



Nutrient retention and availability of biochars prepared by co-pyrolysis of vinasse with sugarcane filter cake

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Abstract

The disposal of vinasse, a nutrient-rich by-product of ethanol production, is challenging because of the low pH and emissions of harmful gases and smells. Here, biochars were produced by pyrolysis of mixtures of filter cake and vinasse (0.25 w/v to 1 w/v) at 550°C. The effects of filter cake to vinasse ratios on the biochar yield, pH, ash content, total nutrient (P, K, Ca, and Mg) content, and nutrient availability were investigated. Increasing the filter cake to vinasse ratio increased the biochar yield and ash content and lowered the biochar pH from 10.3 for 0.25-BC to 8.2 for filter cake biochar (FC-BC). Lower filter cake to vinasse ratios increased the total K content from 7.9 g·kg⁻¹ for FC-BC to 75.9 for 0.25-BC. Nutrient recovery in the biochars was high (79.5% to 130.2%). Whereas P, Ca, and Mg extractability in water was <5%, the K extractability was 80% for 0.25-BC and decreased to 7.6% for FC-BC. Extractability of K, P, Ca, and Mg in 2% formic acid from vinasse-containing biochars was high (>50%). These results highlight the potential suitability for use in agricultural applications. Conversion of vinasse into value-added biochar could reduce waste treatment cost and improve soil health.

1. Introduction

Thailand is among the top 5 sugar producers in the world with a total production of 8.8 million metric tons of sugar in 2023/2024 [1]. After harvesting the produced sugarcane is transported to the sugar industries to produce sugar and ethanol. In addition to the main products, large amounts of by-products are also produced. For example, filter cake is the solid residue from cane juice clarification and filtration process in sugar production [2] and 10 L to 15 L of vinasse is generated from fermentation and distillation for each liter of ethanol that is produced [3]. The sugar industries invest significant resources in the disposal of filter cake and vinasse. Because of their low value, these byproducts are commonly deposited in the field to improve soil fertility. However, the direct soil application of vinasse is unsuitable because of its low pH of approximately 4.5 to 5.5 [4-6], emission of greenhouse gases, and unpleasant smell [7]. To mitigate environmental impacts, it is essential to develop new waste treatment and management processes that maximize the utilization of vinasse and filter cake as value-added materials.

Filter cake and vinasse contain essential nutrients for plants such as phosphorus (P), potassium (K), magnesium (Mg), and calcium (Ca) [4,8,9]. Thermal processing could be a sustainable approach for recovery of nutrients from these wastes in the form of a biochar fertilizer or soil amendment. In addition, transforming vinasse into biochar can significantly reduce the emission of greenhouse gases

such as methane and ammonia compared to unmodified vinasse. During pyrolysis, biomass is converted into biochar at elevated temperatures in limited oxygen condition [10]. Pyrolysis increases the concentrations of inorganic nutrients like P, K, Mg, and Ca in vinasse [11], and previous studies reported that pyrolysis temperature [11] and additives [12] can have beneficial effects on nutrient content and nutrient retention in vinasse biochar. However, vinasse suffers from swelling behavior during the pyrolysis process due to the release of large quantities of water and volatiles. To overcome this, previous studies have evaluated mixing the vinasse with other biomasses like bagasse pith [13] and filter cake [14]. Amin studied the effect of bagasse pith mixed with dried vinasse at the ratio 1:2 (w/w) on carbon emission and nutrient availability in sandy soil and found a reduction in carbon emission and increase in nutrient (K and P) availability [13]. A similar result was observed by Türk and Arslanoğlu [14], who reported that the water-extractable K in the mixed vinasse and carbonation cake (filter cake) biochar increased at increased pyrolysis temperatures (400°C to 600°C) and heating times (2 h to 6 h). In contrast, the water-extractable K content was reduced when the cake to vinasse ratio was increased. However, it is unclear if the lower K extractability in DI water was related to the tendency of slow release or caused by the lower total K content in biochar.

The objectives of this work are (1) to prepare biochars with different filter cake to vinasse ratios (0.25 w/v to 1 w/v) at a pyrolysis temperature of 550°C, (2) to study the effect of filter cake to vinasse ratio on the

nutrient concentration and recovery in the biochar, and (3) to assess the nutrient extractability in DI water and 2% formic acid as a potential indicator for leaching risk and phytoavailability.

2. Experimental

2.1 Collection and characterization of filter cake and vinasse

Filter cake and vinasse were kindly supplied by Mitr Phol sugar factory (Chaiyaphum province, Thailand). The filter cake was air dried, ground and stored in zip lock bags until use. The vinasse was collected in a closed container and used as obtained. All solutions were prepared with deionized (DI) water (18.2 MΩ·cm).

The moisture content of the filter cake and vinasse were determined in triplicate by drying 0.2 g of filter cake and vinasse at 80°C until constant weight. The moisture content was calculated by dividing the weight loss by the initial sample weight and multiplied by 100%. To measure the pH, triplicate samples of 0.3 g raw filter cake were mixed with 30 mL of DI water followed by 10 min ultrasonication and shaking for 30 min at 120 rpm by orbital shaker. The suspension was filtered through Whatman no. 42 filter paper and the pH of the solution was measured by the pH meter (OHAUS Starter 3100) [15]. The pH of as-received vinasse was measured directly.

Thermal degradation of the filter cake and vinasse mixtures was evaluated by thermogravimetric analysis (TGA, Shimadzu DTG 60H). The samples were heated to 800°C (heating rate 10°C·min⁻¹) under N₂ atmosphere (60 mL·min⁻¹). After reaching 800°C, the atmosphere was changed to O₂ (60 mL·min⁻¹) and maintained for 20 min to determine the ash content in the samples.

The total concentrations of P, K, Ca, and Mg in the filter cake and dry vinasse were measured in triplicate after dry ashing, digestion with HNO₃ and H₂O₂, and dissolution and dilution in 5% HNO₃ [15]. The P concentration in solution was determined by the molybdenum blue method using UV-Vis spectroscopy at 880 nm [16]. The K concentration was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES, PerkinElmer Avio 200). The Mg and Ca concentrations were determined by atomic absorption spectroscopy (AAS, PerkinElmer PinAAcle 900 F) with external calibration [16].

2.2. Biochar preparation

First, 240 g of filter cake was mixed with 960, 480, 320, or 240 mL of vinasse, resulting in filter cake to vinasse ratios of 0.25, 0.5, 0.75, and 1 (w/v), respectively. These mixtures were named 0.25FV, 0.5FV, 0.75FV, and 1FV, respectively. Each mixture was left to stand for 3 h to ensure complete wetting of the filter cake and then oven-dried at 60°C overnight. Pyrolysis of the mixtures was carried out in a laboratory scale electric furnace at 550°C (heating rate 10°C·min⁻¹) for 3 h. After pyrolysis, the produced biochars were allowed to cool down to room temperature, weighed, and kept in zip lock bags until use. Triplicate biochar samples were prepared to confirm reproducibility, and the biochar yield was calculated by Equation (1):

$$\text{Yield (\%)} = \frac{w_{\text{BC}}}{w_0} \times 100\% \quad (1)$$

Here, w_{BC} (g) is the weight of the produced biochars and w_0 (g) is the initial biomass weight. The produced biochars were designated as 0.25-BC, 0.5-BC, 0.75-BC and 1-BC according to the ratio between filter cake and vinasse. The biochar produced from pure filter cake was named FC-BC.

2.3 Biochar characterization

The pH of the biochars was measured in triplicate as described for the raw filter cake (0.3 g biochar in 30 mL DI water, 10 min ultrasonication, 30 min shaking at 120 rpm) [15]. The crystal structures of the biochars were studied by X-ray diffraction (XRD, PANalytical EMPYREAN) with Cu K α radiation at $2\theta = 5^\circ$ to 70° (step size at 0.01 $^\circ$). Peak identification was done using X'pert HighScore software. Fourier transform infrared spectroscopy (FTIR, Bruker TENSOR27) analysis of the biochars was done over the wavenumber range of 600 cm⁻¹ to 4000 cm⁻¹ by accumulating 32 scans at 4 cm⁻¹ resolution.

The extractability of the nutrients (P, Mg, Ca, and K) was measured in triplicate in DI water and 2% formic acid. Here, 0.3 g of biochar was mixed with 30 mL of extractant (DI water or 2% formic acid). The mixture was ultrasonicated for 10 min and shaken for 30 min at 120 rpm by an orbital shaker, after which the suspensions were separated through the filter paper (Whatman no. 42) [17]. The P, K, Mg, and Ca concentrations in the solution were measured with UV-Vis spectroscopy (P), ICP-OES (K), and AAS (Mg and Ca) as described previously for the filter cake and vinasse. The nutrient recovery in the biochar after pyrolysis was calculated by Equation (2) [18]:

$$\text{Recovery (\%)} = \frac{c_{\text{BC}}}{c_0} \times \text{Yield} \quad (2)$$

Here, c_{BC} is the nutrient concentration in the biochar (g·kg⁻¹) and c_0 is the nutrient concentration in the raw material (g·kg⁻¹). Nutrient concentrations in the filter cake/vinasse mixtures were calculated based on the measured nutrient concentrations in the filter cake and vinasse.

3. Results and discussion

3.1 Properties of filter cake and vinasse

The properties and nutrient concentrations of filter cake and vinasse are shown in Table 1. The pH of filter cake and vinasse was 7.7 and 4.5, respectively, which is in line with previous studies [4,19]. The more acidic pH of vinasse was caused by the alcoholic fermentation process, which requires acidic conditions for yeasts to metabolize sugar to ethanol, and the presence of organic acids [20]. The moisture contents of the filter cake and vinasse were 8.3% and 83.1%, respectively, and the ash contents were 46.8% and 26.4%. The higher ash content in filter cake compared to the vinasse was possibly due to the higher inorganic material in filter cake, which is in agreement with previous works [19,21].

According to Table 1, the primary nutrient in filter cake was Ca (59.0 g·kg⁻¹), followed by K (21.0 g·kg⁻¹), P (13.4 g·kg⁻¹), and Mg (8.4 g·kg⁻¹). The high Ca content in filter cake and vinasse occurred

by the juice clarification process, where calcium hydroxide and carbon dioxide were added to neutralize the organic acids and to remove the impurity from the juice by sedimentation and vacuum filtration [9,22]. For vinasse, the primary nutrient was K ($80.0 \text{ g}\cdot\text{kg}^{-1}$), followed by Ca ($45.6 \text{ g}\cdot\text{kg}^{-1}$), Mg ($25.1 \text{ g}\cdot\text{kg}^{-1}$), and P ($4.9 \text{ g}\cdot\text{kg}^{-1}$). The K content of vinasse was substantially higher than that of filter cake. These concentrations are in agreement with previous works [8,9]. The composition of filter cake and vinasse may depend on several factors such as sugarcane quality, soil quality, and juice clarification process [2,23].

Pyrolysis of (dried) vinasse alone could not be carried out due to the excessive swelling caused by the loss of water and volatiles, and vinasse was mixed with filter cake to reduce the swelling. To understand how the mixing of filter cake with vinasse would influence the thermal degradation behavior, TGA experiments were carried out in N_2 atmosphere (Figure 1). At temperatures below 120°C a small mass weight loss of 2.7% to 8.2% took place by removal of moisture. The second weight loss step of approximately 25% to 30% at 120°C to 410°C was ascribed to the thermal degradation of cellulose and hemicellulose [21]. In this region, higher vinasse concentrations resulted in lower onset temperatures of 120°C (0.25FV) and 180°C (0.75FV) compared to FC at 210°C . The degradation at lower temperatures may be due to decomposition of small organic molecules and non-fibrous material in vinasse [9,23]. The reduced degradation temperature is also seen in the peak weight loss temperatures of 310°C for both 0.25FV and 0.75FV, and 345°C for FC by the degradation of cellulose and hemicellulose. This is in accordance with Da Silva *et al.* [9,23]. The weight loss above 410°C due to degradation of lignin [21] was observed for 0.25FV, 0.75FV, and FC. After reaching 800°C the atmosphere was switched to O_2 and the char was converted to ash with an ash content of 32.8%, 42.5%, and 47.1% in 0.25FV, 0.75FV, and FC, which is in the range of the ash contents of filter cake and vinasse (Table 1).

3.2 Properties of biochars prepared at different filter cake to vinasse ratios

The yield, pH, and ash contents of the biochars at different filter cake to vinasse ratios are summarized in Table 2. The biochar yield slightly increased at higher ratios, from 54.4% to 58.6% for 0.25-BC to 1-BC and 59.4% for FC-BC, and are in the same range as previous studies on biochars produced from filter cake [24,25] and vinasse [21]. The slight increase in yield by increasing the filter cake to vinasse ratio was due to the higher ash content in the filter cake compared to the vinasse (Table 1). At the same time, the ash content increased at higher

filter cake to vinasse ratios in the range of 75.8% to 81.3% for 0.25-BC to 1-BC and 84.7% for FC-BC. Filter cake contains substantial quantities of inorganic compounds such as SiO_2 and CaCO_3 that are retained in the biochar after pyrolysis, resulting in an increased biochar yield at a higher filter cake to vinasse ratio. The biochar pH decreased with increasing filter cake to vinasse ratios, from 10.3-9.5 for 0.25-BC to 1-BC and 8.2 for FC-BC. This was due to the decomposition of the organic acids in raw vinasse during pyrolysis and the retention of alkaline salts containing K, Ca, and other alkaline earth elements in the biochar [14]. Thus, despite the low pH of the raw vinasse (Table 1), higher vinasse contents resulted in more alkaline biochars.

The XRD patterns of the biochars are shown in Figure 2. Quartz (SiO_2) was the main crystalline phase in all biochars as observed by the sharp peaks at $2\theta = 20.8^\circ, 26.6^\circ, 36.4^\circ, 42.4^\circ, 45.8^\circ, 54.8^\circ, 59.9^\circ, 67.7^\circ$ and 68.2° [24]. The peak intensity of SiO_2 increased at higher filter cake to vinasse ratios, suggesting that the majority of SiO_2 originated from the filter cake. The same trend was also found for calcium carbonate (CaCO_3) at $2\theta = 29.4^\circ, 39.4^\circ, 43.3^\circ, 47.4^\circ, 48.5^\circ$ [26]. The dominant presence of CaCO_3 in all biochar samples is consistent with the higher Ca contents in the raw materials (Table 1) [25]. The formation of KCl (sylvite) was also observed by the peak at $2\theta = 28.4^\circ, 40.6^\circ$, and 58.8° , and was previously observed in vinasse ash [27]. The intensity of KCl decreased when the filter cake and vinasse ratio increased, which is in agreement with the high K content in vinasse (Table 2). The small peaks at $2\theta = 19.7^\circ$ ($\text{Ca}_2\text{P}_2\text{O}_7$) and 31.6° (CaMgP_2O_7) may suggest that all biochars contained a crystalline Ca/Mg pyrophosphate.

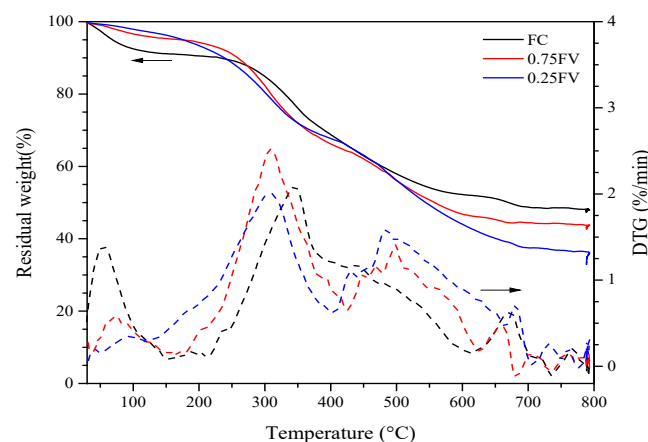


Figure 1. Thermogravimetric analysis of filter cake (FC) and the mixtures of filter cake and vinasse in N_2 atmosphere. The weight loss at a constant temperature of 800°C was in O_2 atmosphere.

Table 1. Physicochemical properties and main nutrient concentrations of filter cake and vinasse. The ash content and nutrient concentrations are based on the dry weight of the raw material.

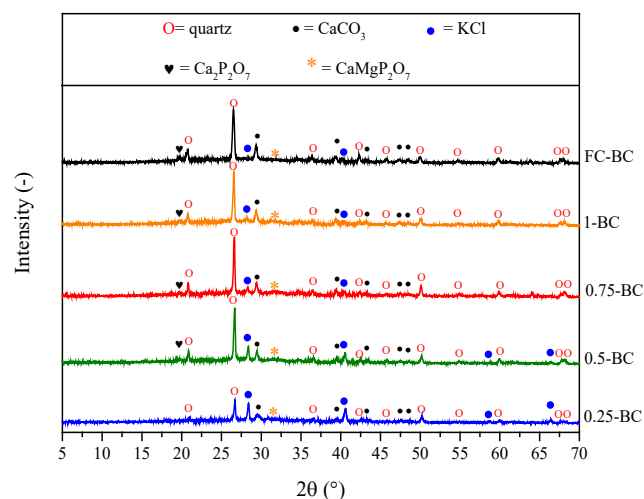
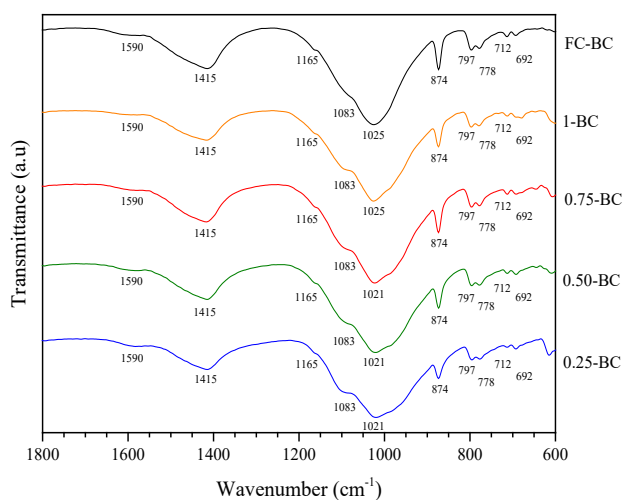
Characteristics	Filter cake	Vinasse
pH	7.7 ± 0.3	4.5 ± 0.1
Moisture content (%)	8.3 ± 0.8	83.1 ± 0.0
Ash content (%)	46.8 ± 1.0	26.4 ± 1.0
P ($\text{g}\cdot\text{kg}^{-1}$)	13.4 ± 0.5	4.9 ± 0.1
K ($\text{g}\cdot\text{kg}^{-1}$)	21.0 ± 1.5	80.0 ± 1.1
Ca ($\text{g}\cdot\text{kg}^{-1}$)	59.0 ± 6.7	45.6 ± 5.9
Mg ($\text{g}\cdot\text{kg}^{-1}$)	8.4 ± 0.6	25.1 ± 0.3

Table 2. Physicochemical properties of biochars prepared from different filter cake to vinasse ratios.

Samples	Characteristics		
	Yield (%)	pH (-)	Ash content (%)
0.25-BC	54.4±0.3	10.3±0.0	75.8±1.6
0.5-BC	56.0±0.3	9.9±0.0	79.7±0.6
0.75-BC	58.4±0.6	9.8±0.1	79.8±2.8
1-BC	58.6±0.4	9.5±0.3	81.3±0.3
FC-BC	59.4±0.4	8.2±0.0	84.7±1.0

Table 3. The total nutrient concentrations and nutrient recovery in the produced biochars.

Sample	Total P (g·kg ⁻¹)	P recovery (%)	Total K (g·kg ⁻¹)	K recovery (%)	Total Mg (g·kg ⁻¹)	Mg recovery (%)	Total Ca (g·kg ⁻¹)	Ca recovery (%)
0.25-BC	18.0±1.3	99.4±8.6	75.9±2.0	115.9±14.7	14.3±0.4	102.8±7.1	79.2±0.4	80.7±13.9
0.5-BC	19.1±0.5	95.7±4.9	56.0±0.9	130.2±16.3	12.3±0.2	108.9±7.2	78.7±1.9	79.5±13.8
0.75-BC	18.6±1.6	92.4±8.7	36.5±2.3	113.3±15.8	10.3±0.5	104.3±8.2	86.2±2.7	89.2±15.6
1-BC	18.4±2.0	89.1±10.5	30.0±1.9	111.7±15.6	9.5±1.2	101.7±14.1	86.7±4.1	89.2±15.9
FC-BC	21.0±1.9	93.0±9.1	7.9±0.8	107.2±17.1	7.2±0.5	100.5±7.4	106.3±1.5	107.0±12.3

**Figure 2.** XRD patterns of produced biochar at different filter cake to vinasse ratios. The following phases were identified: SiO₂ (quartz) (JCPDS No: 00-046-1045), CaCO₃ (calcite) (JCPDS No: 01-072-1652), KCl (sylvite) (JCPDS No: 01-075-0296), Ca₃P₂O₇ (JCPDS No: 00-033-0297), and CaMgP₂O₇ (JCPDS No: 00-024-0135).**Figure 3.** FTIR spectra of the biochars produced with different filter cake to vinasse ratios.

The FTIR spectra of the biochars at 1800 cm⁻¹ to 600 cm⁻¹ are shown in Figure 3. The high intensity peaks at 1021 cm⁻¹ to 1025 cm⁻¹ in all samples were assigned to C–O–C vibrations [28]. The peak at 1590 cm⁻¹ was ascribed to COOH [28]. The presence of C–O bonds was indicated at 1415 cm⁻¹ [29] and 1165 cm⁻¹ (C–O stretching) [29]. The peak at 1085 cm⁻¹ was related to OH– vibrations [29]. The sharp peak at 874 cm⁻¹ and 712 cm⁻¹ indicated the presence of carbonate [15,29], and the decrease of peak intensity of carbonate by the increase of filter cake and vinasse ratio was in accordance with the XRD result of CaCO₃ (Figure 2). The peaks at 797 cm⁻¹ and 778 cm⁻¹ were related to C–H [29] and the peak at 692 cm⁻¹ was ascribed to Si–O vibrations [25].

3.3 Total nutrient concentrations and nutrient recovery in biochars

Total nutrient concentrations and nutrient recovery in the biochars are provided in Table 3. After pyrolysis, the P concentrations have increased from 4.9 g·kg⁻¹ to 13.4 g·kg⁻¹ in the raw materials (Table 1) to 18.0 g·kg⁻¹ to 21.0 g·kg⁻¹ in the biochars, without any clear dependence on the raw material composition. The total K concentrations in the biochars, on the other hand, were highly dependent on the filter cake to vinasse ratios and ranged from 7.9 g·kg⁻¹ for FC-BC to 75.9 g·kg⁻¹ for 0.25-BC. Higher vinasse concentrations in the biomasses resulted in higher K concentrations because of the higher K content in vinasse compared to filter cake (Table 1). These results are in line with previous work that reported an increase in total K concentration from 27.5 g·kg⁻¹ in bagasse pith mix with vinasse 1:2 (w/w) to 45.0 g·kg⁻¹ in biochar after pyrolysis at 240°C [13]. Similarly, the Mg concentrations reduced with increasing filter cake to vinasse ratios, from 14.3 g·kg⁻¹ to 9.5 g·kg⁻¹ for 0.25-BC to 1-BC and 7.2 g·kg⁻¹ for FC-BC. The total Ca concentrations in the produced biochars, on the other hand, increased with the filter cake to vinasse ratios, from approximately 79 g·kg⁻¹ to 106.3 g·kg⁻¹ for FC-BC, and was ascribed to the higher Ca content in the filter cake compared to vinasse (Table 1). The recovery of each nutrient in the biochars was calculated based on the nutrient concentrations in the raw materials and biochars according to Equation (2). All four nutrients were largely recovered in the biochars, ranging from 89.1% to 99.4% for P, 107.2% to 130.2%

for K, 100.5% to 108.9% for Mg and 79.5% to 107.0% for Ca. The nutrients were retained in solid phase (biochar), which is in agreement with the study by Dirbeba *et al.* [11] who reported that approximately 85% of K from vinasse was retained in biochar after pyrolysis at 400°C and 500°C. Also Wang *et al.* [30] reported that P, K, Mg, and Ca were retained in biochars prepared by pyrolysis of swine manure at 300°C to 750°C. These results suggested that the recovery of P, K, Mg, and Ca in filter cake and vinasse was successful by pyrolysis.

3.4 Nutrient extraction in DI water and 2% formic acid

To assess the availability and potential nutrient leaching risk, the extractable nutrient concentrations were measured in DI water and 2% formic acid (Figure 4). The P extractability in water was low (0.02 g·kg⁻¹ to 0.12 g·kg⁻¹) and accounted for less than 1% of total P in the biochars (Figure 4(a)). The extractable P by 2% formic acid was significantly higher and ranged from 9.5 g·kg⁻¹ to 12.3 g·kg⁻¹ (53-75% of the total P). The 2% formic acid extraction has been proposed as an indicator for P availability to crops [17], and the high extractability in 2% formic acid may thus suggest that the P in the biochars is available to plants. At the same time, the low extractability in DI water indicates that the P has a low leaching risk [15,24,25]. The different amounts of extractable P by DI water and 2% formic acid could have occurred due to formation of low solubility compounds such as Ca₂P₂O₇ and CaMgP₂O₇, which were indicated to be present in XRD results (Figure 2).

The extractable K in DI water (Figure 4(b)) strongly decreased upon increasing the filter cake to vinasse ratio, from 60.9 g·kg⁻¹ (80.4% of total K) for 0.25-BC to 0.6 g·kg⁻¹ (7.6% of total K) for FC-BC. The same trend was seen in extractable K by 2% formic acid. The high

extractability in DI water in the vinasse-rich biochars was ascribed to the prominent presence of water-soluble KCl in the XRD patterns (Figure 2). Similar results were found in a previous study on biochar production from vinasse at 400°C to 500°C by fast pyrolysis, where it was concluded that all K in vinasse biochar was in KCl form which is available to plants [11]. The extractable K in 2% formic acid was >90% for the biochars prepared from the filter cake-vinasse mixtures but dropped to 35.8% in FC-BC. This may suggest that the K in the vinasse biochar is readily extractable, whereas the K in the filter cake biochar is present in a poorly extractable form.

The extractable Mg in DI water (Figure 4(c)) was in the range of 0.18 g·kg⁻¹ to 0.30 g·kg⁻¹ (1.3% to 1.9% from total Mg), indicating poor solubility and low leaching risk. The extractable Mg in 2% formic acid was higher at 4.6 g·kg⁻¹ to 8.7 g·kg⁻¹ and decreased as the filter cake and vinasse ratio was increased, which was mainly due to the lower Mg contents in the filter cake-rich biochars (Table 3). Normalized by the total Mg concentrations, the extractable Mg in 2% formic acid was 61% to 64% of the total Mg and with only slight dependency on raw material composition.

Similar to Mg, the extractable Ca in DI water was low (2.9 g·kg⁻¹ to 3.4 g·kg⁻¹, 2.6% to 3.7% of total Ca, Figure 4(d)). The extractable Ca in 2% formic acid was 65.8 g·kg⁻¹ to 79.0 g·kg⁻¹ (68.1% to 91.8% of total Ca) and did not show a clear dependence on the biochar composition. Based on the presence of Ca₂P₂O₇ and CaMgP₂O₇ in the XRD pattern (Figure 2) it seems likely that the Mg and Ca extractability in both extractants was partially controlled by binding of Mg and Ca to P. Furthermore, the low Ca extractability in DI water may be due to the formation of crystalline CaCO₃. The greater nutrients extractable (P, K, Mg, and Ca) in 2% formic acid than in DI water was also found in sewage sludge biochar at 700°C [31].

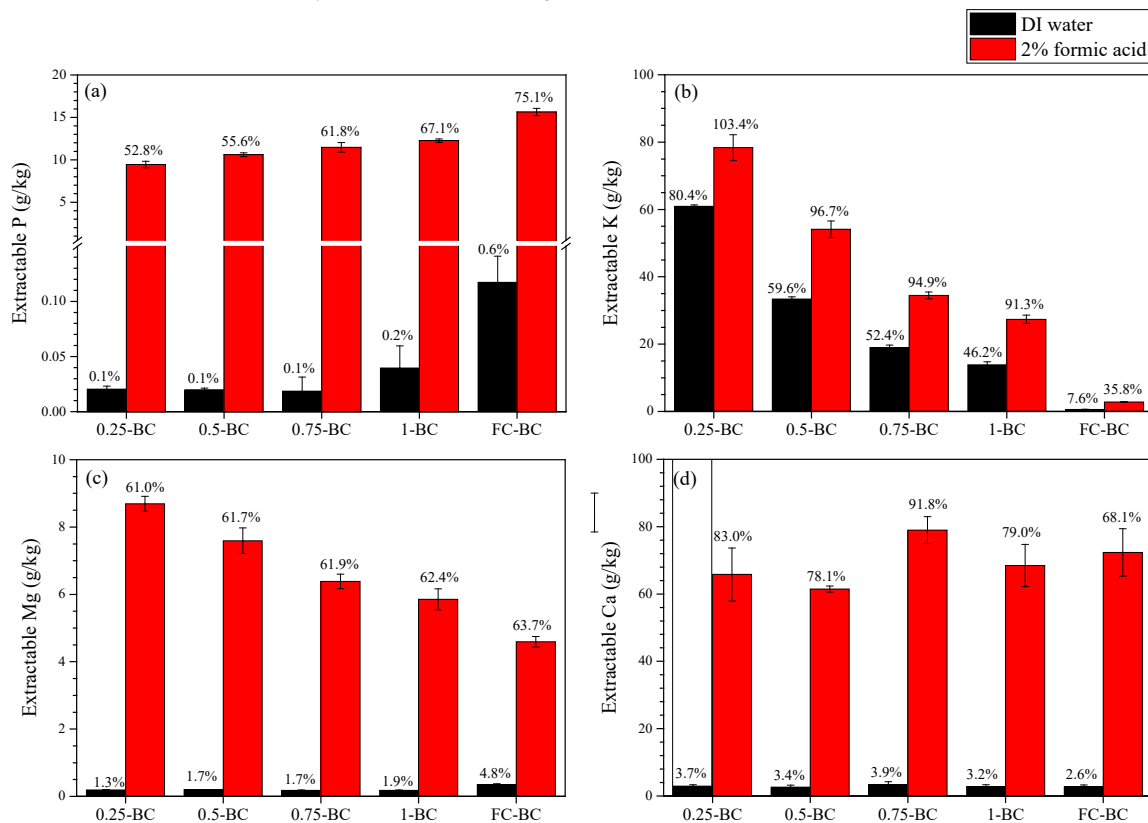


Figure 4. Extractability in DI water and 2% formic acid of a) phosphorus (P), b) potassium (K), c) magnesium (Mg), and d) calcium (Ca) from the biochars.

The nutrient extractability in water is directly related to its leaching risk because the quantity of each nutrient that dissolves in water can be readily lost through runoff (and move to surface waters) or into groundwater. However, solubility of a nutrient in water is also a prerequisite for plant uptake, since plant roots can only absorb dissolved nutrients. Plants, however, do not require their nutrients immediately upon application but rather throughout (specific periods of) the growth season that takes several weeks/months (depending on the crop). A slower nutrient release is thus preferential. Thus, by reducing the water solubility of a nutrient (which is done in our study through pyrolysis), its leaching risk is reduced, while the nutrients may still be absorbed by the crop. The availability of each nutrient is also highly dependent on a number of parameters such as crop species and soil properties, which should be confirmed in a plant trial.

4. Conclusions

Biochar prepared from vinasse and filter cake is a promising material to retain essential nutrients (P, K, Mg and Ca) as fertilizer or soil amendment. The total nutrient content of the prepared biochars strongly depended on the filter cake to vinasse ratio. The K content in the biochars was remarkably enhanced by the vinasse content, highlighting the importance of optimizing feedstock to target specific nutrient profiles. The potential phytoavailability of essential nutrients (P, K, Mg, and Ca) as indicated by their extractability using water and 2% formic acid suggested that pyrolysis efficiently retained these nutrients in an available form. The biochar prepared with a filter cake to vinasse ratio of 0.25 exhibited the highest total nutrient content (P, K, Mg, and Ca) and may prolong the runoff by water leaching. The valorization of vinasse and filter cake as biochar may reduce the cost of waste treatment in the sugar industry and provide a sustainable circular economy by applying the produced biochar on the sugarcane field. Future research should focus on optimization of pyrolysis conditions to maximize nutrient retention and biochar quality for fertilizer applications.

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References

- [1] USDA, "Sugar: World Markets and Trade 2023 / 24," Foreign Agric. Serv. <https://apps.fas.usda.gov/psdonline/circulars/sugar.pdf>, no. November, pp. 1-9, 2023, [Online]. Available: <https://fas.usda.gov/data/sugar-world-markets-and-trade>
- [2] R. D. M. Prado, G. Caione, and C. N. S. Campos, "Filter cake and vinasse as fertilizers contributing to conservation agriculture," *Applied and Environmental Soil Science*, vol. 2013, no. 1, p. 581984, 2013.
- [3] F. Santos, P. Eichler, G. Machado, J. De Mattia, and G. De Souza, *By-products of the sugarcane industry*. Elsevier Inc., 2019.
- [4] L. L. Campiteli, R. M. Santos, G. Lazarovits, and E. C. Rigobelo, "The impact of applications of sugar cane filter cake and vinasse on soil fertility factors in fields having four different crop rotations practices in Brazil," *Cientifica*, vol. 46, no. 1, pp. 42-48, 2018.
- [5] C. A. Melo, F. H. S. Junior, M. C. Bisinoti, A. B. Moreira, and O. P. Ferreira, "Transforming sugarcane bagasse and vinasse wastes into hydrochar in the presence of phosphoric acid: An evaluation of nutrient contents and structural properties," *Waste and Biomass Valorization*, vol. 8, no. 4, pp. 1139-1151, 2017.
- [6] E. Arslanoğlu, M. Ş. A. Eren, H. Arslanoğlu, and H. Çiftçi, "Fabrication, characterization, and adsorption applications of low-cost hybride activated carbons from peanut shell-vinasse mixtures by one-step pyrolysis," *Biomass Convers. Biorefinery*, vol. 13, no. 3, pp. 2321-2335, 2023.
- [7] T. F. Abbruzzini, M. D. Oliveira Zenero, P. A. M. de Andrade, F. Dini Andreote, J. Campo, and C. E. Pellegrino Cerri, "Effects of biochar on the emissions of greenhouse gases from sugarcane residues applied to soils," *The Journal of Agricultural Science*, vol. 08, no. 09, pp. 869-886, 2017.
- [8] M. J. Dirbeba, A. Brink, N. DeMartini, D. Lindberg, and M. Hupa, "Sugarcane vinasse CO₂ gasification and release of ash-forming matters in CO₂ and N₂ atmospheres," *Bioresource Technology*, vol. 218, pp. 606-614, 2016.
- [9] D. R. Da Silva, M. S. Crespi, P. C. G. M. Crnkovic, and C. A. Ribeiro, "Pyrolysis, combustion and oxy-combustion studies of sugarcane industry wastes and its blends," *Journal of Thermal Analysis and Calorimetry*, vol. 121, no. 1, pp. 309-318, 2015.
- [10] R. Chatterjee, B. Sajjadi, W. Y. Chen, D. L. Mattern, N. Hammer, V. Raman, and A. Dorris, "Effect of pyrolysis temperature on physicochemical properties and acoustic-based amination of biochar for efficient CO₂ adsorption," *Frontiers in Energy Research*, vol. 8, p. 85, 2020.
- [11] M. J. Dirbeba, A. Aho, N. Demartini, A. Brink, I. Mattsson, L. Hupa, and M. Hupa, "Fast pyrolysis of dried sugar cane vinasse at 400 and 500°C: Product distribution and yield," *Energy and Fuels*, vol. 33, no. 2, pp. 1236-1247, 2019.
- [12] N. Kamali, A. RashidiMehrabadi, M. Mirabi, and M. A. Zahed, "Synthesis of vinasse-dolomite nanocomposite biochar via a novel developed functionalization method to recover phosphate as a potential fertilizer substitute" *Frontiers of Environmental Science & Engineering*, vol. 14, no. 4, p. 70, 2020.
- [13] A. E. E. A. Z. Amin, "Bagasse pith-vinasse biochar effects on carbon emission and nutrient release in calcareous sandy soil," *Journal of Soil Science and Plant Nutrition*, vol. 20, no. 1, pp. 220-231, 2020.
- [14] F. N. Türk and H. Arslanoğlu, "Recovery of potassium from pyrolysis product of sugar fabrication waste carbonation cake and vinasse mixture and production of adsorbent for wastewater treatment," *Journal Sugar Tech*, vol. 26, no. 2, pp. 478-488, 2024.
- [15] S. Suwanree, J. T. N. Knijnenburg, P. Kasemsiri, W. Kraithong, P. Chindaprasirt, and K. Jetsrisuparb, "Engineered biochar from sugarcane leaves with slow phosphorus release kinetics," *Biomass and Bioenergy*, vol. 156, no. March 2021, p. 106304, 2022.
- [16] S. Suwanree, K. Jetsrisuparb, P. Kasemsiri, P. Tharamas, H. Uyama, S. Kuboon, and J. T. N. Knijnenburg, "Influence of

- magnesium content and phosphoric acid treatment on cadmium adsorption onto sugarcane leaf biochar,” *Research on Chemical Intermediates*, vol. 50, no. 8, pp. 3981-4001, 2024.
- [17] T. Wang, M. Camps-Arbestain, M. Hedley, and P. Bishop, “Predicting phosphorus bioavailability from high-ash biochars,” *Plant and Soil*, vol. 357, no. 1, pp. 173-187, 2012.
- [18] K. Sun, M. Qiu, L. Han, J. Jin, Z. Wang, Z. Pan, and B. Xing, “Speciation of phosphorus in plant- and manure-derived biochars and its dissolution under various aqueous conditions,” *Science of the Total Environment*, vol. 634, pp. 1300-1307, 2018.
- [19] S. Meunchang, S. Panichsakpatana, and R. W. Weaver, “Co-composting of filter cake and bagasse; by-products from a sugar mill,” *Bioresource Technology*, vol. 96, no. 4, pp. 437-442, 2005.
- [20] L. A. G. de Godoi, P. R. Camiloti, A. N. Bernardes, B. L. S. Sanchez, A. P. R. Torres, A. da C. Gomes, and L. S. Botta, “Seasonal variation of the organic and inorganic composition of sugarcane vinasse : Main implications for its environmental uses generating as byproduct a viscous phase called molasses,” *Environmental Science and Pollution Research*, vol. 26, pp. 29267-29282, 2019.
- [21] J. S. Devia-Orjuela, C. E. Alvarez-Pugliese, D. Donneys-Victoria, N. M. Cabrales, L. E. B. Ho, B. Brém, A. Sauciuc, E. Gál, D. Espin, M. Schichtel, D. Lang, S. Giardinelli, and M. Briceno, “Evaluation of press mud, vinasse powder and extraction sludge with ethanol in a pyrolysis process,” *Energies*, vol. 12, no. 21, pp. 1-21, 2019.
- [22] H. M. Tun, H. Myat, T. Swe, N. Wah, and P. S. Win, “Software development of distributed control system-based sugar mill using visual studio. net,” *ITS*, vol. 5, no. 2, pp. 2617-4537, 2021.
- [23] D. R. da Silva, M. S. Crespi, C. A. Ribeiro, and J. M. V. Capela, “Thermal decomposition kinetics of sugarcane mills wastes,” *Journal of Thermal Analysis and Calorimetry*, vol. 131, no. 1, pp. 811-822, 2018.
- [24] K. Jetsrisuparb, T. Jeejaila, C. Saengthip, P. Kasemsiri, Y. Ngernyen, P. Chindaprasirt, and J. T. N. Knijnenburg, “Tailoring the phosphorus release from biochar-based fertilizers: role of magnesium or calcium addition during co-pyrolysis,” *RSC Advances*, vol. 12, no. 47, pp. 30539-30548, 2022.
- [25] J. T. N. Knijnenburg, P. Kasemsiri, W. Kaewpradit, T. Tarinta, W. Jantapa, T. Jeejaila, C. Saengthip, and K. Jetsrisuparb, “Co-pyrolysis of biomass with magnesium and phosphorus: Effect of magnesium content on phosphate release from biochar-based fertilizers,” *Biomass Conversion and Biorefinery*, vol. 14, no. 14, pp. 15351-15361, 2024.
- [26] M. J. Buer Boyetey, S. Torgbo, P. Sukyai, N. Watthanasakphuban, and N. Kamonsutthipajit, “Filter cake-derived calcium carbonate polymorphs from sugar refinery for hydroxyapatite production as a sustainable material for biomedical application,” *Ceramics International*, vol. 49, no. 14, pp. 23417-23425, 2023.
- [27] M. J. Dirbeba, A. Brink, M. Zevenhoven, N. Demartini, D. Lindberg, L. Hupa, and M. Hupa, “Characterization of vinasse for thermochemical conversion - fuel fractionation, release of inorganics, and ash-melting behavior,” *Energy and Fuels*, vol. 33, no. 7, pp. 5840-5848, 2019.
- [28] T. K. Choudhary, K. S. Khan, Q. Hussain, M. Ahmad, and M. Ashfaq, “Feedstock-induced changes in composition and stability of biochar derived from different agricultural wastes,” *The Arabian Journal of Geosciences*, vol. 12, no. 20, 2019.
- [29] G. Bekiaris, C. Peltre, L. S. Jensen, and S. Bruun, “Using FTIR-photoacoustic spectroscopy for phosphorus speciation analysis of biochars,” *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, vol. 168, pp. 29-36, 2016.
- [30] K. Wang, N. Peng, G. Lu, and Z. Dang, “Effects of pyrolysis temperature and holding time on physicochemical properties of swine-manure-derived biochar,” *Waste and Biomass Valorization*, vol. 11, no. 2, pp. 613-624, 2020.
- [31] W. Buss, A. Bogush, K. Ignatyev, and O. Mašek, “Unlocking the fertilizer potential of waste-derived biochar,” *ACS Sustainable Chemistry & Engineering*, vol. 8, no. 32, pp. 12295-12303, 2020.