical composition determined by X-ray fluorescence.

Oxide	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂
Concentration (%)	14.30	3.56	6.56	3.31	1.27	0.13	3.13	0.26	64.80	0.86

The mass spectrometry analysis results showed that the sample is mainly composed of Fe, K and Ca (Figure 1). These results reinforce the results obtained in the X-ray fluorescence measurements, because the oxides of interest in this study, present in higher quantities in the samples are Fe, K, and Ca, from augite, sanidine and anorthite and minerals found in the X-ray diffraction analyses.

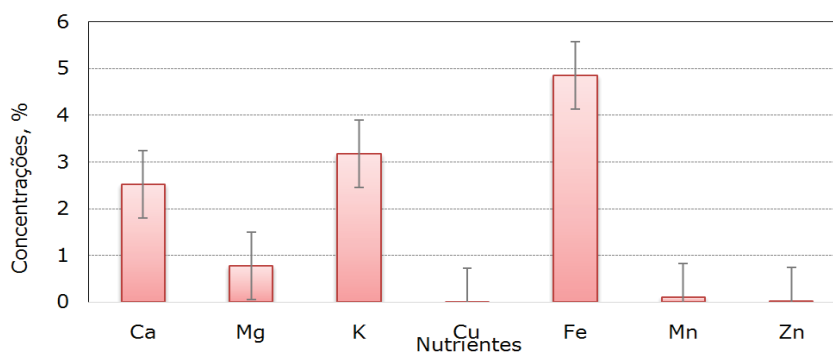


Figure 1. Nutrient concentration of the rock dust sample.

The particles had a surface area of 203 m²/g (\pm 0.73 m²/g), which is considered to be a high value for adsorption mechanisms. This may result in a high porosity of the particles, facilitating hydrolysis mechanisms and consequent mineral weathering, the result of which provides nutrients to the soil (Osterroht, 2003).

The cation exchange capacity (CEC) of the sample was determined at 2.4 meqNH₄⁺/g (\pm 0.01). This result is consistent with the

theoretical CEC of acidic volcanic rock, which is approximately between 1 and 3 meq/g, as shown by Andrade (1995).

These results may be related to the presence of certain minerals such as clays and zeolites. These results may be related to the presence of certain minerals⁴ such as clays and zeolites that promote high capacity ion exchange in solid/liquid interface (Luz, 1995).

Nutrient Extraction Studies

The results of the nutrient extraction studies of the particles for the acidic aqueous phases are shown in Figure 2.

In this case, it is possible to show that the extraction of Ca showed a similar behavior in relation to the temperature in the two types of acids studied. However, for the CA the extraction showed an increase of over 60%.

The release of Mg in the presence of CA at 50 °C was 25% greater than at 25 °C. This extraction solution was 57% more efficient than the OAR solution at different temperatures. In contrast, K leaching by OAR was two times higher than the CA in the two temperature conditions. Furthermore, the particles showed a high potential for release in both solutions.

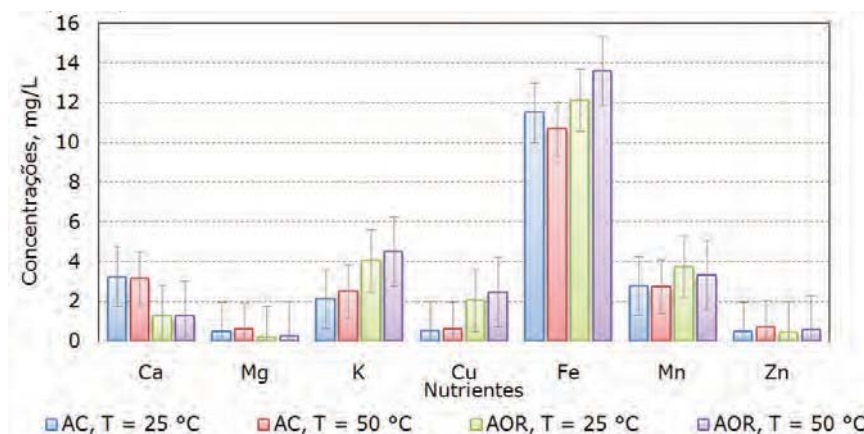


Figure 2. Concentration of the major nutrients available in the extracting solutions. Experimental error: ± 0.02



The release of Cu and Mn in the presence of OAR showed a similar behavior in relation to the temperature, but differed depending upon the type of acid, showing an increase of more than 73% Cu and more than 25% Mn for OAR.

The concentration of Fe released for both of the extracting solutions was higher when compared to other nutrients. This fact can be attributed to the properties of this nutrient being leached in an acidic environment (Oliveira et al., 2005).

The release of Zn showed an increase of 10% at 50 °C for CA.

These results show that the sample has the agronutrients required by the plants, but in apparently low levels. Thus, there will possibly be a need to use a larger amount of particles, or an adequate soil correction before application of the stonemeal technique.

Conclusion

The evaluated characteristics of the particles of acidic volcanic rock mining residue showed that all of the macronutrients and most of the micronutrients described in the literature are present in varying amounts in the sample studied. This indicates a possible potential for nutrient release to the soil. Additionally, the use of organic acid solutions of low molecular weight, tested in this study as extraction agents, were effective in providing mineral nutrients to plants, unless temperatures exceeded 50 °C.

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