IMPACTS OF SUGARCANE VINASSE AND ZEOLITE LOADED WITH VINASSE NUTRIENTS ON A TYPICAL TROPICAL SOIL PROPERTIES

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ABSTRACT

The intensive use of vinasse in fertigation can cause adverse environmental impacts due to its high organic matter content and acidic pH, despite its nutrient content, including potassium, nitrogen, and phosphorus. In this context, strategies that promote the recovery of nutrients from vinasse and its more controlled application, such as the use of zeolite enriched with vinasse-derived nutrients (ZV), are promising alternatives. This study comparatively evaluated the effects of applying sugarcane vinasse and zeolite with nutrients recovered from vinasse on the fertility of a typical tropical soil, such as an Oxisol. Natural zeolite samples (1 to 4 mm) adsorbed nutrients from vinasse by column percolation until saturation, recovering 44.22 mg g^{-1} of K$^+$ and 3.06 mg g^{-1} of NH$_4^+$. Column tests were then conducted to evaluate the application of raw vinasse and nutrient-loaded zeolite (ZV) in soil. When added to the soil, vinasse increased K$^+$ and Ca^{2+} concentrations by 20x and 1.5x, respectively, whereas ZV increased them by 7x and 6.2x. The Ca^{2+} ions released by ZV displaced H$^+$ from the colloidal exchange sites of the soil, raising its pH from 4.1 to 5.6, whereas the addition of vinasse increased the pH of the soil only to 4.7 due to the high level of organic acids. Consequently, base saturation (V) of ZV and vinasse soils increased from 10% to 79% and 41%, respectively. ZV improved soil fertility more than vinasse since V>50%, without increasing organic matter. The direct use of vinasse, although beneficial in the short term, poses environmental risks from nutrient leaching and soil acidification. In contrast, the use of ZV can increase soil nutrient availability and promote their gradual release, making this process a more sustainable alternative for agricultural management.

Keywords: Zeolite; Vinasse; Recovery; Nutrients; Tropical soil.

RESUMO

IMPACTOS DA VINHAÇA DE CANA-DE-AÇÚCAR E DA ZEÓLITA SATURADA COM NUTRIENTES DA VINHAÇA NAS PROPRIEDADES DE UM TÍPICO SOLO TROPICAL. O uso intensivo da vinhaça na fertirrigação pode causar impactos ambientais negativos devido ao seu alto teor de matéria orgânica e pH ácido, apesar de possuir nutrientes como potássio, nitrogênio e fósforo. Nesse contexto, estratégias que promovam a recuperação de nutrientes da vinhaça e sua aplicação mais

controlada, como o uso de zeólita enriquecida com os nutrientes da vinhaça (ZV), são alternativas promissoras. Este estudo avaliou comparativamente os efeitos da aplicação de vinhaça de cana-de-açúcar e zeólita enriquecida com nutrientes recuperados da vinhaça na fertilidade de um solo tropical típico, como o Latossolo. As amostras de zeólita natural (1 a 4 mm) adsorveram nutrientes da vinhaça por percolação em coluna até a saturação, recuperando 44,22 mg g^{-1} de K$^+$ e 3,06 mg g^{-1} de NH$_4^+$. Em seguida, foram realizados testes em coluna para avaliar a aplicação da vinhaça bruta e da zeólita enriquecida com nutrientes da vinhaça (ZV) no solo. Quando adicionada ao solo, a vinhaça aumentou as concentrações de K$^+$ e Ca^{2+} em 20x e 1,5x, respectivamente, enquanto a ZV as aumentou em 7x e 6,2x. Os íons Ca^{2+} liberados pela ZV deslocaram o H$^+$ dos sítios de troca dos coloides do solo, elevando seu pH de 4,1 para 5,6, enquanto a adição de vinhaça aumentou o pH do solo apenas para 4,7 devido ao elevado teor de ácidos orgânicos. Consequentemente, a saturação de bases (V) dos solos com ZV e vinhaça aumentou de 10% para 79% e 41%, respectivamente. A ZV melhorou a fertilidade do solo mais do que a vinhaça, uma vez que V>50%, sem aumentar a matéria orgânica. O uso direto da vinhaça, embora benéfico a curto prazo, apresenta riscos ambientais relacionados à lixiviação de nutrientes e à acidificação do solo, enquanto o uso da ZV pode promover o aumento da disponibilidade de nutrientes ao solo e sua liberação gradual, tornando esse processo uma alternativa mais sustentável para o manejo agrícola.

Palavras-chave: Zeólita; Vinhaça; Recuperação; Nutrientes; Solo tropical.

RESUMEN

IMPACTOS DE LA VINAZA DE CAÑA DE AZÚCAR Y DE LA ZEOLITA SATURADA CON NUTRIENTES DE LA VINAZA SOBRE LAS PROPIEDADES DE UN SUELO TROPICAL TÍPICO. El uso intensivo de vinaza en fertirrigación puede provocar impactos ambientales negativos debido a su alto contenido en materia orgánica y pH ácido, a pesar de contener nutrientes como potasio, nitrógeno y fósforo. En este contexto, las estrategias que promueven la recuperación de nutrientes de la vinaza y su aplicación más controladas, como el uso de zeolita enriquecida con nutrientes de la vinaza (ZV), son alternativas prometedoras. Este estudio evaluó comparativamente los efectos de la aplicación de vinaza de caña de azúcar y zeolita enriquecida (ZV) con nutrientes recuperados de la vinaza sobre la fertilidad de un suelo tropical típico, como el Latosol. Las muestras de zeolita natural (1 a 4 mm) adsorbieron nutrientes de la vinaza mediante percolación en columna hasta la saturación, recuperando 44,22 mg g^{-1} de K$^+$ y 3,06 mg g^{-1} de NH$_4^+$. Posteriormente, se realizaron ensayos en columna para evaluar la aplicación de vinaza cruda y de la zeolita enriquecida con nutrientes (ZV) en el suelo. Cuando se añadió al suelo, la vinaza aumentó las concentraciones de K$^+$ y Ca^{2+} en 20 y 1,5 veces respectivamente, mientras que la ZV las aumentó en 7 y 6,2 veces. Los iones Ca^{2+} liberados por la ZV desplazaron al H$^+$ de los sitios de intercambio coloidal del suelo, elevando su pH de 4,1 a 5,6, mientras que la adición de vinaza aumentó el pH del suelo solo hasta 4,7 debido al alto nivel de ácidos orgánicos. En consecuencia, la saturación de bases (V) de los suelos con ZV y vinaza aumentó del 10 % al 79 % y al 41 %, respectivamente. El ZV mejoró la fertilidad del suelo más que la vinaza, ya que V>50 %, sin aumentar la materia orgánica. El uso directo de la vinaza, aunque beneficioso a corto plazo, presenta riesgos ambientales relacionados con la lixiviación de nutrientes y la acidificación del suelo, mientras que el uso de la ZV puede promover una mayor disponibilidad de nutrientes en el suelo y su liberación gradual, convirtiendo este proceso en una alternativa más sostenible para el manejo agrícola.

Palabras clave: Zeolita; Vinaza; Recuperación; Nutrientes; Suelo tropical.

1 INTRODUCTION

Sugarcane is a key renewable energy source, with Brazil among the leaders in ethanol production. The country ranks second, behind only the United States, where production is based mainly on corn (Fuess et al., 2017; Renewable Fuels Association [RFA], 2023). Even so, productivity in ethanol generation from sugarcane is higher (about 7 m³ ha⁻¹) when compared to other raw materials, such as corn and cassava (between 3 and 4 m³ ha⁻¹) (Fuess et al., 2017). This alternative, however, also implies an increase in the volume of vinasse generated in the sugar and alcohol industries (Silva et al., 2021).

Approximately 300 billion liters of vinasse are generated in Brazil each year (Silva et al., 2019). The primary use of vinasse is fertigation, a low-cost operation that does not require sophisticated technologies (Carpanez et al., 2022). The management of vinasse transport and application to the soil is relatively simple and is carried out with the aid of trucks or infiltration pipes (Fuess et al., 2021; Gloeden et al., 1991). For these reasons and due to the prohibition of vinasse discharge into water bodies in Brazil since 1978, fertigation has been widely used in Brazil since the 1980s. However, this practice has caused pollution, mainly in groundwater and surface water, and has consequently led to the deaths of aquatic animals (Cruz et al., 1991).

Over the last two decades, the sugar-energy sector has had the most significant impact on water resources (67.4%), followed by soil (22.6%) and the atmosphere (10.07%) (Rebelato et al., 2016). To prevent increased contamination of water and soil, it is necessary to control the application of vinasse based on each soil's characteristics, as the amount of effluent should not exceed its ion retention capacity (Silva et al., 2007). The primary issue to be considered regarding the use of vinasse in fertigation is, therefore, the balance between its advantages for the agro-industrial sector and the negative environmental impacts associated with its disposal. While studies demonstrate the short-term benefits of fertigation with vinasse (Fuess et al., 2021), there is also a need to deepen our understanding of its effects on the soil and, consequently, on groundwater.

Given the widespread use of fertigation with vinasse in agriculture, it is necessary to develop sustainable technologies that utilize its nutrients without contaminating soil, surface water, and groundwater. An alternative to using vinasse without releasing other contaminants directly into the soil is to use minerals that can remove nutrients from vinasse, such as zeolites. Zeolites, with their abundant pores and channels, provide a high surface area that can reach hundreds of m² per gram of zeolite (Soltys et al., 2020) and can effectively recover nutrients, such as K^+ and NH_4^+. This property, combined with the generation of negative charges resulting from the replacement of part of Si^{+4} by Al^{+3} in the framework, gives zeolites a high cation-exchange capacity and, thus, several applications (Pabalan & Bertetti, 2001). The addition of zeolites to the soil enhances soil sorption capacity, reduces soil acidification, increases nutrient use efficiency, enables higher yields, and reduces nutrient dispersion into the environment (Jarosz et al., 2022). In this context, this study aims to analyze the main effects of direct vinasse percolation in an Oxisol, compared with the alternative addition of zeolites enriched vinasse-derived nutrients, using experimental data.

2 MATERIALS AND METHODS

2.1 Materials

The vinasse sample was provided by the sugar and ethanol industry, "Alcoeste Bioenergia Fernandópolis S/A", in Fernandópolis, São Paulo State. The zeolite used in this study originates from volcano-sedimentary deposits in Cuba and was supplied by Indústria Celta Brasil Ltda. This sample has a particle size between 1 and 4 mm and is composed of 67% clinoptilolite, 20% mordenite, and 13% muscovite.

To analyze and compare the effects of directly using vinasse in soil versus adding zeolites enriched with nutrients from vinasse (ZV), tests were conducted in columns containing nutrient-poor soil, such as Oxisol, which is abundant in Brazil. Oliveira et al. (2016) previously collected and analyzed this soil sample from the city of Piracicaba (São Paulo State).

2.2 Methods

2.2.1 Vinasse, Zeolite, and Oxisol characterization

The vinasse chemical composition was determined in the laboratories of the Departamento de Ciência do Solo of Escola Superior de Agricultura Luiz de Queiroz of Universidade de

São Paulo (ESALQ/USP). The analysis included total nitrogen (sulfuric digestion/Kjeldahl), potassium and sodium (acid digestion or in water and determination by flame photometry), phosphorus (acid digestion and determination by colorimetry), calcium (acid digestion and determination by atomic absorption), sulfur (acid digestion and determination by the gravimetric method of barium sulfate), organic carbon (by wet method – extraction with dichromate and determination by titrimetry), organic matter (combustion – loss on ignition) and pH (pH meter equipment). The ammonium concentration was determined by spectrophotometry using the Nessler reagent method.

Both the zeolite and the soil were analyzed before and after being used in the column tests (item 2.2.2). The chemical composition of the zeolites was determined before and after saturation with vinasse. The samples were fused with lithium tetraborate and compared with certified reference materials in the QZF1 calibration (Quartz and Feldspar) by X-ray fluorescence spectrometry (XRF). The equipment used was a Malvern Panalytical spectrometer, Zetium model, from the Laboratório de Tecnologia Mineral (LCT) of the Escola Politécnica/Universidade de São Paulo. The loss on ignition (LOI) was determined by the gravimetric method at 1020 °C for 2 h in an electrical oven. To determine the cation exchange capacity (CEC), the zeolite was saturated with 1 mol L^{-1} potassium chloride, then with 1 mol L^{-1} ammonium acetate. After centrifugation, the potassium ions displaced from the zeolite by ammonium ions into the supernatant solution were quantified by flame photometry. The result of this potassium concentration was used to calculate the CEC. This test was based on the method proposed by Hesse (1971).

The soil samples were dried in an oven at 60 °C for 48 h to determine physicochemical and chemical parameters. The analyses were performed at the Laboratório de Fertilidade do Solo of the Instituto Agronômico de Campinas (IAC) and included: pH (in CaCl$_2$ and determination by potentiometry), organic matter content (by the colorimetric method by extraction with sodium dichromate and determination by colorimetry), phosphorus, potassium, calcium, magnesium (by ion exchange resin extractor) and phosphorus determination by colorimetry (molybdenum blue method), H+Al (Shoemaker-McLean-Pratt (SMP) buffer solution and determination by potentiometry)

and cation exchange capacity (CEC) calculated in mmol$_c$ kg^{-1} from the Ca+Mg+K+(H+Al) contents.

2.2.2 Column tests

Two types of column tests were conducted. The first type of test involved saturating the zeolite exchange sites with vinasse nutrients via adsorption (recovery of vinasse nutrients). The second type of test examined how the percolation of raw vinasse and the addition of natural zeolite (Z) or zeolite loaded with vinasse nutrients (ZV) can affect soil properties.

a) Recovery of nutrients from vinasse by zeolite

A column test was conducted to evaluate the recovery of K$^+$ and NH$_4^+$ from vinasse by zeolite until its exchange sites were saturated. A mass of 50.0 g of natural zeolite (Z) was compacted into an acrylic cylinder (3 cm internal diameter and 15 cm height), resulting in a length of 8 cm. Coarse glass beads (average diameter of 3 mm) were placed at both ends of the column as a support medium and to provide uniform flow distribution. Silicone tubing (diameter of 3 mm) was connected to the extremities of the column. A vinasse upward flow was established using a peristaltic pump (Watson Marlow - 120S) at a flow rate of 11 mL min^{-1}. Effluent samples were collected every 10 minutes during the first three hours of the test, then every 20 minutes thereafter. Samples were analyzed for pH, potassium, sodium, and ammonium. The test duration was 10 h and 20 min, until the breakthrough curve was stable. The breakthrough curves show the ratio of the cation concentration in the effluent sample (C) to the initial concentration of the same cations in the vinasse (C$_0$) over time. When C/C$_0$ equals 1, the exhaustion point is reached, corresponding to the zeolite's maximum saturation capacity (Borba et al., 2006).

After saturation, the chemical composition of the zeolite sample containing the vinasse nutrients (ZV) was investigated by X-ray fluorescence spectrometry (XRF), as described in the previous section 2.2.1.

b) Addition of vinasse and zeolite samples (Z and ZV) in soil

Five columns were prepared in acrylic cylinders as previously described, adding Oxisol – which was crushed, homogenized, sieved (< 2 mm), and quartered. Glass wool was placed at the bottom of the column, followed by a 2 cm layer

of 3 mm-diameter coarse glass beads and a 2 cm layer of sand (0.6–1.5 mm), before the addition of the soil. In total, 200 g of soil was added (except in columns 4 and 5), corresponding to a thickness of approximately 23 cm of the column (Figure 1).

All tests were performed at room temperature (~25 °C) using five setups. Column 1 served as the control, in which soil was percolated with distilled water (DI water) to identify the primary compounds leached from the soil. Columns 2 and 3 evaluated the impact of vinasse addition. In column two, vinasse was percolated to evaluate its impact on soil properties and nutrient leaching. In column three, 5 g of natural zeolite without nutrients was mixed with 10 g of soil and placed at the top of the column, which was also percolated with vinasse. Columns four and five were used to evaluate the impact of adding ZV and its ability to release the nutrients retained in its structure. In both columns, 25 g of ZV were placed at the top; column four was packed with 50 g of Oxisol, while column five was packed with 50 g of fine glass beads (FGB). Then, these columns were percolated with tap water to simulate irrigation water. This water had an electrical conductivity of 164.04 μS cm^{-1}, concentrations of K$^+$ of 2.07 mg L^{-1}, Na$^+$ of 12.86 mg L^{-1}, and a pH of 7.7.

The results of these tests were analyzed using breakthrough curves. The porosity (n) and the time to replace one pore volume (t_{PV}) were determined for all tests. The n was calculated using equation 1, and t_{PV} was obtained using equation 2.

$$n = V_{pore} \div V_{total\ column} \qquad \text{(Eq. 1)}$$

$$t_{PV} = V_{pore} \div Q \qquad \text{(Eq. 2)}$$

where V_{pore} is the pore volume (mL) and $V_{total\ column}$ is the total column volume (mL), Q corresponds to the volumetric flow rate (mL/min).

In addition, the cumulative mass of nutrients leached from the columns (Ma) was calculated using equation 3, based on the flow rate (Q) and the effluent concentration (C_i) at a given time interval (Δt_i).

$$Ma = \sum_{i=1}^{n} Q_i \times C_i \times \Delta t_i \qquad \text{(Eq. 3)}$$

After the tests, the soil samples were collected, separated from the fractions with zeolite (when present), and dried in an oven at 60 °C for 48 h to determine physicochemical and chemical parameters, as reported in section 2.2.1.

3 RESULTS AND DISCUSSION

3.1 Zeolites and vinasse characterization

The chemical analysis (Table 1) showed that zeolite is mainly composed of SiO$_2$, followed by Al$_2$O$_3$, CaO, Na$_2$O, K$_2$O, Fe$_2$O$_3$, MgO, MnO, and TiO$_2$. Si^{4+} and Al^{3+} belong to the tetrahedral structure, while Ca^{2+}, Na$^+$, K$^+$, and Mg^{2+} occupy

TABLE 1 – Chemical composition of natural zeolite. Loss on ignition (LOI) at 1020 °C.

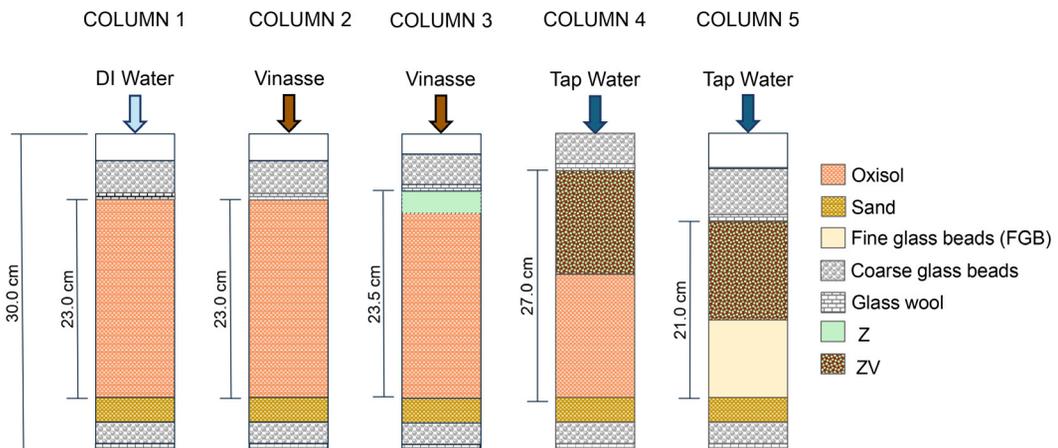| wt %					
LOI	10.40	Na$_2$O	1.95	MnO	0.30
SiO$_2$	68.30	K$_2$O	1.77	TiO$_2$	0.23
Al$_2$O$_3$	11.00	Fe$_2$O$_3$	1.69	ZrO$_2$	0.01
CaO	2.94	MgO	0.82	P$_2$O$_5$	<0.05

FIGURE 1 – Column tests 1 to 5 setup. Z= natural zeolite; ZV= vinasse nutrients-loaded zeolite

the zeolite exchange sites (pores and cavities). Furthermore, the loss on ignition value of 10.4% is attributed to the mass of volatile compounds, such as water molecules, in the samples.

The CEC result obtained for zeolite (1.1 meq g^{-1} – which corresponds to 110 cmol$_c$ kg^{-1}) is consistent with those reported by Qi et al. (2005) and Diaz-Nava et al. (2005), who obtained CEC values of 1.03 and 1.09 meq g^{-1} in samples predominantly containing clinoptilolite.

Table 2 presents details of the chemical composition of vinasse. Vinasse has an acidic pH (4.5) and is rich in organic matter (8.69 mg L^{-1}) and organic carbon (4.83 g L^{-1}). It also contains macronutrients – such as potassium (2.60 g L^{-1}), phosphorus (0.05 g L^{-1}) and nitrogenous compounds (0.9 g L^{-1}) – and some micronutrients, such as calcium (1.31 g L^{-1}), iron (2.50 mg L^{-1}), manganese (2.50 mg L^{-1}), copper (0.25 mg L^{-1}), zinc (0.25 mg L^{-1}) and magnesium (0.01 mg L^{-1}). The ammonium ions (NH_4^+) concentration determined by the Nessler method was 589.7 mg L^{-1}. These nutrient values are slightly higher than those reported in other studies, as expected, since vinasse composition varies depending on the process and the origin of the raw material (Silva et al., 2023). Compared with these data, the nutrient concentrations in our study are higher, especially for potassium.

TABLE 2 – Chemical composition of vinasse. OM= organic matter; OC= organic carbon

Total solids	OM	CO	K₂O	Ca	N	SO₄	P₂O₅
			(g L⁻¹)				
6.37	8.69	4.83	2.60	1.31	0.90	0.40	0.05
NH₄	Na	Fe	Mn	Cu	Zn	Mg	pH
			(mg L⁻¹)				
589.70	67.50	2.50	2.50	0.25	0.25	0.01	4.50

3.2 Column tests

3.2.1 Recovery of nutrients from vinasse by zeolite

The recovery of nutrients from vinasse using zeolite was evaluated in a column test. It was observed that the breakthrough curves for potassium and ammonium ions are similar, both increasing until stabilizing at a C/C_0 ratio of 1 (Figure 2). The sodium ion behaved differently, because it was released from the zeolite into the solution, whereas the K^+ and NH_4^+ ions were retained by the zeolite.

After the first 200 minutes (3 h 20 min) of the test, the potassium concentration nearly stabilized, with a C/C_0 ratio of 0.7, while the exhaustion point ($C/C_0 = 1$) was reached only after 420 minutes (7 h). During this period (7 h), 44.22 mg K^+ g^{-1} was removed, totaling 2211 mg of potassium removed from 6 L of vinasse per 50 g of zeolite. In contrast, the ammonium ions reached stability after 70 minutes, with a C/C_0 ratio already close to 1. A total of 3.06 mg g^{-1} was removed (1 h 10 min), totaling 153.37 mg of ammonium retained within the column. The NH_4^+ recovery from an activated sludge effluent using a zeolite column reported by Sayavedra et al. (2024) was slightly higher (4.9 mg g^{-1}). This is probably because the NH_4^+ and K^+ concentrations in this effluent were the same (25 mg L^{-1}), in contrast to vinasse, where the K^+ content differs significantly (2,600 mg L^{-1}) from NH_4^+ (~590 mg L^{-1}).
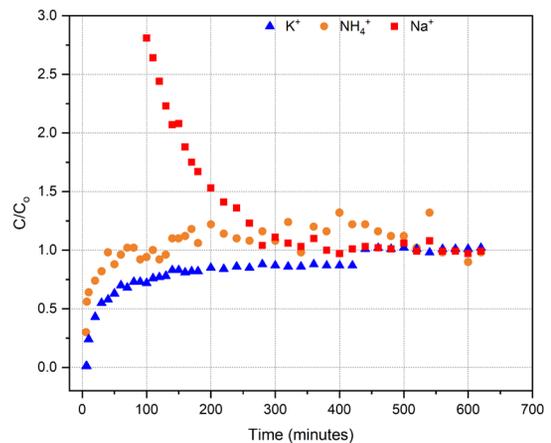

FIGURE 2 – Breakthrough curves for K^+, NH_4^+, and Na^+ ions in a coarse zeolite column percolated with vinasse.

For sodium, the concentration in the column effluent was higher than the initial concentration in the vinasse, due to ion exchanges with the zeolite itself. Initially, the sodium levels were higher ($C/C_0 > 2.5$) but decreased as the exchange mechanisms also decreased and the zeolite's exchange sites became saturated with the vinasse components. Stabilization occurred after 260 minutes (4 h 20 min), with the sodium concentration eventually approaching the initial vinasse concentration.

The chemical composition of the zeolite saturated with vinasse was analyzed by XRF to determine the amount of nutrients adsorbed. A increase of 2.3 times in the K_2O content (from 1.77 to 4.09 wt%) and a decrease of 2.2 times in the

Na$_2$O (from 1.95 to 0.90 wt%) and 0.9 times in the CaO contents (from 2.94 to 1.92 wt%) were observed when compared to the zeolite data before (Table 1) and after treatment with vinasse in the column (Table 3). Although this chemical composition (obtained by XRF) does not take NH$_4^+$ ions into account, it is known from adsorption test data that there is around 0.3% NH$_4^+$ in the zeolite structure.

TABLE 3 – Chemical composition of the vinasse nutrient-loaded zeolite (ZV), in weight percent (wt%). Loss on ignition (LOI) at 1020 °C.

	wt%				
LOI	10.50	*CaO*	1.92	*TiO$_2$*	0.23
SiO$_2$	68.40	*Fe$_2$O$_3$*	1.61	*P$_2$O$_5$*	0.07
Al$_2$O$_3$	11.20	*Na$_2$O*	0.90	*MnO*	0.01
K$_2$O	4.09	*MgO*	0.73	*ZrO$_2$*	0.01

These results indicate that K$^+$ was the main cation removed from the vinasse by exchange with other zeolite cations, mainly Na$^+$ and to a lesser extent Ca^{2+}. This exchange mechanism reflects well the selectivity order of clinoptilolite - Cs$^+$ >Rb$^+$ >K$^+$ >NH$_4^+$ >Ba^{2+} >Sr^{2+} >Na$^+$ >Ca^{2+} >Fe^{2+} >Al^{3+} >Mg^{2+} >Li$^+$ (Ames, 1960) – where the K$^+$ and NH$_4^+$ ions are more favored to occupy the exchange sites of the zeolite than Na$^+$ and Ca^{2+} since they have lower charge density than other ions (Zhang et al., 2024). In this sense, the ZV sample was enriched in potassium while still having some calcium ions in its exchange sites. The decrease in Na$^+$ was

significant because this ion does not contribute to soil fertility, unlike K$^+$ and Ca^{2+}.

The increase in phosphorus content was unexpected. One possible explanation is the physical retention of phosphorus in the solid fraction of the vinasse, since the zeolite (ZV) used in column 5 was not washed prior to chemical analysis. In this case, phosphorus ions may have formed complexes with organic compounds of the solid phase of vinasse (Prado et al., 2013). In addition, according to Saifuddin et al. (2019), phosphorus can also bind to Fe sites on the zeolite surface through ligand-exchange mechanisms, where phosphate replaces surface –OH groups coordinated to Fe. Therefore, part of the detected phosphorus may reflect not only superficial residues but also chemical association with iron present in the vinasse.

3.2.2 Addition of vinasse and zeolite samples (Z and ZV) in soil

a) Addition of vinasse and Z

In column 2 (Figure 3), the soil was percolated with 0.7 L of vinasse with a flow rate of 2.8 mL min^{-1}, with porosity = 56.4%, and t_{PV} = 24 min. Potassium and ammonium had C/C$_0$ values close to 0.5 at the time of 1 pore volume (PV). So, the retardation factor (R) was close to one, indicating low interaction and retention of these compounds in the soil. Stability was observed at approximately 40 minutes (1.6 PV) for potassium ions and 30 minutes (1.3 PV) for ammonium, both with C/C$_0$ ratios of 0.9. The exhaustion point was reached at
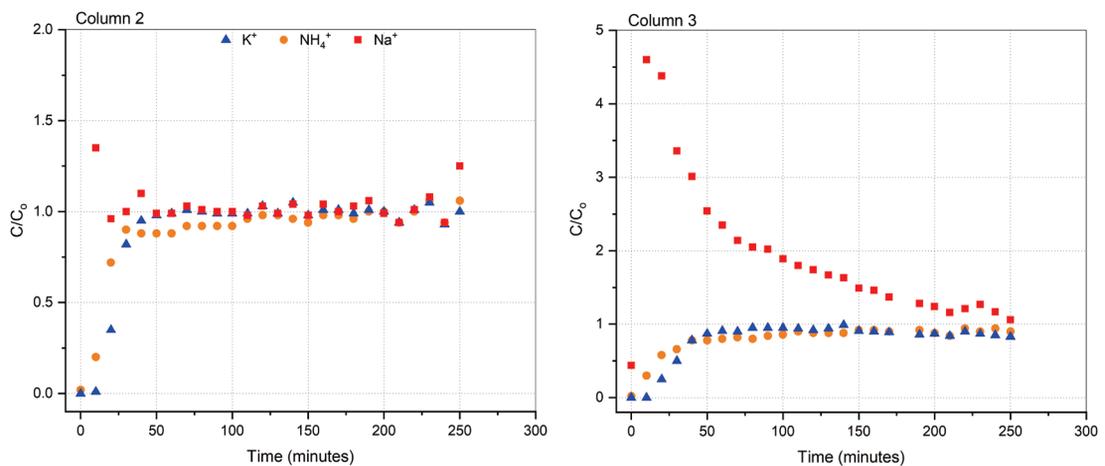

FIGURE 3 – Breakthrough curves for K$^+$, NH$_4^+$, and Na$^+$ in columns 2 and 3. Initial concentrations: 2160 mg L^{-1} of K$^+$, 250 mg L^{-1} of NH$_4^+$, and 67.5 mg L^{-1} of Na$^+$.

70 minutes (2.9 PV) for potassium and 190 min (7.9 PV) for ammonium.

During the first 10 minutes, the sodium content was slightly elevated in the solution percolated in both columns. However, this ion was not determined in the soil composition; this increase may be due to its leaching from the soil components in column 2. Then, the concentration decreased, stabilizing at C/C_0 equal to 1 after 20 minutes, indicating that this soil type does not retain Na^+ ions significantly. The mass balance stated a loss of 2.16 mg of sodium from the soil during the test. As for potassium, the total mass retained in the column was 147 mg, and that of ammonium was 18.5 mg ($\sim$0.79 mg g^{-1} and 0.27 mg g^{-1}, respectively). The pH varied from 5.41 at the beginning of the test to 4.74 at the end, with the final pH closer to that observed for vinasse, 4.5 (Table 2). This decrease in pH is likely due to the acidic pH of the vinasse itself.

In column 3 (Figure 3), containing 5 g of zeolite mixed with 10 g of soil at the top of the column, 0.8 L of vinasse was percolated. The irregularity of the zeolite grains, along with the fraction of suspended solids in the vinasse, may have caused the reduction in permeability, and therefore, it was necessary to adjust the flow rate. Initially, the flow rate was 3.2 mL min^{-1} (t_{PV}=18.7 min) until 40 min, then it was reduced to 2.8 mL min^{-1} (t_{PV}=21.4 min), and after 2 h and 40 min of testing, the flow rate was decreased to 2.4 mL min^{-1} (t_{PV}=25 min). Due to the addition of zeolite, the retardation factor for potassium was higher (1.6), indicating greater retention of this compound in the porous medium. Concentration stability was reached at 60 min for potassium, with a C/C_0 ratio of $\sim$0.8, and at 100 min for ammonium, with a C/C_0 of 0.9. The potassium mass retained in column 3 (312 mg) was more than twice that in column 2, further evidence of cation retention by the zeolite. Likewise, there was an increase in ammonium retention (33.2 mg) in column 3. This greater retention agrees with the higher retardation factor observed. In addition to the high potassium retention by the zeolite, a slight increase in the soil potassium content was observed, from 21.6 mg kg^{-1} in column 2 to 22.9 mg kg^{-1} in column 3, because this soil was not analyzed together with the layer where the zeolite was added to the column.

As in column 2, an initial increase in sodium content was also observed in column 3, but at more than 3x the level. The mass balance between the sodium input and output from the column also indicated a more significant sodium loss than in

column 2, reaching 10.37 mg. The higher values were caused by the release of sodium from the zeolite structure due to exchange with K^+ and NH_4^+ ions. Sodium concentration decreased throughout the test, reaching a C/C_0 of 1.06 after 4 h 20 min. The release of sodium from zeolite into the leaching solution could lead to salinization effect. However, previous studies indicated that this was unlikely to have negative impacts on the soil (Soltys et al., 2020). The pH of the leached solution ranged from 4.4 at the start to 4.6 at the end of the test.

Therefore, the results of columns 2 and 3 tests show the advantage of adding zeolites to the soil to retain vinasse nutrients and reduce/avoid their leaching. Amin (2024) also observed the effectiveness of zeolites (among other adsorbents) in reducing the leaching of vinasse components, such as dissolved organic carbon and ammonium, and the significant increase in the available potassium in calcareous sandy soils compared to the control treatment. On the other hand, a study of the effects of 50 years of vinasse fertigation on groundwater quality in east-central Mexico revealed contamination of the aquifer by dissolved soil manganese during the oxidation of organic matter introduced by vinasse percolation (González & Mejía, 2014). This suggests that, despite soil nutrient retention, oxidation of organic matter from vinasse can negatively impact groundwater quality.

b) Addition of ZV

The cumulative release curves of K^+ and NH_4^+ ions from columns 4 (ZV and soil) and 5 (ZV and fine glass beads) were determined (Figure 4) to observe the ion release from the nutrient-loaded zeolite over time (around 18 days) and to investigate the differences caused by soil retention (comparing column 4 to column 5). The flow rate of tap water through both columns was 2.8 mL min^{-1}.

The total mass of potassium and ammonium released in column 4 was 806 mg and 67.6 mg, respectively. In column 5, the total mass of potassium and ammonium released from ZV was higher, respectively, 1337 mg and 83.7 mg. Considering the potassium and ammonium content in 25 g of ZV (917 mg of K^+ and 101.5 mg of NH_4^+), there was a release of 145.8% and 82.3%, respectively, in column 5. Therefore, the excess potassium ions released in column 5 likely originate from the tap water composition ($\sim$2.1 mg L^{-1} K^+), and without the soil, the ions were released at a higher rate in this column. This also indicates
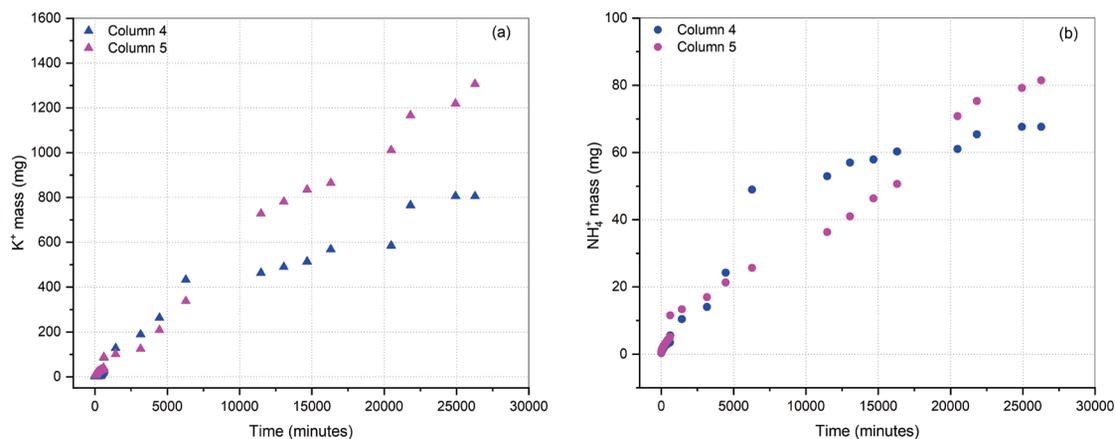
FIGURE 4 – Cumulative mass (mg) of K^+ (a) and NH_4^+ (b) released from columns 4 and 5 over time. Initial mass in 25 g of ZV: 917 mg of K^+ and 101.5 mg of NH_4^+.

that 87.9% of potassium and 66.6% of ammonium were released from soil column 4 after 18 days.

In tests conducted in pots containing sandy soil (nutrient-poor soil) under non-saturated conditions, Santos et al. (2024) found that clinoptilolite enriched with potassium and ammonium from synthetic solutions lost far fewer nutrients (15.5% K^+ and 22.4% NH_4^+) over three months than chemical fertilizers (92.9% K^+ and 54% NH_4^+). They observed no difference in the kale growth between soils that received enriched nutrients from zeolites and synthetic fertilizers. Eslami et al. (2018) also prepared zeolites (clinoptilolite and chabazite) with synthetic NH_4^+ and K^+ solutions for use as slow-release fertilizers in sandy soils; however, under saturated conditions. They observed leaching losses of 88% for K^+, and 84% for NH_4^+ from chemical fertilizers, and 14% for K^+ and 29% for NH_4^+ from enriched clinoptilolite. Zeolites enriched with

nutrients from vinasse can therefore slowly release K^+ and NH_4^+ under both unsaturated and saturated soil conditions, providing these nutrients to plants over a long period.

3.2.3 Effect of addition of vinasse and zeolite samples (Z and ZV) on the soil properties

The chemical properties of the soil samples collected after the column tests are presented in Table 4. The percolation of distilled water (DI) through the Oxisol (column 1: $n = 56.4\%$ e $t_{PV} = 31$ min) practically did not change the soil parameters, with only a decrease in potassium and calcium content observed, due to their high solubility and, consequently, mobility.

In contrast, comparing the data from the soil columns that received vinasse (columns 2 and 3) with those from the DI percolated soil (column 1) significant modifications in several parameters were

TABLE 4 – Physical-chemical and chemical parameters of the soils used in the column tests. DI: Distilled water; Z: natural zeolite; ZV: nutrient-loaded zeolite; OM: organic matter; SB: sum of bases; CEC: cation exchange capacity; BS: base saturation; V: base saturation in percentage.

Parameters	Oxisol (soil)	Column 1 (soil+DI)	Column 2 (soil+vinasse)	Column 3 (Z+soil+vinasse)	Column 4 (ZV+soil+tap water)
pH	4.1	4.0	4.8	4.7	5.6
OM (g kg^{-1})	12.0	12.0	17.0	17.0	13.0
H+Al (mg kg^{-1})	97.0	91.0	83.0	89.0	23.0
P (mg kg^{-1})	5.0	5.0	19.0	14.0	9.0
K (mg kg^{-1})	1.1	0.4	21.6	22.9	6.9
Ca (mg kg^{-1})	12.0	9.0	17.0	19.0	74.0
Mg (mg kg^{-1})	1.0	1.0	20.0	20.0	8.0
SB (mg kg^{-1})	14.1	10.4	58.6	61.9	88.9
CEC (mmol$_c$ kg^{-1})	111.1	101.4	141.6	150.9	111.9
V (%)	13.0	10.0	41.0	41.0	79.0

observed (Table 4). The soil parameters of columns 2 and 3 are similar, because both samples were collected after soil saturation ($C/C_0=1$). However, the addition of zeolite before saturation with vinasse (column 3) has a noticeable effect. This is because the soil layer where the zeolite was mixed retained the vinasse cations until its saturation, and this layer was separated from the portion of soil analyzed at the end of the test; therefore, the cations removed from the vinasse by the zeolite were not determined in this soil sample.

There was a slight increase in soil pH from 4.1 to 4.8 (column 2) and 4.7 (column 3), but it remained as acidic as vinasse (4.5) (Table 2). The increase in organic matter content (~42%) in these soils may have kept the pH acidic due to the presence of a variety of organic acids in the vinasse, such as acetic acid, butyric acid, caproic acid, citric acid, lactic acid, propionic acid, succinic acid, valeric acid, among others (Bernardes et al., 2021). Jiang et al. (2012) also observed that continuous application of vinasse for 2–3 years at two sites in China slightly increased the soil pH from 4.36 to 4.93 and from 4.56 to 4.89, respectively, while the vinasse pH was 4.35.

The soils of columns 2 and 3 also showed significant increases in the concentrations of potassium (~20x), magnesium (20x), phosphorus (~3x), calcium (~1.5x), and the CEC (~1.3x). However, as the total CEC refers to the sum of the exchangeable cations of the soil (Ca^{2+}, Mg^{2+}, K^+, H^+, and Al^{3+}), most of this value comes from $H^+ + Al^{3+}$, which, although slightly reduced by the addition of vinasse, is still high and potentially toxic to plants (Ronquim, 2010). On the other hand, Galdeano et al. (2021) observed low fertility conditions in soils fertilized with vinasse for 5 years, due to increase H+Al content, despite a high CEC value. Therefore, these results show the importance of analyzing additional parameters to assess soil fertility, not just nutrient content, such as K^+ content.

The sum of exchangeable bases (SB = Ca^{2+} + Mg^{2+} + K^+), in turn, rose significantly from 14.1 mg kg^{-1} to around 60 mg kg^{-1} in soils of columns 2 and 3. Consequently, as the base saturation (V) corresponds to the percentage of the soil's cation exchange capacity (CEC) that is occupied by basic cations, this parameter also increased in columns 2 and 3 (Table 4) from 10% (column 1 soil) to 41%. However, as base saturation is an excellent indicator of soil fertility, these soils cannot be considered fertile, as the V value must be ≥ 50% (Ronquim, 2010). However, the contribution of H^+ and Al^{3+}

to the exchange complex remained high, thereby reducing fertility and increasing soil acidity and toxicity. On the other hand, the phosphorus content increased in soils of columns 2 and 3, probably due to its adsorption by Oxisol components, such as iron oxides/hydroxides, whose pH$_{PZC}$ values are usually high – around 7 to 7.5 (Pouran et al., 2014). At a pH around 4.5, the soil's iron components can acquire positive surface charges, which favour the adsorption of phosphate anions. This behavior had also been observed by Parfitt (1977) in an Oxisol from Papua New Guinea, where phosphate adsorption by iron and aluminum oxides/hydroxides increased with decreasing soil pH.

Despite this, compared to chemical fertilizers, the benefits of vinasse as an organic amendment are superior because it improves physicochemical and biological properties of the soil (Stephen et al., 2024). In fact, a study carried out on the long-term effects of applying vinasse to two types of soil, one clayey (for 10 years) and the other sandy (for 15 years), showed an improvement in both soil health components, especially in soil organic carbon content, nutrient recycling, and soil physical quality (Luz et al., 2024). Therefore, it is important to mention that the main changes observed in the soils of columns 2 and 3 were related to the application of vinasse until the soil was completely saturated, i.e., when the concentrations of the K^+ and NH_4^+ solutions percolating into the soil were equal to those of the original vinasse ($C/C_0=1$). Therefore, vinasse can also bring benefits by controlling its dosage (Yin et al., 2019; Ebaid et al., 2024), as its sustainable use is essential to promote a harmonious balance between agricultural productivity and environmental well-being (Stephen et al., 2024).

In general, the results of column tests using vinasse showed that the main effects on soil fertility are related to the increase in the levels of potassium, magnesium, phosphorus and calcium. While there are short-term improvements in soil fertility, there are potential risks of groundwater contamination and acidification due to the high organic matter content. Therefore, vinasse application rates must be carefully regulated and monitored according to soil properties.

On the other hand, the soil in column 4, which received the nutrient-loaded zeolite (ZV), presented OM content similar to that of the soil in column 1 (control). Its potassium content increased approximately 7x (6.9 mg kg^{-1}) compared to the control soil (0.4 mg kg^{-1}), but it was approximately 3x lower than in soils where the vinasse was applied

(around 22 mg kg^{-1}). Magnesium concentration in the soil of column 4 increased 8x (from 1 to 8 mg kg^{-1}), and the phosphorus rose from 1.8x (5 to 9 mg kg^{-1}). The highest increase observed was in the calcium content, which reached 74 mg kg^{-1}, the highest value among all tests, corresponding to 6.2x the control soil (9 mg kg^{-1}). The ZV itself may have contributed to the increase in calcium, since zeolite initially contains Ca^{2+} within its structure, and most of these ions were retained even after treatment with vinasse (Tables 1 and 3).

As calcium is preferentially adsorbed by soil colloids to a greater extent than potassium (Jakobsen, 1993), the Ca^{2+} ions from the ZV may have displaced and be exchanged with the H^+ and Al^{3+} from the colloidal phases of the soil. This would explain why the pH of the soil in column 4 increased from 4.1 to 5.6, the highest of all the tests (Table 3), and the pH of the leached solution also increased from 5 to 6-7, after 10 hours. The presence of bicarbonate and basic functional groups can also neutralize H^+, as commonly observed in calcium-induced deacidification reactions. Consequently, the decrease in exchangeable H^+ was accompanied by an increase in soil pH, consistent with the greater availability of Ca^{2+} and the lower Al+H values observed in column 4.

In ion-exchange studies involving K-Ca systems, Cofie and Pleysier (2004) also found that the organic and clay fractions preferred Ca^{2+} over K^+ throughout the soil, while Filcheva and Tsadilas (2002) reported that clinoptilolite zeolite increased soil pH and exchangeable potassium. Therefore, in our study, Al+H of soil column 4 is the lowest (23 mg kg^{-1}) of all the tests. On the other hand, the addition of natural zeolite in column 3 did not increase the soil pH. As the soil was percolated with vinasse, the high concentrations of organic acids in the solution may have suppressed the ability of Ca^{2+} to displace H^+ ions from the soil colloids. So, after percolation of vinasse, similar pH values (4.7–4.8) were recorded in the soils of columns 2 and 3.

Due to the increase in Ca^{2+} in the soil in column 4, its sum of exchangeable bases (SB = Ca^{2+} + Mg^{2+} + K^+) was significantly higher (88.9 mg kg^{-1}), and its base saturation (79%) also increased more than the other soils, making it the most fertile soil in the test. On the other hand, ZV also contributed to the increase in phosphorus content in the soil of column 4, since these ions remained physically retained on the surface of the zeolites (Table 3). Therefore, these results suggest that nutrient-loaded zeolite (ZV) can provide nutrients that, although present in lower quantities than pure vinasse, are available to plants more gradually and over a longer period, minimizing their loss through leaching. Furthermore, the addition of ZV increased the fertility of the Oxisol (V%) and pH, since there was no increase in organic matter. Overall, the use of ZV had greater positive impacts compared to vinasse, including greater nutrient availability, a lower risk of groundwater contamination and soil acidification, and a general improvement in soil health.

4 CONCLUSIONS

Zeolites can effectively recover potassium and ammonium ions from sugarcane vinasse. These ions are important plant nutrients and can slowly release from the ZV structure into the soil.

The addition of ZV to a tropical soil (Oxisol) increased the concentrations of potassium (~7x) and calcium (~6.2x) and the pH (4.1 to 5.6), and, consequently, base saturation (V) to almost 80%, improving soil fertility without increasing organic matter content.

On the other hand, the direct addition of vinasse to Oxisol did not significantly alter the pH, keeping it acidic (~4.7) and rich in H+Al, although it increased the K^+ (~20x) and Ca^{2+} (~1.5x) contents. Despite the increase in nutrient levels, the fertility of the Oxisol did not improve, as H+Al remained high and, consequently, V< 50%.

Therefore, the main benefits of using zeolite loaded with vinasse nutrients in soil are its ability to increase pH levels, slowly and continuously release nutrients, improve fertility, and reduce nutrient loss.

Additionally, future studies should examine the combination of this nutrient source with others, as well as its impact on soil microbial communities.

5 ACKNOWLEDGMENTS

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