Applied Environmental Science and Engineering for a Sustainable Future

Zainul Akmar Zakaria
Cristobal N Aguilar
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Valorisation of Agro-industrial Residues – Volume II: Non-Biological Approaches

Springer

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Chapter 10
Valorization of Sugarcane-Based Bioethanol Industry Waste (Vinasse) to Organic Fertilizer

Ratna Dewi Kusumaningtyas, Dhoni Hartanto, Hasan Abdul Rohman, Mitamaytawati, Nur Qudus, and Daniyanto

Abstract Indonesia is among the top ten sugarcane-producing countries in the world. Among the important sugarcane-based industry is bioethanol production. Bioethanol is recently experiencing significant growth due to the increase in need of renewable energy. However, this industry faces a challenge since it produces a huge amount of liquid waste, namely vinasse. The production of 1 L of bioethanol generates 12 L of vinasse. Vinasse is pollutant due to its high value of chemical oxygen demand (COD) and biological oxygen demand (BOD), high salt content, unpleasant odor, high acidity, and dark color. Therefore, it should be treated before releasing to the environment. However, pretreatment of vinasse is not economical. The more feasible way to handle vinasse is shifting it into valuable product. Vinasse contains nutrients which are necessary for improving soil fertility and useful for plant fertilization. There are some methods to convert vinasse to organic fertilizer. This chapter shows one case study of formulating vinasse with filter cake of sugar factory, and agricultural wastes to produce liquid organic fertilizer (LOF). LOF was synthesized via anaerobic fermentation of vinasse in the presence of promoting microbes and formulation of fermented vinasse with filter cake, lead tree leaves, and banana peel to produce LOF. The LOFs were characterized to determine the values of organic C, C/N ratio, and the contents of N, P, and K elements. LOFs were applied on the tomato plant to enhance plant growth. The more advanced process of vinasse valorization is converting it into slow release solid organo-mineral fertilizer (SR-OMF).

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Keywords Vinasse · Filter cake · Organic fertilizer · Tomato plant · Slow release organo-mineral fertilizer

10.1 Introduction

Indonesia is among the major sugarcane producing countries in the world. In Indonesia, sugarcane (*Saccharum officinarum*) is mostly utilized as raw material in sugar industry. There are 62 sugar industries for sugarcane, and 10 refined sugar industries. In Manufacture Year 2017/2018, Indonesian white sugar production increased to 2.2 MMT, while sugarcane production was stable at 28.0 MMT (Wright and Meylinah 2014). Among the major residues of sugar refinery is filter cake and molasses. Filter cake is a waste of sugarcane juice filtration, which contains organic compounds and phosphorus. Hence, this waste is potential to be converted into fertilizer (Prado et al. 2013). On the other hand, molasses is usually used for the production of ethanol (Obono et al. 2016). Sugarcane ethanol is a well-established industry and it is recently experiencing significant growth due to the increase in need of renewable energy. However, this industry faces a challenge since it produces a huge amount of liquid waste, namely vinasse.

Vinasse is the bottom effluent of distillation column in sugarcane ethanol purification process. The production of 1 L of ethanol from sugarcane generates up to 12 L of vinasse (Cassman et al. 2018). Vinasse is pollutant to the environment due to its high value of Chemical Oxygen Demand (COD) up to 140 g/L, high value of Biological Oxygen Demand (BOD), high salt content, strong unpleasant odor, very high acidity (pH 3.5–5), and heavy dark color (Hoarau et al. 2018). Therefore, it should be treated before releasing to the environment, or otherwise it will pollute surface and groundwater, as well as harm aquatic biota. However, pretreatment process of vinasse waste prior to its disposal is not economical since it is produced abundantly. The more feasible way to handle vinasse is shifting this liquid waste into valuable product.

Despite its polluting characteristic, vinasse contains nutrients which is necessary for improving soil fertility, such as nitrogen (up to 4.2 g/L), phosphorus (up to 3.0 g/L), or potassium (up to 17.5 g/L) as reported by Hoarau et al. (2018). Vinasse also comprises magnesium, calcium, and organic matters (organic acids, amino acids, sugars, polysaccharides, and proteins) which are useful for plant fertilization. This feature demonstrates that valorization of vinasse to organic fertilizer is prospective. Application of vinasse for organic fertilizer of several types of plants (sugarcane, corn, tomato, watermelon) has been studied previously.

There are some methods of applying vinasse as organic fertilizer, such as fertigation or direct application of untreated vinasse to the soil (Jiang et al. 2012), application of concentrated vinasse (Lourenço et al. 2019), formulation of vinasse-based organo-mineral fertilizer (Kusumaningtyas et al. 2017). Fertigation is simple and easy to apply. However, the direct application of unprocessed vinasse to the land shows several drawbacks to the environment, such as the increasing salt level in the soil, groundwater pollution, and greenhouse gas emissions. Besides that, untreated vinasse contains high amount of water. Thus, fertilization needs large volume of untreated vinasse. This condition causes costly expense of vinasse transportation (Bettani et al. 2019). To overcome this obstacle, vinasse is concentrated through vaporization before being applied as organic fertilizer. This is the efficient way to lessen the volume of vinasse in order to decrease transportation cost without losing its nutrients (Lourenço et al. 2019). However, in some countries, characteristic of solitary concentrated vinasse fertilizer does not fulfill the national standard parameter of organic fertilizer properties, such as nitrogen (N), phosphorus (P), and potassium (K) contents, as well as C/N (carbon/nitrogen) ratio value. Hence, concentrated vinasse should be combined with other material to improve its characteristic as organic fertilizer. In the previous work, concentrated vinasse was blended with 3, 6, and 9% commercial NPK fertilizer to produce vinasse-based organo-mineral fertilizer (OMF). OMF was successfully employed for improving the growth of tomato and watermelon plant.

In this work, vinasse was combined with other sugar industry waste (filter cake) and agricultural wastes to produce liquid organic fertilizer (LOF) through microbiological process. Microbiological process was applied to help the decomposition of solid organic matters and transform them into organic fertilizers which are useful for improving soil fertility and plant productivity. Filter cake and agricultural wastes (lead tree leaves and banana peel) were added in formulation to enhance the quality of vinasse-based fertilizer. Filter cake is a good source of phosphorus. Phosphorus is important for supporting photosynthesis process and stomatal conductance, as well as promoting root growth (Vasconcelos et al. 2017). The improved stomatal conductance is essential for increasing transpiration rates. On the other hand, the optimum growth of root will enhance the root exploration capability, leading to increased water absorption.

Lead tree (*Leucaena leucocephala*) is a plant that is widely grown in Indonesia and commonly used for greening purpose. This plant produces lots of leaves, but this plant leaves have not been optimally utilized. In fact, lead tree leaves contain high nitrogen, phosphorus, potassium, carbon, and oxygen elements, which are necessary for supporting plant growth. ter Meulen et al. (1979) reported that lead tree leaves (LTL) contain 19.0 g/kg calcium, 2.16 g/kg phosphorus, and 17.0 g/kg potassium. It was also described that fermented LTL can be applied as liquid organic fertilizer (ter Meulen et al. 1979). The other agricultural waste employed for LOF formulation in this work was banana peels. Banana peel is potential to be used for organic fertilizer since it contains nutrients for plant. Kalemelawa (2012) stated that solid organic fertilizer made of banana peel was a potential source of K and N (Kalemelawa et al. 2012).

10.2 Vinasse

The bioethanol industry is growing because people are focusing on finding renewable energy sources. The most developed bioethanol industry in Indonesia is molasses-based bioethanol. Molasses is sugar syrup which does not crystallize after the crystallization process. Molasses which is usually reddish brown is a by-product of the sugar industry which still contains sucrose. Although there are other raw materials, generally bioethanol manufacturers prefer using molasses because molasses is cheaper and easier to obtain, the process of making molasses-based bioethanol is simpler, it contains high sucrose and nitrogen, phosphorus, sulfur, minerals, and vitamins required by yeast. However, the molasses-based bioethanol industry creates a problem of producing liquid waste called vinasse in very large quantities and it is polluting the environment.

Vinasse is the liquid waste resulting from the bottom product of distillation in the maisch column during the production of bioethanol from molasses. Vinasse contains a chemical compound that causes Chemical Oxygen Demand (COD) to increase more than 50,000 ppm and Biological Oxygen Demand (BOD) to increase more than 30,000 ppm. This waste cannot be directly discharged into the water environment or river, because it will eliminate the dissolved oxygen in it which ultimately damages the ecosystem of the biota. The main impacts caused by vinasse waste in soil and groundwater resources are salinity and increased concentrations of nitrates, nitrite, ammonia, magnesium, phosphate, aluminum, iron, manganese, chloride, and organic carbon. Metal mobilization/dissolution such as iron, copper, cadmium, chromium, cobalt, nickel, tin, and zinc can occur, as well as changes in pH in soil and ground water. The bioethanol plant produces vinasse as its liquid waste of 12 times more than the volume of bioethanol production (Leme and Seabra 2016). The characteristics of vinasse waste can be seen in Table 10.1.

Vinasse waste has high organic matter and low acidity with pH around 3.9–4.3 (Parnaudeau et al. 2008). The problem caused by the low acidity of vinasse waste is the difficulty of nutrient adsorption by plants. Nutrients can be easily absorbed by plants at pH 6–7, because at that level of acidity, most nutrients can dissolve easily in water. The level of pH in the soil also indicates the presence of toxic substances for plants. Al (aluminum) elements are found in acid soil which can both poison plants

Table 10.1 Characteristics of vinasse

Character	Information
Debit	±480 m^3 per day
pH	3.9–4.3
Suspended residue	High
NH_3	200 ppm
BOD, 20 °C	Very high
COD	Very high
Color	Dark brown to black

Source: Madubaru (2008)

Fig. 10.1 Untreated vinasse

and bind phosphorus which causes plants to be unable to absorb it. In addition to acidic soil, too many microelements can poison plants. As for alkaline soil, there are many elements of Na (Sodium) and Mo (Molybdenum). The condition of soil acidity also determines the development of microorganisms in the soil. Mushrooms and organic matter-decomposing bacteria can grow well in the environment with pH 5.5–7. In addition, microorganisms which are beneficial to roots of plant can also develop well (Gyaneshwar et al. 2002). Vinasse waste also has a reddish brown color and is malodorous (Fig. 10.1). One of the negative effects of vinasse waste on rice plants is that it causes the color of the grains of rice to become brownish and malodourous, making rice less suitable for consumption. One of the efforts to handle vinasse waste is by using vinasse as organic fertilizer. Vinasse has macro- and micronutrients including N, P, K, Ca, Mg, Fe, Mn, Zn, and Cu which are useful and required for plant to grow (Madubaru 2008). Vinasse has been used as solid organo-mineral fertilizer (Kusumaningtyas et al. 2017). Vinasse can also be processed into liquid organic fertilizer through fermentation and non-fermentation process.

The production of organic fertilizer through fermentation process is usually conducted in the presence of Promi (Promoting Microbes). Promi is active microbes that can stimulate the plant growth. Microbes in promi involve three types of microbes, namely *Aspergillus* sp., *Trichoderma harzianum* DT 38, *Trichoderma harzianum* DT 39, and microbial weathering. *Aspergillus* sp. has an ability to solve phosphate from the insoluble sources. *Trichoderma harzianum* DT 38 has a role in stimulating plant growth. Furthermore, *Trichoderma harzianum* DT 39 is a natural agent to resist infectious soil diseases.

10.3 Organic Fertilizer

Organic fertilizers are plant fertilizers that originate from organic sources, such as animal and plant matters, human excreta, manure, etc. It commonly contains various important nutrients needed by plants, both macro and micro. The macroelements required by plants include nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg). Furthermore, microelements are iron (Fe), copper (Cu), zinc (Zn), chlorine (CI), boron (B), molybdenum (Mo), and aluminum (AI) (Chang et al. 2007). Vinasse waste, which is derived from agro-industrial process, is among the potential feedstock for composing organic fertilizer. To improve its properties as organic fertilizer, vinasse can be combined with other organic fertilizer sources, for example filter cake and agricultural wastes.

Filter cake is one of the wastes produced by sugar mills in the process of manufacturing sugar. This waste comes out of the process in solid form containing water, still has high temperature, and in the form of soil. The filter cake is actually sugarcane fiber mixed with dirt and separated from the sap. The filter cake composition consists of coir, wax and crude fat, crude protein, sugar, total ash, SiO_2, CaO, P_2O_5, and MgO. The composition of the filter cake has different percentage of content from one sugar mill to another, depending on the production pattern and origin of the sugarcane (Prado et al. 2013).

The filter cake is generally used as an organic fertilizer. The filter cake of some sugar mills are recycled as fertilizer, which is then used for fertilizing sugarcane in sugarcane plantation areas. The process of using organic fertilizer is not complicated. The fertilizer undergoes drying process for a few weeks/months for aeration in an open area. The drying process is aimed to reduce the temperature and the excessive content of nitrogen in the filter cake. By continuing to use inorganic fertilizers as a starter, the use of filter cake organic fertilizer can still be accepted by the community (Prado et al. 2013). The filter cake can be used directly as fertilizer, because it contains nutrients required by the soil. To enrich the N element, it is composted with bagasse and kettle ash. Administering 100 tons of filter cake or its compost per hectare to sugarcane can significantly increase the weight and yield of sugarcane. Besides, combining filter cake with vinasse to produce organic fertilizer is considered attractive as well.

Beside filter cake, the other potential organic substance which can be formulated with vinasse to prepare organic fertilizer is agricultural wastes. As an agricultural country, Indonesia has various and abundant sources of organic fertilizer from crops, among the others are banana peels and lead tree (*Leucaena leucocephala*) leaves. Bananas and banana peels are rich in minerals such as potassium, magnesium, phosphorus, chloride, and iron. The contents of banana peel can be seen from Table 10.2.

Lead tree leaves are widely available in Indonesia and are used for reforestation. This plant contains high levels of nutrients required by plants. Lead tree leaves contain 19.0 g/kg calcium, 2.16 g/kg phosphorus, and 17.0 g/kg potassium (ter Meulen et al. 1979). According to Kang (1981), the organic fertilizer in the form of lead tree leaves can improve soil fertility and affect the growth of plants (Kang et al. 1981).

Table 10.2 Mineral and nutrient contents in banana peel

Mineral and nutrient contents of banana peel	Total
Water (%)	68.90
Carbohydrates (%)	18.50
Fat (%)	2.11
Protein (%)	0.32
Potassium (mg/100 g)	71.5
Phosphorus (mg/100 g)	11.7
Iron (mg/100 g)	1.6
Vitamins:	
B (mg/100 g)	0.12
C (mg/100 g)	17.5

Source: Essien (2005)

10.4 Case Study: Formulation of Vinasse, Filter Cake, and Agricultural Wastes to Liquid Organic Fertilizer

One case study of vinasse valorization is the formulation of vinasse, filter cake, and local agricultural wastes (banana peels and lead tree leaves) to produce liquid organic fertilizer (LOF). In this case, vinasse was obtained from Micro, Small, and Medium Enterprises (MSME) of bioethanol production in Sukoharjo, Central Java, Indonesia. Meanwhile the filter cake was supplied by PT Madubaru Sugar Factory, Yogyakarta, Indonesia.

10.4.1 Methods

The main raw materials of the process were vinasse, filter cake (FC), banana peels (BP), and lead tree leaves (LTL). The raw materials were formulated with and without fermentation process. The fermentation was performed in the presence of promoting microbes (promi). The formulations were conducted at various compositions of feedstocks and operation condition, as shown in Table 10.3.

The conversion of vinasse into LOF was conducted through the following procedure. Vinasse (100 mL) was prepared in the beaker glass. The acidity (pH) of vinasse was adjusted by the addition of 40% NaOH solution until it reached pH 7 (neutral). Subsequently, vinasse was evaporated at the temperature of 100 °C for 1 h to remove the water and volatile compounds content until the volume of vinasse reached 80 mL (Kusumaningtyas et al. 2017). After being cooled, vinasse was then mixed with the other feedstocks as depicted in Table 10.3. Promi as much as 2 g was added for the fermentation process. The fermentation was conducted as set in Table 10.1 and in the anaerobic condition. The LOFs resulted from this process were then characterized to determine the values of N, P, and K contents, organic C content, and C/N ratio. The values were compared to the Indonesian Standard quality

Table 10.3 Formulation of liquid organic fertilizer (LOF) from vinasse

Types of LOF	Composition of raw materials				Texture	Length of fermentation, days
	V, mL	FC, g	BP, g	LTL, g		
LOF 1	100	–	–	–	Smooth	–
LOF 2	100	–	–	–	Smooth	7
LOF 3	100	12	6	12	Rough	7
LOF 4	100	12	6	12	Rough	14
LOF 5	100	12	6	12	Smooth	7
LOF 6	100	–	30	–	Smooth	7
LOF 7	100	–	–	30	Smooth	7
LOF 8	100	30	–	–	Smooth	7
LOF 9	Blending of LOF 6 + LOF 7 + LOF 8					–

Table 10.4 Indonesian Standard Quality of organic fertilizer (SNI 19-7030-2004)

No	Parameter	Unit	Minimum	Maximum
1	Water content	%	–	50
2	Temperature	°C	–	Water temperature
3	Color		–	Black brownish
4	pH		6.8	7.49
5	Impurities	%	–	1.5
	Macro element			
6	Organic compounds	%	27	58
7	Nitrogen	%	0.40	–
8	Organic C (carbon)	%	9.80	31
9	Phosphorus	%	0.10	–
10	C/N—Ratio	%	10	20
11	Kalium	%	0.20	–

of organic fertilizer (Table 10.4) in terms of the tested parameters. Next, the LOFs were applied to fertilize the tomato plant.

To examine the effectiveness of LOFs in fertilizing tomato plant, firstly, 22 pots were filled with soil and prepared as plant growing media. Seeding of tomato plant seedlings were carried out on the growing media. After 14 days, 15 mL each type of LOF was added on two pots of tomato plants for the first time. It was called as Period 1 of Fertilization. The next fertilizing periods were conducted every 10 days until it reached the sixth period of fertilization (60 days after the first period of fertilization). On each period, the growth of tomato plants was observed in terms of the height of tomato plant, diameter of stem, number of the leaves, first time of flowering, first time of fruiting, as well as the number and diameter of fruit on the last period of fertilization. An identical procedure was also performed for the tomato plant fertilized by commercial NPK fertilizer and the plant without fertilization for comparison.

10.4.2 Characterization of Liquid Organic Fertilizers (LOFs)

The physical properties of LOFs in terms of main N, P, and K contents, organic C content, and C/N ratio are demonstrated in Table 10.5.

Production of liquid organic fertilizer (LOF) can be conducted with or without fermentation. However, anaerobic fermentation in the presence of promi could accelerate the formation of fertilizer and enhance the quality of LOF (Pangnakorn et al. 2009). In the anaerobic vinasse fermentation, specific gasses, i.e., methane (CH_4) and carbon dioxide (CO_2), were released (Sydney and Sydney 2013).

The first experiment was the preparation of LOF without fermentation process (LOF 1). In this case, the solely vinasse was simply treated with 40% NaOH solution to adjust the pH and evaporated to reduce the water content. It was found that LOF 1 has fulfilled the standard parameter of N, P, K, organic C, and C/N ratio. However, when the anaerobic fermentation process was carried out on the vinasse (LOF 2) for 7 days, the NPK and organic C content were significantly improved as it is presented in Table 10.5. Besides, the C/N ratio also increased. C/N ratio is among the important parameters to control the quality of organic fertilizer (Chanyasak and Kubota 1981).

To enhance the properties of organic fertilizer, especially the content of NPK and organic C, vinasse was combined with filter cake (FC) and agricultural wastes, i.e., banana peel (BP) and lead tree leaves (LTL), with the specific formulation of LOF 3, LOF 4, and LOF 4 as depicted in Table 10.3. In LOF 3, agricultural wastes were blended with the other feedstocks in a rough texture and fermented for 7 days. A similar composition was also applied for LOF 4, but it was fermented for a longer period (14 days). It was revealed that the simultaneous blend of vinasse with FC, BP, and LTL could not provide a higher NPK and organic C content compared to the pure vinasse and fermented vinasse fertilizer (LOF 1 and LOF 2). Moreover, the C/N ratio value of LOF 3 and LOF 4 are too high (excess carbon). If the C/N ratio is too high, the decomposition will slow down. It was also found that the longer fermentation time than 7 days did not improve the quality of LOF. Hence, 7 days of fermentation is considered efficient.

Table 10.5 Properties of various types of liquid organic fertilizer (LOF)

No	Types of LOF	NPK content, %			Organic C content, %	C/N ratio
		N	P	K		
1	LOF 1	0.63	0.42	0.38	12.35	19.60
2	LOF 2	0.68	0.48	0.43	14.20	20.88
3	LOF 3	0.65	0.46	0.36	13.30	21.45
4	LOF 4	0.59	0.56	0.29	13.13	22.55
5	LOF 5	0.56	0.52	0.35	12.63	22.55
6	LOF 6	0.68	0.63	0.61	13.25	19.48
7	LOF 7	0.71	0.54	0.59	12.30	17.32
8	LOF 8	0.66	0.56	0.59	12.90	19.55
9	LOF 9	0.75	0.67	0.70	14.28	19.05

To examine the effect of agricultural wastes texture, the identical formulation of vinasse, FC, BP, and LTL was blended together, but the agricultural wastes were added in a smooth texture (LOF 5). The smooth form of material was expected to result in a more homogeneous mixture. The mixture was then fermented for 7 days. However, the changing of the texture yet did not enhance the NPK content. The value of C/N ratio was also higher than the Indonesian National Standard of organic fertilizer product.

To explore the better quality of organic fertilizer, vinasse was mixed with the BP, LTL, and FC separately as demonstrated in the LOF 6, LOF 7, and LOF 8 formulation, respectively (Table 10.3). Each mixture was fermented for 7 days. It was shown that a single blending of vinasse with BP, TLT, and FC resulted in the significant improvement of NPK and organic C contents. The value of C/N ratio also met the Indonesian standard of organic fertilizer. However, the best enhancement was given by blending LOF 6, LOF 7, and LOF 8 with ratio of 1:1:1 to obtain LOF 9. LOF 9 demonstrated the highest NPK and organic C content. The C/N ratio of LOF 9 satisfied the standard as well. Among all the types of LOF, LOF 9 has shown the best properties in terms of NPK content, C organic content, and C/N ratio. To investigate the effectiveness of vinasse-based organic fertilizer, all types of LOFs were applied for fertilizing tomato plant.

10.4.3 Application of Liquid Organic Fertilizers (LOFs) on Tomato Plants

LOFs produced in this work were applied to tomato plants. The effects of fertilization using LOFs on the tomato plants in terms of the height of tomato plant, diameter of stem, number of the leaves, first time of flowering, first time of fruiting, as well as the number and diameter of fruit on the last period of fertilization were observed. Tomato plant is selected as the medium for applying LOFs because tomato plant has a fast growth period. LOFs were primarily applied to the tomato plants which were approximately 14 days old. At this age, tomato plants already had complete growth organs. The fertilizing period was conducted every 10 days with the LOFs dose of 15 mL. There were totally six periods of fertilization during this observation, meaning that the observation was conducted for 60 days. As control, observation was also performed for the plants fertilized by commercial NPK fertilizer and plants without fertilization.

Plant height is an important parameter in plant ecological aspect. It is generally related to the life span, seed mass, and time to maturity, and is an essential factor of plant's capability to struggle for light (Moles et al. 2009). The height of tomato plants fertilized by LOFs, commercial NPK fertilizer, and without fertilization for each period of fertilization is shown in Fig. 10.2. It was disclosed that all types of LOFs provide the higher stem height of tomato plants. However, LOF 9 has shown the best enhancement on the stem height growth compared to that of the other types

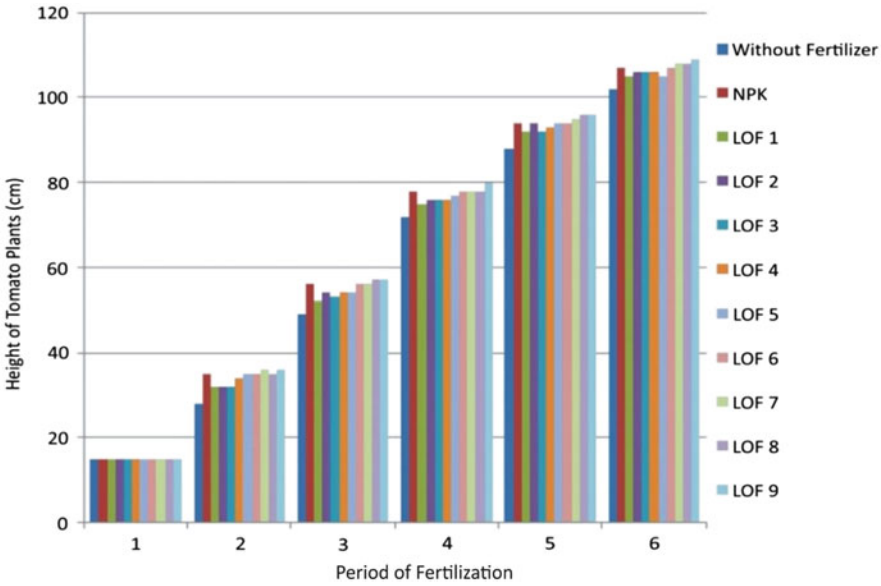

Fig. 10.2 The effect of LOFs fertilization on the height of tomato plants for each period of fertilization

of LOFs and commercial NPK fertilizer. It is due to the fact that LOF 9 contained higher organic C, N, P, and K elements than the other types of LOFs. Meanwhile, commercial NPK fertilizer has high element of N, P, K, but it does not contain organic C. Tomato plant needs nutrients such as N, P, K, and C for growing, flowering, and fruiting.

Organic C has an important function to support the photosynthesis process (Xu et al. 2015). C element can be absorbed by the plant from the air (CO_2) or from the soil (HCO_3^-). Deficiency of C element could interrupt photosynthesis process. On the other hand, the N element is important as the precursor of protein in the plant. It is also essential in the chlorophyll formation. Thus, N has a vital role to create the green color of the plant's organs. Besides, N element has a function to enhance the plant's growth, such as the growth of stem, branch, and leaves, and improve the quality of the plant (Dobermann and Fairhurst 2001). N element is absorbed by the plant in the form of NH_4^+ or NO_3^-. The lack of nitrogen brings about the symptoms of slow or dwarf growth, withering of plants, and the lack of chlorophyll, which cause the old leaves to quickly turn into yellow and die.

The effect of tomato plant fertilizing using LOFs on the growth of stem diameter is shown in Fig. 10.3. It was revealed that the addition of fertilizer increased the rate of stem growth. However, the best rate of stem growth was provided by the fertilization using NPK and LOF 9. It is not surprising since NPK and LOF 9 comprised the highest content of N, P, and K elements. In addition, LOF 9 contained the highest substance of C, compared to the other types of LOFs. Beside N, plants also need a considerable amount of P and K elements to support

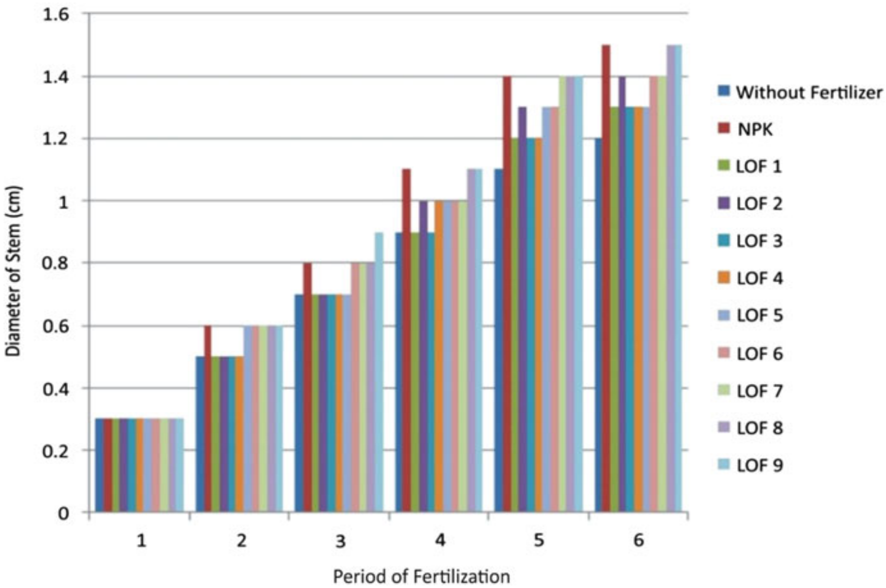

Fig. 10.3 The effect of LOFs fertilization on the stem diameter of tomato plants for each period of fertilization

their growth. The P element is principal to maintain the development of carbohydrate and to ensure the efficient mechanism of the chloroplast activity. It also plays an important role in the metabolism activity (Dobermann and Fairhurst 2001). P is beneficial to stimulate root growth and plant growth as well as supports the formation of flowers and seeds. Moreover, it accelerates fruit ripening so that it speeds up the harvest period. The lack of P causes the incomplete plant roots, dwarf, and thin plants. It also makes the leaves to become dry, and the color becomes reddish and brown.

Figure 10.4 demonstrates the influences of fertilization using LOFs on the number of leaves of tomato plants. The highest number of leaves was provided by the tomato plants fertilized by commercial NPK and LOF 9. NPK and LOF 9 had the highest content of potassium (K) element. Potassium elements are usually available for plants nutrient in the form of K^+ cations. The existence of adequate K is crucial since this element plays an important role in the carbohydrate formation, promoting the production of chlorophylls and flower, increasing root absorption to nutrients capability, and improving the plant's resistance to diseases. Inadequate K supply to the plant will bring about several indications, for instance, slow stem formation and dwarf plants, yellowing shoots like burning at the edges, the death of roots and hair roots, and the disruption on nutrient absorption (Xu et al. 2015).

Fertilization using LOF also affected the flowering and fruiting time of the tomato plants. The addition of fertilizer enhances the flowering and fruiting speed. It can be seen in Table 10.6 and Fig. 10.5 that the tomato plants which had been given LOFs

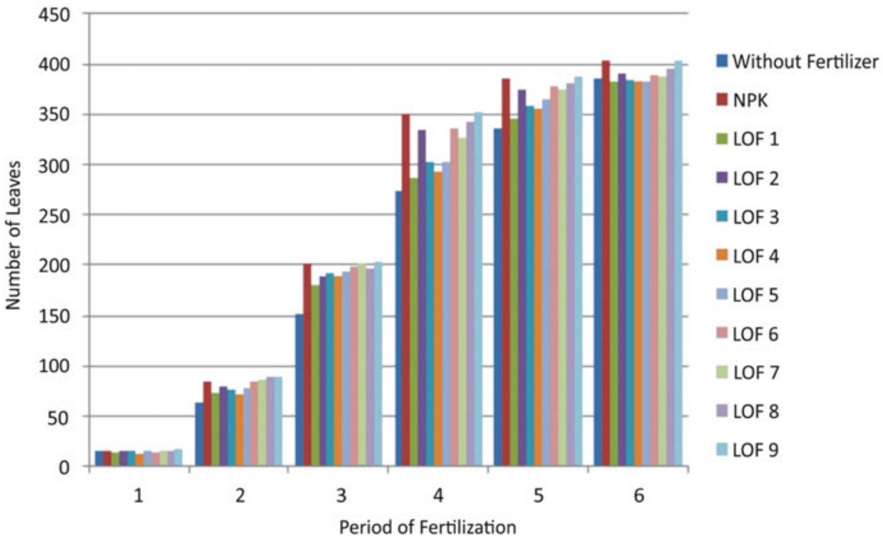

Fig. 10.4 The effect of LOFs fertilization on the number of leaves of tomato plants for each period of fertilization

Table 10.6 Flowering and fruiting time of tomato plant fertilized by LOF

Types of fertilizer	Flowering time (days)
Without fertilizer (control 1)	50
NPK (control 2)	46
LOF 1	48
LOF 2	47
LOF 3	48
LOF 4	47
LOF 5	48
LOF 6	47
LOF 7	47
LOF 8	48
LOF 9	46

needed flowering time less than 50 days. At this time, very small fruits were also found on the tomato plants. Among the others, LOF 9 has shown the earliest time of flowering and fruiting (46 days). It was due to the fact that LOF 9 had the highest content of N, P, K, and C elements, which are important for supporting the plant growth.

The flowering and fruiting speed of the tomato plants has a significant impact on the fruits produced by the plant, especially in terms of the number and diameter of the fruit as indicated in Table 10.7 and Fig. 10.6. It was demonstrated that LOF 9 produced the highest number of fruits (9) with a big diameter of fruit (4.1 cm). For comparison, tomato plants fertilized by commercial NPK could produce a slightly

Fig. 10.5 The flower and small fruit on the tomato plant fertilized by LOF at the age less than 50 days

Table 10.7 Number and diameter of tomato fruit

Types of fertilizer	Number of fruit	Diameter (cm)
Without fertilizer (control 1)	3	3.5
NPK (control 2)	8	4.2
LOF 1	5	3.7
LOF 2	7	4
LOF 3	5	3.6
LOF 4	6	3.6
LOF 5	4	3.7
LOF 6	6	3.7
LOF 7	7	3.9
LOF 8	7	3.8
LOF 9	9	4.1

higher diameter of fruit (4.2 cm), but the number of fruits was only eight. As control, tomato plant without any fertilization barely produced three fruits having a small diameter (3.5 cm).

The experimental result has denoted that vinasse-based organic fertilizers could promote the growth of the tomato plant in terms of height, stems, leaves, the speed of flowering and fruiting time of tomato plants, as well as the quality and quantity of the fruits. This innovation is a prospective alternative to give added value to vinasse waste. It is also an appropriate option to provide an economical organic fertilizer for farmers, which will support the government in increasing food security.

10.5 Future Trend: Slow Release Solid Organic Fertilizer

10.5.1 Vinasse-Based Slow Release Organo-Mineral Fertilizer

Upgrading vinasse to organic fertilizer has a high economic potency. Vinasse can be converted to liquid or solid organic fertilizer. Solid organic fertilizer provides advantages compared to liquid organic fertilizer to some extent, such as: it is easy in handling and transportation, it is more stable, and has a longer life time than LOF. Vinasse-based solid organic fertilizer, which was called organo-mineral fertilizer (OMF), has been developed by (Kusumaningtyas et al. 2017). It has been proved that OMF contained high N, P, K, and organic C and it was effective in improving the tomato and watermelon plants. However, there are some issues related to the losses of N during the application of OMF in soil for plant fertilization.

N element is important since one of the essential and limit nutrient required in agriculture production is nitrogen (Qiu et al. 2018). N fertilizer is commonly used to improve crop production. Therefore, it is produced in a huge amount to fulfill the demand of the agricultural production worldwide. The conventional use of N fertilizer becomes inefficient because more than 42–47% of N fertilizer will be leached, denitrified, or volatile (Zhang et al. 2015; Bouwman et al. 2017; Zhu et al. 2018; Siva et al. 1999). The loss of N causes some environmental pollution such as the contamination of groundwater by nitrate leaching and even causes greenhouse gas emission (Zhang 2017). It also can increase the cost in agriculture production but give less effect to the yield. Therefore, it is important to prevent the N loss through some pathways to increase the use efficiency of N fertilizer.

Some research has been conducted to develop the strategies in N fertilizer loss prevention. The biochar addition with urea can reduce the loss of N through ammonia volatilization (Zhu et al. 2018). Biochar combined with water treatment has high capabilities to decrease N loss through leaching (Zhu et al. 2018). Slow release of fertilizer from urea can also be used as a treatment to decrease the loss of nitrogen through N leaching and ammonia emission with a high yield of the crop (Yang et al. 2017; Tian et al. 2018).

Organo-mineral fertilizer (OMF) is becoming a popular strategy to enhance the efficiency of the use of fertilizer and increase the crop yields and soil health compared to the use of organic or inorganic fertilizer because of its slow release properties (Buss et al. 2019). OMF provides nutrients simultaneously for the crops through controlling the nutrient release to the soil, surface water, groundwater, and atmosphere. OMF which was made of biochar-ash composite increased the crop yields and P uptake compared with the conventional phosphate fertilizer (Buss et al. 2019). It was also used to enhance the use efficiency of N, N uptake, plant photosynthesis, and N availability during plant cycle compared to commercial organic fertilizer (Nguyen et al. 2017). Brown coal mixed with urea as a slow release organo-mineral fertilizer reduced the loss of gaseous N and increased crop yields and N uptake (Saha et al. 2019). Fly ash in a coal power plant also has potential as a slow-release fertilizer even in calcareous soils (Hermassi et al. 2017). Slow-release fertilizer is also applied in a mixed of mono-ammonium phosphate, triple superphosphate, and phosphoric acid, with and without the addition of magnesium oxide with poultry litter yielding the slow release of P which makes potential in tropical soils (Lustosa Filho et al. 2017).

The technique of slow-release fertilizer for improving the quality of vinasse-based OMF has not been previously developed. On the other hand, the use of vinasse with the controlled-release characteristic becomes critical to enable the effective use of the nutrient as soil fertilizer. In this study, novel slow-release organo-mineral fertilizer from vinasse or vinasse-based slow release solid organo-mineral fertilizer (SR-OMF) with the chitosan–bentonite matrix was developed to investigate the nitrogen release performance in soil fertilized.

10.5.2 Methods

The first step of SR-OMF production is preparation of vinasse organo-mineral fertilizer (OMF). Initially, vinasse of 100 g was dissolved in NaOH to adjust the pH of vinasse to 7. The solution was evaporated in the temperature range of 80–90 °C for about 30 min to remove 80% water from the solution. Then, NPK was added to the vinasse-rich solution and stirred at a constant speed until NPK completely dissolved. The solution was heated using the oven in a constant temperature of 110 °C and stopped when the weight remains constant.

The second step is chitosan–bentonite matrix composite production. Primarily, chitosan solution (1% w/v) was prepared by dissolving 1 g of chitosan in 100 mL of acetic acid (2% w/v) and stirred at a constant speed. Subsequently, chitosan–bentonite matrix composite was prepared by dissolving bentonite in a chitosan solution to obtain the various concentrations of 2%, 3%, and 5%. The solution was stirred for about 5 h and then 2 drops of Tween 80 surfactant were added to the solution followed by stirring for about 1 h.

The third step, the final step, is SR-OMF production. SR-OMF was prepared by mixing OMF which consists of 9% NPK with the chitosan–bentonite matrix in a ratio of 7:3. The solution is stirred using magnetic stirrer for about 2 h at a temperature of 25 °C and then heated in a temperature of 50 °C until the mass of the solution remains constant. The SR-OMF was then obtained. It was then characterized to determine the content of N element and the N release rate.

The nitrogen release rate was conducted using incubation method in an open space in the laboratory. Dry soil of 113.79 g was undertaken in low-density polyethylene tubes of 6.0 cm diameter and 6.70 cm height. SR-OMF 1 g was mixed with dry soil of 200 g and then added to each tube. During the incubation, the leaching of nitrogen for each tube will be analyzed at days 0, 7, 14, 21, 28, and 60 through watered method. The nitrogen compositions dissolved in water was analyzed through Kjeldahl method. The carbon compositions was analyzed using a UV/Vis spectrophotometer.

10.5.3 Nitrogen Release Pattern of SR-OMF

The nitrogen concentrations were initially analyzed for the vinasse SR-OMF which consists of the mixture of the vinasse OMF and chitosan–bentonite matrix. The ratio of chitosan–bentonite was 7:3. The effect of chitosan–bentonite matrix concentration in a vinasse OMF is shown in Fig. 10.6. The concentration of chitosan–bentonite matrix added in a vinasse OMF were 0, 1, 2, 3, and 5%w/v which produced nitrogen of 0.5, 1.51, 1.66, 1.91, and 2.10%w/w, respectively. Figure 10.7 shows that the increase of the chitosan–bentonite matrix concentration can increase the total nitrogen. The maximum total nitrogen achieved in a chitosan–bentonite matrix concentration was 5%w/v.

The nitrogen release rate was analyzed through the incubation method to obtain the amount of nitrogen released to the soil. The nitrogen release rate of SR-OMF was compared to the OMF. The comparison between two fertilizers for the nitrogen release and the interval comparison before and after incubation is listed in Table 10.1 which shows that the nitrogen dissolved in water for the OMF are 0.011, 0.01, 0.008, and 0.006%w/w in 3, 6, 9, and 12 days, respectively. The total nitrogen dissolved is 0.035%w/w which is about 6.36% compared to the nitrogen concentration before the incubation. In a SR-OMF, the nitrogen dissolved is 0.01, 0.08, 0.004, and 0.003%w/w in 3, 6, 9, and 12 days, respectively. The total nitrogen dissolved in water is 0.025 which is smaller compared to the total dissolved nitrogen in OMF. This number is about 1.19% from the nitrogen concentration before the incubation. Thus, the addition of the chitosan–bentonite matrix to the fertilizer causes the decrease of the nitrogen release rate to the water because the nitrogen release is controlled by the matrix.

The nitrogen release profile for both fertilizers is shown in Fig. 10.8 which indicates the decrease of nitrogen as the day increases. The decrease in nitrogen happened because of the less nitrogen dissolved in water. This condition occurred due to the volatilization of nitrogen to the air. Nitrogen is a volatile compound which is easy to be released from the soil to the air.

Fig. 10.6 The fruit produced by the tomato plant fertilized by LOF

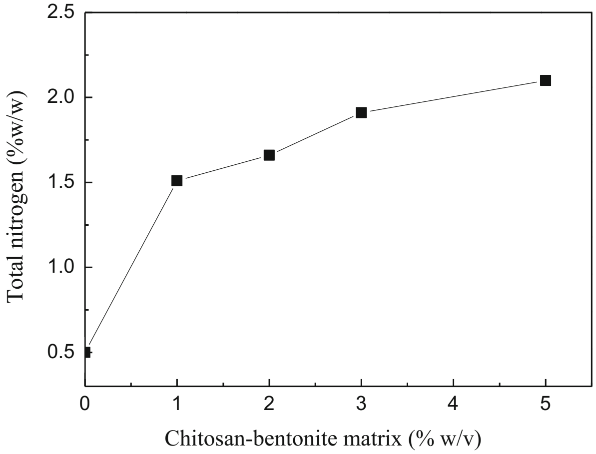

Fig. 10.7 Total N in a vinasse SR-OMF mixed with chitosan-bentonite matrix

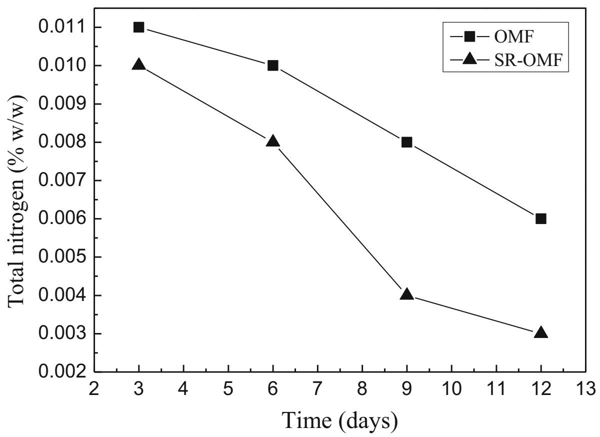

Fig. 10.8 The release rate of nitrogen for a vinasse SR-OMF and OMF

10.6 Conclusion

Vinasse waste of bioethanol industry is potential to be upgraded into liquid organic fertilizer as well as solid organic fertilizer. The ability of vinasse-based organic fertilizer to promote the growth of the tomato plant in terms of height, stems, leaves, the speed of flowering and fruiting time of tomato plants, as well as the quality and quantity of the fruits is evidence. Combination of vinasse with co-feedstocks (filter cake, banana peels, and lead tree leaves) could improve the properties of vinasse-based liquid organic fertilizer. The best way of LOF formulation vinasse, banana peels, and lead tree leaves is through the blending and fermentation process of vinasse with each feedstock separately, resulting in LOF 6, LOF 7, and LOF 8. Subsequently, the three types of LOFs (LOF 6, LOF 7, and LOF 8) were mixed together to produce LOF 9, which becomes the best formulation of vinasse and filter cake–banana peels–lead tree leaves. On the other hand, the conversion of vinasse into solid fertilizer (OMF) is also an attractive option. To improve the effectiveness of OMF in fertilization, development of the slow-release organo-mineral fertilizer from vinasse becomes of increasing interest in research. In this work, the soil fertilized is used and analyzed to understand the nitrogen release behavior. The increase of the chitosan–bentonite matrix concentration causes the increase of the nitrogen with the maximum concentration of the matrix is 5%w/v yielding 2.1%w/w of nitrogen. The nitrogen release rate of SR-OMF is slower compared to OMF. It shows that SR-OMF from vinasse has a promising potential as a fertilizer which allows nitrogen release control to optimize the nutrient use efficiency in agricultural crops.

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