Analysis and Characterization of Solid and Liquid Organic Fertilizer from Hydrothermal Carbonization (HTC) of Chicken Feather and Blood Waste

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Abstract: *Conversion of feather and blood from chicken slaughterhouse waste for producing solid and liquid organic fertilizer excluding composting process with a variation of the mass ratio of feather and blood of a chicken has been conducted. The nitrogen, sulfur, and iron content in the solid and liquid product of the hydrothermal carbonization process were analyzed to identify and characterize the possibility of hydrolysate as a source of nitrogen, sulfur, and iron in soil fertilizer. Feather and blood of chicken waste were introduced to a hydrothermal carbonization reactor with the addition of limestone at a temperature range of 160–170 °C for the preparation of solid and liquid organic fertilizer. According to the FTIR interpretation, the solid product had functional groups such as NH, OH, CH sp^3, SH, C=O, C=C, C–O–C, and C–H aromatic. The nitrogen, sulfur, and iron content of the optimal ratio in the solid phase were 4.67%, 1.63%, and 3694.56 ppm, while their contents in the liquid fertilizer were 3.76%, 1.80%, and 221.56 ppm, respectively. The vibration of 478 cm^{-1} is attributed to Fe–O paramagnetic (Fe_2O_3) confirmed by TEM images showed the diameter size less than 20 nm indicating the presence of superparamagnetic material.*

Keywords: *hydrolysate; hydrothermal carbonization; feather; blood*

INTRODUCTION

The composting process requires a very long time to produce organic fertilizer; otherwise, it is only several hours if the hydrothermal carbonization (HTC) process is used. Production of organic fertilizer from poultry feather wastes, excluding the composting process of chicken feathers generated in large quantities by the poultry industry, are hazardous for the natural environment because of their poor digestibility and their potential as a source of microbiological pathogens [1]. Mazzoto et al. [2] explained that chicken meat consumption increases the waste problem like feathers and blood. This waste produced by chicken slaughterhouse waste causes terrible odor due to releasing NH_3 and H_2S gas. The soil undergoes hardening when this waste disposes directly into the soil (especially for feathers waste) due to disulfide bonds (S–S). Meanwhile, the chicken slaughter waste, such as poultry litter and manure, and feathers can be functioned as a soil amendment [2] due to the high nitrogen, sulfur and iron chelate organic complex contents [2,4-6].

Kuncaka [7] proposed a synthetic humus preparation technique called New Road of Synthetic Humification, which explained how to make synthetic humus by Partial Hydrothermal Carbonization (PHTC). This technique produces a high aromatization degree called hydrochar and some materials like carbohydrate, protein, and lipid or hydrolysate material like amino acid and fatty acid. These molecules interact with each other using hydrogen bonding [8]. This humus like structure has suitable to the modern humus definition [8]. This humus like structure is called a Slow Release Organic Paramagnetic (SROP) Fertilizer.

Adiabati et al. [8] explained feather waste contains protein about 80–90%, while blood contains protein about 4.5–5.2 g/L [9]. Both proteins in feather and blood are useful as a source of nitrogen [3-5]. Feather is the main sulfur source in disulfide bonds (S–S), contained in a feather as much as 17% [2]. Blood contains hemoglobin as much as 8.65 g/L [10-11]. Each hemoglobin contains iron in the heme protein [5]. Based on this, a combination of feather and blood can be converted into hydrolysate. Suwardi and Wijaya [12] studied one of the problems in Indonesian soil is leveling off. This condition occurs when the soil organic matter (SOM) is very low. SOM is classified into three categories according to soil organic carbon (SOC) content, i.e., low (less than 2%), normal (2–3%), and high (up to 3%) [13]. Indonesia's soil agriculture, around 73%, has a low SOC [14].

Chicken feathers and blood waste contain many microbes, pathogens, and parasites in raw biomass; then this study aims to develop hydrothermal carbonization (HTC) using feather and blood chicken waste as a precursor for producing solid and liquid organic fertilizer instead of the composting process. The nitrogen, sulfur, and iron content in the solid and liquid organic fertilizer were analyzed to identify and characterize the possibility of hydrolysate as nitrogen, sulfur, and iron source in solid and liquid organic fertilizer. In this research, feathers and blood of chicken waste as precursors were obtained from the Ar-Royan Chicken Slaughterhouse, Yogyakarta province, Indonesia.

■ EXPERIMENTAL SECTION

Materials

The materials used in this research were feather and blood of chicken waste (obtained from the Ar-Royan Chicken Slaughterhouse, Bantul, Yogyakarta, Indonesia), limestone (CaO), universal pH indicator, filter paper, distilled water, H_2SO_4 96%, $Fe(NO_3)_3$, H_3BO_3, NaOH, $Na_2S_2O_3$, K_2SO_4, HgO, HCl 37%, HNO_3 68%, $BaCl_2$, and Mr-BCG indicator (a mixture of methyl red and cresol green bromine) from Sigma Aldrich in pro analysis grade.

Instrumentation

The solid organic fertilizer was characterized by Fourier Transform Infra-Red spectrophotometry (FTIR, Prestige-21) with KBr pellet and Transmission Electron Microscopy (TEM, JEOL-JEM1400). The liquid organic fertilizer was characterized by High Performance Liquid Chromatography (HPLC, Dionex Ultimate-3000). The content of nitrogen (N), sulfur (S), and iron (Fe) in both solid organic and liquid organic fertilizer were determined using the Kjeldahl method, gravimetric method, and atomic absorption spectrophotometer, respectively.

Procedure

Hydrolysate preparation

Feather and blood of chicken waste were mixed with a mass ratio of feather and blood, i.e., 500 g of feather and 500 g of blood (1:1), 750 g of feather and 250 g of blood (3:1), and 250 g feather and 750 g of blood (1:3). Limestone (CaO) was added to the mixture of feather and blood until a pH of 12–13 showed by universal pH indicator. Then, the mixture was introduced to HTC Reactor without a stirring system, as shown in Fig. 1. The HTC process using this reactor was done at temperatures around 160–170 °C and pressure of 9–10 atm for 3 h. HTC products were separated using the Buchner filter. The solid phase was dried using an oven at 100 °C for 24 h. The dry matter was weighed with an analytical balance. The liquid phase obtained was placed in a bottle for further analysis.

Nitrogen determination by Kjeldahl method

Nitrogen determination was carried out for a solid organic fertilizer and liquid organic fertilizer. The Kjeldahl method consists of 3 stages, i.e., destruction, distillation, and titration. For the first stage, destruction, 0.2 g of sample was put into 30 mL Kjeldahl flask. As much as 0.7 g of N catalyst (a mixture of K_2SO_4 and HgO with a ratio of 20:1), 4 mL of concentrated H_2SO_4 solution,

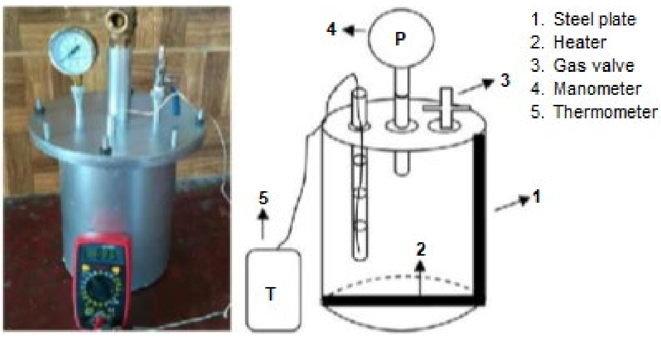

Fig 1. Scheme of HTC Reactor without stirring system

and boiling chips were added to the Kjeldahl flask. The flask was then boiled in a fume hood for 1 h until the sample turns green clearly. After this, the flask was cooled until it reaches room temperature. Ten milliliters of distilled water was added to the cold Kjeldahl flask. The second step is distillation; the product of destruction was moved from the Kjeldahl flask to the distillation flask. Erlenmeyer 125 mL was placed under the condenser. The Erlenmeyer was then filled with 4% H_3BO_3 solution and 4 drops of the Mr-BCG indicator. The tip of the condenser must be submerged in Erlenmeyer. A solution of 20 mL of NaOH-thiosulfate (a mixture of NaOH 40% and $Na_2S_2O_3$) was put into a distillation flask which had been filled with a sample that had been destroyed. The distillation process was carried out until 60 mL of distillate was obtained in Erlenmeyer (the color changed from red to blue). The third stage is titration; a standard of 0.02 M HCl solution was used for the titration process until the color of the sample was changed from blue to red. Nitrogen percentage (%N) was calculated by using this equation:

$$\%N = \frac{v \times M \times Ar_N}{w} \times 100\%$$

where v is the volume of HCl solution used for titration (mL), M is the concentration of HCl used (0.02 M), Ar_N is the relative mass of nitrogen (14.007 g/mol), and w is the mass of sample (mg).

Sulfur determination by gravimetric method

Sulfur determination was carried out for a solid organic fertilizer and liquid organic fertilizer. A total of 2 g of sample (solid phase) was inserted into the porcelain dish. Then, the sample was heated in a muffle furnace to give ash. Ash was crushed by porcelain mortar and then was added with 25 mL of HNO_3 (1:3). The solution was filtered using filter paper. Five milliliters of the filtrate was taken and then put into 5 mL centrifuge tube. The tube was centrifuged to form a sediment, and the sediment was separated using filter paper. The sediment obtained was then dried in an oven until it reached a constant mass. The sulfur percentage (%S) was calculated using this equation:

$$\%S = \frac{m \times \frac{Ar_S}{Mr_{BaSO_4}}}{w} \times 100\%$$

where m is the mass of sediment (g), Ar_S is the relative atomic mass of S, Mr_{BaSO_4} is the relative mass of $BaSO_4$, and w is the mass of sample (g).

Iron (Fe) determination

The Fe containing in each solid organic fertilizer and liquid organic fertilizer (3:1, 1:1, 1:3) was determined using Atomic Absorption Spectrophotometer (AAS). A standard curve of $Fe(NO_3)_3$ was used for the quantitative analysis of Fe.

■ RESULTS AND DISCUSSION

FTIR Characterization of Solid Aggregate of Hydrolysate

The solid organic fertilizer was characterized by an FTIR spectrophotometer to show the functional group changes during the HTC process. FTIR spectra were showed in Fig. 2. The broad band at 3400 cm^{-1} was attributed to O–H stretching vibration in carboxyl and hydroxyl groups from an amino acid in polyaromatics structure. This band can be correlated to the hydrophilic surface of polyaromatic compounds in a solid aggregate of hydrolysate [15]. The band at 2924 and 2855 cm^{-1} were attributed to the vibration of the CH sp^3 group. This band was associated with an aliphatic group from an amino acid in the polyaromatics structure of a solid organic fertilizer.

The band at 2515 cm^{-1} was associated with the thiol group (–SH), which is appeared due to the hydrolysis process of a disulfide bond (S–S) from keratin. The formation of a thiol group (–SH) indicated the loss of undegradable character in chicken feathers [16]. Thiol group (–SH) was associated with cysteine adsorbed in polyaromatic structure in solid organic fertilizer. The band at 1651 cm^{-1} was associated with the C=O bond from the polyaromatic surface as the product of polycondensation of hydroxymethylfurfural (HMF) [15]. This band proved that the surface of polyaromatic was hydrophilic.

A new band that appeared at 1623 cm^{-1} was attributed to the stretching vibration of the C=C aromatic bond from a polyaromatic structure. The aromatic structure was present in a solid aggregate of hydrolysate strengthened by a new band at 872 cm^{-1} attributed to the vibration of CH aromatic. Both of these

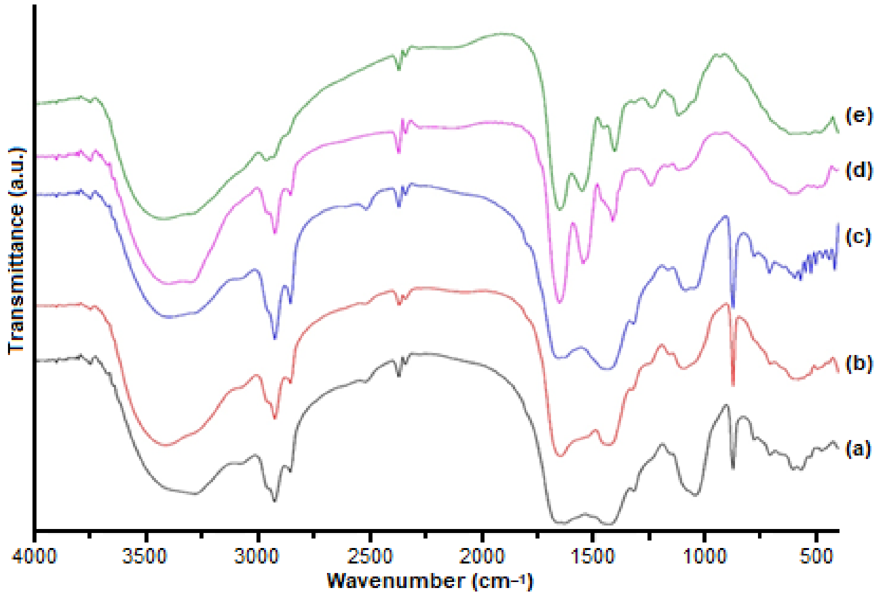

Fig 2. FTIR spectra of solid aggregates of hydrolysates of (a) 1:3, (b) 1:1, (c) 3:1, (d) chicken feather raw material, and (e) chicken blood raw material

new bands indicated the aromatization process during HTC. The aromatization was also present in the previous study [15-18]. Polyaromatic structure in solid aggregate of hydrolysate plays a role in bonding some nutrients such as nitrogen and sulfur in the soil. In this study, amino acid and the polyaromatic structure were bonded via hydrogen bonds through an amine, carboxyl, and hydroxyl groups from the amino acid. In addition, the band at 1080 cm^{-1} was attributed to the vibration of the C–O–C bond from the product of HMF polycondensation in the polyaromatic surface. The band at 478 cm^{-1} was attributed to Fe–O vibration from paramagnetic material (Fe_2O_3) in a solid organic fertilizer, and the band located at 500–700 cm^{-1} in raw chicken feather and raw blood were attributed to N–H vibration.

This solid organic fertilizer should also be able to play a role as soil amendments. The requirement of soil amendment material was the high aromatization degree [17]. The two bands that showed the aromatization degree were at 1623 and 872 cm^{-1}. After making a comparison of the fives sample, it was found that the characteristics peaks are similar to each other and comparable with other studies except the absorption ratio of band intensity at 872 cm^{-1} and the absorption band of 1080 cm^{-1} was relatively different in 1:3 compare with the ratio of 1:1 and 3:1. Therefore during HTC of ratio 1:1, the deposit of solid organic fertilizer starts to settle well. The difference in aromatization degree in each ratio is caused by the ability of the system to raise sub-critical water conditions that are affected by water content [18]. More water content could cause low sub-critical water conditions. A solid organic fertilizer with a ratio of 1:3 has higher water content (from blood used) in the system than the 1:1 and 3:1 ratio. Therefore, the 1:3 ratio has low subcritical water conditions that cause a low hydrolysis reaction.

TEM Characterization of Solid Aggregate of Hydrolysate

TEM images are shown in Fig. 3. Two agglomeration products have been identified in the TEM images to give a primary and secondary agglomeration. A secondary agglomerate consists of some combined primary agglomerates, while a primary agglomerate consists of some incorporated primary nanoparticles. The agglomeration could occur because the hydroxyl (–OH) and carbonyl (C=O) groups in the surface of polyaromatics undergo dehydration reactions [19]. The diameter of the agglomerate has a size less than 20 nm, and if this result was combined with the result from FTIR vibration of Fe–O at 478 cm^{-1}, it may be assumed that the primary nanoparticles have the superparamagnetic property [19].

Nitrogen and Sulfur Analysis

Each ratio of a solid organic fertilizer and liquid organic was analyzed by Kjeldahl and gravimetric methods to determine the percentage of nitrogen and sulfur. Fig. 4 and 5 represent the percentage of nitrogen and sulfur of each solid organic fertilizer and liquid organic fertilizer, respectively. Nitrogen and sulfur percentage increased in the solid phase from 3:1 to 1:3 ratio, while decreased in the liquid phase from 3:1 to 1:3 ratio. Nitrogen and sulfur in the liquid phase indicated the hydrolysis of protein in chickens' feathers and blood into soluble amino acids [16].

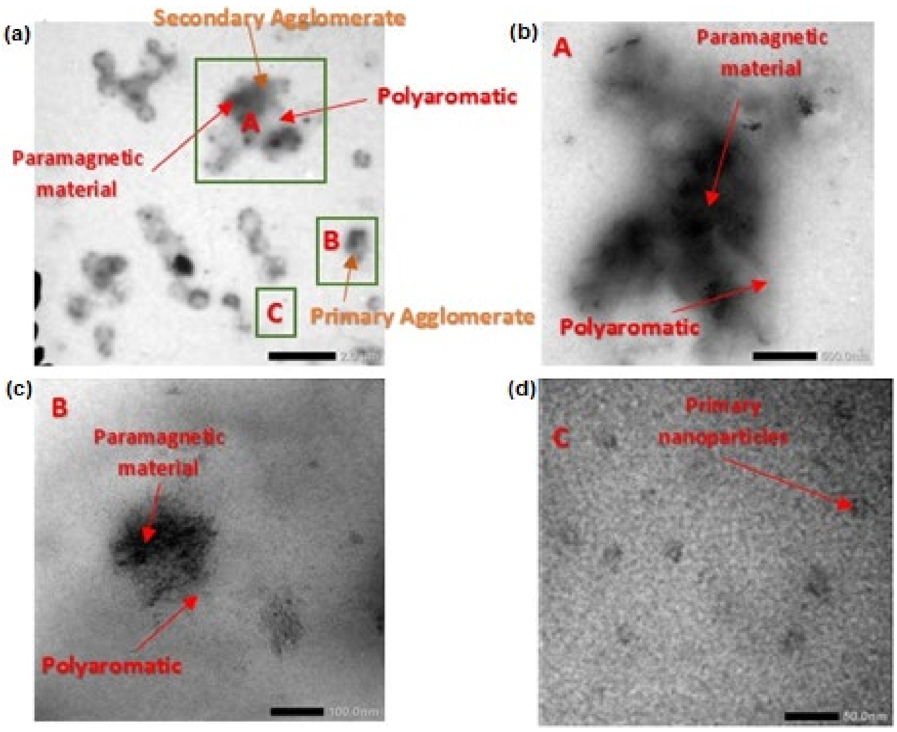

Fig 3. TEM images of solid organic fertilizer with a ratio of 3:1 showing (a) primary and secondary agglomerates, (b) primary agglomerate, (c) secondary agglomerate, and (d) primary nanoparticles

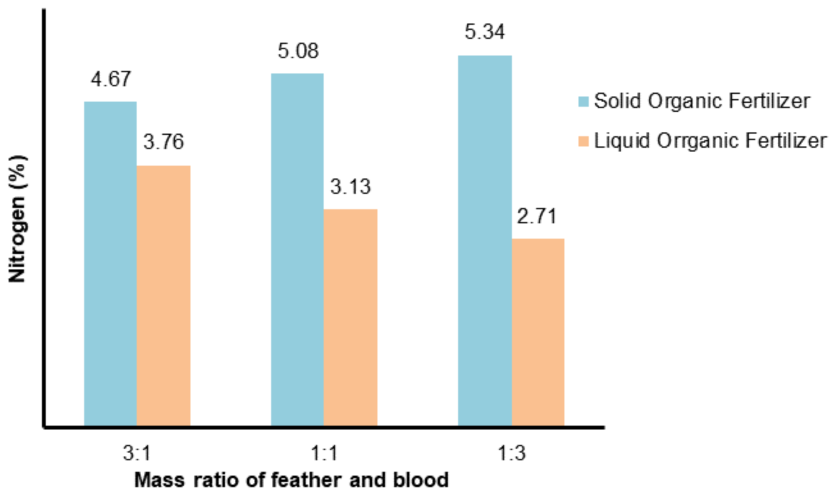

Fig 4. Nitrogen percentage of solid organic fertilizer and liquid organic fertilizer

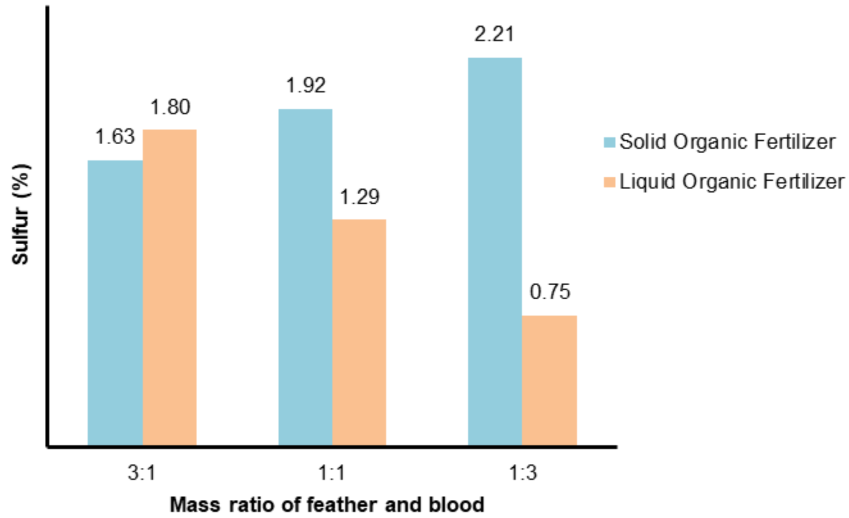

Fig 5. Sulfur percentage of solid organic fertilizer and liquid organic fertilizer

Iron Analysis

The iron (Fe) contents of a solid organic fertilizer and liquid organic fertilizer are given in Table 1. The concentration of iron in the blood is much bigger than in feather, which is 1816.62 ppm [23] and 30 ppm [15] for blood and feather, respectively. It is in line with the AAS analysis of iron content where the ratio of 1:3 has the highest number of iron because it contained the highest amount of blood and a lower amount of feather. Otherwise, the 3:1 ratio has the lowest iron concentration because it contained the lowest amount of blood and a higher amount of feather.

The data was compared to the regulation of the Ministerial of Agriculture in Indonesia. According to the ministerial Regulation of Agriculture number 28 in 2009 on organic fertilizer, bio-fertilizers, and soil repair, which is now revised to Ministerial Regulation of Agriculture in 2011, to have a good quality of solid organic fertilizer, the iron contents should not exceed 9,000 ppm. This regulation necessitates that the formation of iron compounds in fertilizer should be below 9,000 ppm [20].

Based on the requirements above, the concentrations for every raw material and hydrolysate were below 9,000 ppm, which means the concentrations fit the standard regulation from the Ministerial of Agriculture in Indonesia. The solid organic fertilizer has an increment of iron concentration for every variation compared to raw material. Meanwhile, the liquid organic fertilizer has a decrement of iron concentration for every variation compared to raw material. It means that the solid product probably chelated the iron more than the liquid product. The iron contents proved the paramagnetic character present in the solid aggregate of hydrolysate. In a solid organic fertilizer, the function of iron was to prevent the plant from chlorosis [21-22] and to control the electron transfer [21].

Liquid Organic Fertilizer Characterization by HPLC

All ratios of liquid organic fertilizer were characterized by HPLC to determine the amounts and types of amino acids. Table 2 refers to the amounts and types of amino acids in the liquid organic fertilizer. Profile of amino acid content in the liquid phase indicated the potential as a liquid organic fertilizer. The potential of the liquid phase as a liquid organic fertilizer has been discussed in a previous study [16].

Results of nitrogen and sulfur analysis showed that

Table 1. The distribution of iron content in solid organic fertilizer and liquid organic fertilizer

Sample	Concentration (ppm)
Solid 1:1	6238.01
Solid 1:3	6393.86
Solid 3:1	3694.56
Liquid 1:1	307.15
Liquid 1:3	599.74
Liquid 3:1	221.56

Table 2. Amino acid profile of liquid hydrolysate

Amino acid	3:1	1:1	1:3
	Percentage (%)	Percentage (%)	Percentage (%)
Aspartic acid	3.44	7.74	4.08
Glutamic acid	17.70	16.30	17.15
Serine	1.54	2.55	2.69
Histidine	4.36	7.38	2.65
Glycine	9.66	7.32	6.89
Alanine	16.92	11.19	13.76
Tyrosine	1.99	4.72	2.40
Methionine	1.08	0.88	-
Valine	11.41	9.65	8.64
Phenylalanine	7.19	6.03	5.49
Isoleucine	6.52	5.52	0.71
Leucine	12.32	11.27	5.20
Lysine	5.88	9.45	30.33
Total amino acid	100.00	100.00	100.00

hydrolysate of 3:1 ratio undergoes maximum hydrolysis highest amino acid content for most detected amino acids, i.e., glutamic acid, glycine, alanine, methionine, valine, phenylalanine, isoleucine, and leucine, compared to other ratios. This result proved that the 3:1 ratio undergoes maximum hydrolysis.

■ CONCLUSION

The HTC process has an excellent effect on the degradation of keratin chicken feathers and high protein blood of chicken waste to produce solid organic fertilizer and liquid organic fertilizer. According to FTIR spectra of solid organic fertilizer, the functional groups that appeared were NH, OH, C=O, CH sp^3, SH, Fe–O, CH aromatic, C=C aromatic, and C–O groups. TEM images showed the size of paramagnetic material coated by polyaromatic structure is less than 20 nm. A solid organic fertilizer started from a 1:1 ratio was optimally formed, indicated by a high degree of aromatization. Percentage of nitrogen and sulfur in solid organic fertilizer and liquid organic fertilizer were affected by ratios of feather and blood as precursors. HPLC analysis showed the potential of liquid organic fertilizer as a liquid protein source because of the high protein contents.

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■ REFERENCES

[1] Tronina, P., and Bubel, F., 2008, Production of organic fertilizer from poultry wastes excluding the composting process, *Pol. J. Chem. Technol.*, 10 (2), 33–36.

[2] Mazotto, A.M., Coelho, R.R.R., Cedrola, S.M.L., de Lima, M.F., Couri, S., de Souza, E.P., and Vermelho, A.B., 2011, Keratinase production by three *Bacillus* spp. using feather meal and whole feather as substrate in a submerged fermentation, *Enzyme Res.*, 2011, 523780.

[3] Sams, A.R., 2000, *Poultry Meat Processing*, 1st Ed., Eds. Owens, C.M., Alvarado, C., and Sams, A.R., CRC Press, Boca Raton.

[4] Sari, Ö.F., Özdemir, S., and Celebi, A., 2016, Utilization and management of poultry slaughterhouse wastes with new methods, *EurAsia Waste Management Symposium*, 2-4 May 2016, İstanbul, Türkiye.

[5] Yaakob, M.A., Radin Mohamed, R.M.S., Al-Gheethi, A.A.S., and Mohd Kassim, A.H., 2018, Characteristics of chicken slaughterhouse wastewater, *Chem. Eng. Trans.*, 63, 637–642.

[6] Wan, Y., Ghost, R., and Cui, Z., 2002, High resolution

plasma protein fractionation using ultrafiltration, *Desalination*, 144 (1-3), 301–306.
[7] Kuncaka, A., 2014, *Metode Memproduksi Pupuk Organik Paramagnetik Pelepasan Lambat*, IND. Patent No. P00201401530.
[8] Hayes, M.H.B., Swift, R.S., Byrne, C.M., and Simpson, A.J., 2010, The isolation and characterization of humic substances and humin from Grey Brown Podzolic and Grey Grassland Soil, *19th World Congress of Soil Science, Soil Solution for Changing World,* 1-6 August 2010, Brisbane, Australia.
[9] Adiati, U., Puastuti, W., and Mathius, I.W., 2004, Peluang pemanfaatan tepung bulu ayam sebagai bahan pakan ternak ruminansia, *Wartazoa*, 14, 39–44.
[10] Widhyari, S.D., Esfandiari, A., and Herlina, 2011, Profil protein total, albumin dan globulin pada ayam broiler yang diberi kunyit, bawang putih dan Zinc (Zn), *JIPI*, 16 (3), 179–184.
[11] Putriani, S., Soma, I.G., and Ardana, I.B.K., 2012, Nilai hematokrit, kadar hemoglobin, dan total eritrosit ayam pedaging yang diinjeksi kombinasi tylosin dengan gentamicin, *Indones. Med. Veterinus*, 1 (4), 492–504.
[12] Suwardi and Wijaya, H., 2013, Peningkatan produksi tanaman pangan dengan bahan aktif asam humat dengan zeolite sebagai pembawa, *JIPI*, 18 (2), 79–84.
[13] Gitosuwondo, S., 2010, Strategi efisiensi penggunaan bahan organik untuk kesuburan dan produktivitas tanah melalui pemberdayaan sumberdaya hayati tanah, *Jurnal Sumber Daya Lahan*, 4 (1), 13–25.
[14] Las, I., and Setyorini, D., 2010, Kondisi lahan, teknologi, arah, dan pengembangan pupuk majemuk NPK dan pupuk organik, *Prosiding Semnas Peranan Pupuk NPK dan Organik dalam Meningkatkan Produksi dan Swasembada Beras Berkelanjutan*, Balai Besar Litbang Sumberdaya Lahan Pertanian, 24 February 2010, Bogor, Indonesia.
[15] Sevilla, M., and Fuertes, A.B., 2009, The production of carbon materials by hydrothermal carbonization of cellulose, *Carbon*, 47 (9), 2281–2289.
[16] Nurdiawati, A., Nakhshiniev, B., Zaini, I.N., Saidov, N., Takahashi, F., and Yoshikawa, K., 2017, Characterization of potential liquid fertilizers obtained by hydrothermal treatment of chicken feathers, *Environ. Prog. Sustainable Energy*, 37 (1), 375–382.
[17] Gasco, G., Paz-Ferreiro, J., Álvarez, M.L., Saa, A., and Méndez, A., 2018, Biochars and hydrochars prepared by pyrolysis and hydrothermal carbonisation of pig manure, *Waste Manage.*, 79, 395–403.
[18] Donar, Y.O., Çağlar, E., and Sınağ, A., 2016, Preparation and characterization of agricultural waste biomass based hydrochars, *Fuel*, 183, 366–372.
[19] Namanga, J., Foba, J., Ndinteh, D.T., Yufanyi, D.M., and Krause, R.W.M., 2013, Synthesis and magnetic properties of a superparamagnetic nanocomposite "Pectin-magnetite nanocomposite", *J. Nanomater.*, 2013, 137275.
[20] Cahyadi, Yuliani, N., and Srikandi, 2013, Penetapan ambang batas kadar Fe total dalam pupuk organik yang berpotensi menyebabkan keracunan Fe tanaman padi sawah, *Sains Natural*, 3 (2), 135–143.
[21] Fattakhova, L.A., Shinkarev, A.A., Kosareva, L.R., Nurgaliev, D.K., Shinkarev Jr., A.A., and Bagautdinova, Y.S., 2016, Magnetic properties of different-aged chernozemic soil profiles, *ARPN J. Eng. Appl. Sci.*, 19 (11), 11383–11394.
[22] Yunta, F., Di Foggia, M., Bellido-Dıáz, V., Morales-Calderoń, M., Tessarin, P., López-Rayo, S., Tinti, A., Kovács, K., Klencsár, Z., Fodor, F., and Rombola, A.D., 2013, Blood meal-based compound. Good choice as iron fertilizer for organic farming, *J. Agric. Food Chem.*, 61 (17), 3995–4003.
[23] Kovács, K., Czech, V., Fodor, F., Solti, A., Lucena, J.J., Santos-Rosell, S., and Hernández-Apaolaza, L., 2013, Characterization of Fe-leonardite complexes as novel natural iron fertilizers, *J. Agric. Food Chem.*, 61 (50), 12200–12210.