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Effect of Hydrothermal Treatment on Macro/Micro Nutrients Extraction from Chicken Manure for Liquid Organic Fertilizer Production

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Authors' contributions

This work was carried out in collaboration between all authors. This work was carried out in collaboration among all authors. Author JACBP designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors BN, KY and HBG supervised author JACBP. All authors read and approved the final manuscript.

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ABSTRACT

In order to study the influence of the hydrothermal treatment technology (HTT) on macro/micro nutrients extraction from two types of chicken manure (broiler chicken manure (BCM) and laying hen chicken manure (LCM)), hydrothermal treatment followed by the solid/liquid separation of the HTT product was performed with a fixed feedstock to water mass ratio (1:3), 30 min reaction time and three different reaction temperatures (160ºC, 180ºC, 200ºC). More than 50% of N can be extracted from solid to liquid after HTT for both BCM and LCM. Moreover, the organic N content was more than 80% in all liquid samples and it was increasing with the increase of HTT temperature. According to all the results, 180ºC is the optimum temperature for both types of chicken manure and the pH value of the liquid extracted at the optimum temperature was close to 7 for both types of chicken manure. The heavy metal contents in the liquid obtained from BCM and LCM were not detected. It was observed that macro nutrients and micro-nutrients were dissolved in the liquid after HTT.

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Keywords: Chicken manure; hydrothermal treatment; organic nitrogen; macro/micro nutrients.

1. INTRODUCTION

Availability of plant nutrients to feed the world population in the future is one of the main problems addressed by the world. Nitrogen (N), phosphorus (P) and potassium (K) are three essential nutrients for plant growth. The world demand for fertilizer nutrients is estimated to grow at 1.9 percent per annum from 2012 to 2016 [1]. The demand for N, phosphate, and potash is forecasted to grow annually by 1.3, 2.0, and 3.7 percent, respectively, during this period [1]. Over the next five years, the global capacity of fertilizer products, intermediates and raw materials will further increase [1]. Over 90% of the 1 billion poorest people live in these countries where food security is and will remain a serious challenge unless appropriate policy and technical measures are taken to ensure fertilizer security [2]. Very high consumption of artificial, chemical fertilizers is not good to the natural environment [3]. Farm lands are now saturated with chemicals which are mainly phosphates due to high consumption of phosphate fertilizers and artificial soil conditions have caused inadvertent reduction of agricultural yield [3].

Animal and poultry manure have been used as valuable fertilizer for agriculture. This is because valuable and renewable nutrients are contained which have been used successfully to improve the soil fertility for many years [4,5]. With the introduction of low cost chemically synthesized fertilizers suitable for high yield crops varieties, the use of manure became less cost effective, and in some countries, organic manure have been largely replaced [6]. As a result, they have become wastes and have created disposal problems [7]. Due to the low cholesterol content in chicken, the poultry industry is growing very fast as agro-based industries in the world [7]. However, due to large scale accumulation of poultry litter, it is currently facing disposal and environmental pollution problems unless environmentally and economically sustainable management technologies are developed [7-10].

The loss of nutrients is one of the issues associated with the usage of poultry manure, especially significant amount of N losses through ammonia (NH_3) volatilization, denitrification and leaching are of concern because they not only reduce the fertilizer value of the manure, but also deteriorate the quality of the environment [11,12]. There are three main forms of N in the chicken manure: inorganic N, easily decomposable organic N and slowly mineralizable organic N [12]. It is estimated that about 70 to 95% of N in the feed is excreted [12]. A large proportion (80%) of the total N in fresh poultry manure is in the form of uric acid ($C_5H_4N_4O_3$) [12].

The litter and manure component of chicken has a high nutritional value and is used as an organic fertilizer. Since past years, farmers have tried to apply the chicken manure to their land as nutrient source with several methods like direct application and composting. Green-manuring has been applied to recover the soil condition due to the deterioration of the soil after several cropping [13]. This natural process of manure decomposition helps the activity of microorganisms in soil and increases soil productivity [13].

Few options have been considered in proper management of chicken manure: centralized anaerobic digestion, composting and direct combustion with combined heat and power [9]. Composting of organic wastes is leading to a stabilized final product free of phytotoxicity and pathogens and with certain humic properties [14]. However, the composting process requires a large space, longer time before utilization and if the optimum conditions cannot be achieved, N and other nutrients will be lost that could result to bad odor [9].

Anaerobic digestion is used worldwide as a treatment method for industrial, agricultural and municipal wastes [9]. The concentration of ammonia-nitrogen is increased during the anaerobic digestion of poultry liter [9]. Some amount of ammonium ions can be utilized by some anaerobic bacteria, while an excess amount can prevent the destruction of organic compounds, the production of volatile fatty acids and methanogenesis [9]. The dilution of the material to 0.5-3% total solids is a possible solution for the ammonia inhabitation [9]. Nevertheless, dilution of material to 0.5-3% results in a large increase in volume of wastes and makes this method uneconomical [9].

The hydrothermal treatment technology (HTT) is a thermochemical process which employs the combination of heat and water as medium to convert unutilized resources in various shapes and characteristics into uniform products such as fuel and fertilizer. Elevated temperatures and pressures are involved in HTT. Thus, the hot water created can serve as solvent, a reactant and even a catalyst or catalyst precursor. HTT can be utilized to produce organic fertilizer efficiently and effectively [15,16]. There were some previous researches on organic solid and liquid fertilizer production from biomass using HTT [16]. There are a lot of merits of HTT when it is used before composting over traditional composting processes:

1) shorter period of time is required for the composting process [17,15]
2) supply of additional readily bioavailable form of C [17], and
3) stability and maturity reached within short period of time [15]

In addition to that, more nutrients such as N move to liquid and more heavy metals remain in solid in sewage sludge after HTT, suggesting the possibility of liquid fertilizer production [16]. According to previous researches, poultry litter is mainly used for composting, anaerobic digestion and animal feed [7,9,12]. Effect of the separation method on the nutrient extraction was investigated in earlier research for pig slurry [18]. Small amount of nutrients was able to extracted from untreated pig slurry using different separation method [18]. It is possible to extract more nutrients from biomass waste by utilizing HTT [16]. Therefore, the influence of HTT process on the nutrient extraction of chicken manure is showing great interest and the investigation on the nutrient solubilization is of highly pursued [16]. The main purpose of this research is to study the effect of HTT on nutrients (macro and micro) and heavy metal extraction from two kinds of chicken manure (BCM and LCM) to demonstrate the technical feasibility of liquid fertilizer production from chicken manure by employing HTT. Amount of macro and micro nutrients movement, change of the pH value, solubilization ratio, C:N ratio in solid and liquid products, the N distribution as organic N and inorganic N in two types of chicken manure during HTT with different reaction temperatures are discussed. In addition, the optimum reaction temperature for effective nutrient extraction to the liquid product is discussed.

2. EXPERIMENTALS AND ANALYSIS METHODS

2.1 Materials

In this research, BCM and LCM were obtained from an egg and meat producing chicken farm located in the western province of Sri Lanka. The nutrients values including the moisture content and ash percentage was shown in the Table 1 and the experimental procedures to analyze the nutrients of two types of chicken manure before and after HTT are shown in Fig. 1.

2.2 Method

Two types of chicken manures were crushed and sieved (pore size is 710 µm) in order to make sure that all the particles were uniform. The moisture content as shown in Table 1 was determined as received basis. The moisture content of the samples was measured by subtracting the initial weight of the raw samples from the weight after drying inside an oven (ONW-300S, ETTAS, Japan) at 105ºC for 24 hours. The Moisture content analysis was triplicated and elemental analysis and ash percentage analysis was duplicated.

C, N and H were determined using CHNS analyzer (vario EL cube, Elementar, Germany). Ten milligrams of sample was used for C, H, N analysis and it was duplicated. The rest of the nutrients were measured using an energy dispersive X-ray fluorescence spectrometer (S2 Ranger, Bruker AXS, Germany). A muffle oven (NEW-1C, Hayashi Denko, Japan) was used to determine the ash content in all raw and treated materials. Two types of raw materials were burnt inside the oven at 550ºC for 4 hrs. Then, the remaining ash content of raw materials after combustion was measured.

Next, HTT was applied to two types chicken manure with different conditions. The bench scale HT reactor (MMJ-500, OM Labtech Co., Ltd) with 0.5L capacity is utilized as shown in Fig. 2. The reactor is a batch type which is equipped with an automated stirrer, a pressure sensor and a temperature controller. The raw materials and water were introduced into the reactor tube and kept the mass: water ratio (1:3) constant. In order to prevent combustion during reaction, the air inside the reactor was purged by argon gas after sealing the reactor. Initial pressure was set to near atmospheric pressure inside the reactor. After that, heat was applied to generate steam with the average heating rate of 7ºC/min and constant stirring speed of 100 rpm. The reaction temperature was raised up to 160ºC (0.6MPa), 180ºC (1.0 MPa), 200ºC (1.5 MPa) and the set temperature was maintained for 30 minutes. After the holding time, the reactor was cooled down (<95ºC) and depressurized. If any NH_3 was generated, it was trapped in the boric acid (Cat. No-021-02195, WAKO Chemical, Japan) and the amount of NH_3 dissolved in the boric acid was measured. At the end of the HTT process, the condensed liquid and the wet solid residue were collected separately.

Table 1. Moisture content, ash content and elemental analysis

Sample name	Moisture content%	Ash%	N%	C%
Broiler chicken manure	21.43(0.16)	26.00(0.44)	3.54(0.11)	36.95(0.14)
Laying hen chicken manure	17.34(0.18)	47.80(0.34)	2.41(0.10)	28.91(0.10)

(sd) – Standard deviation

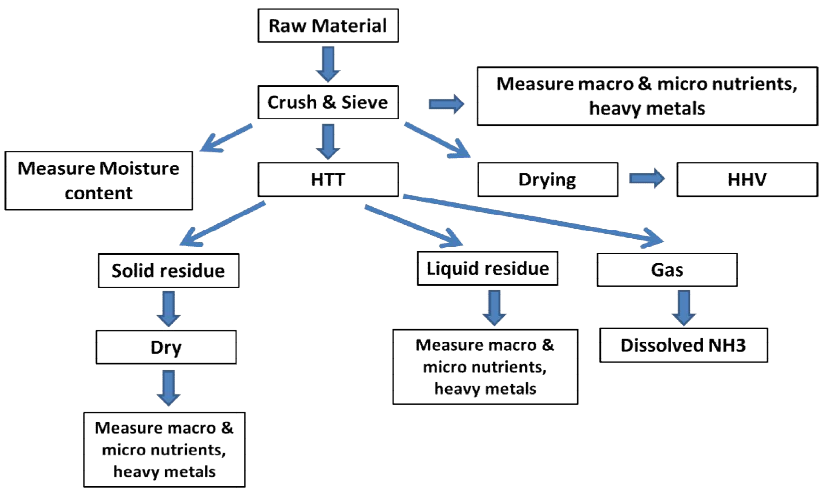

Fig. 1. Flow of experiments

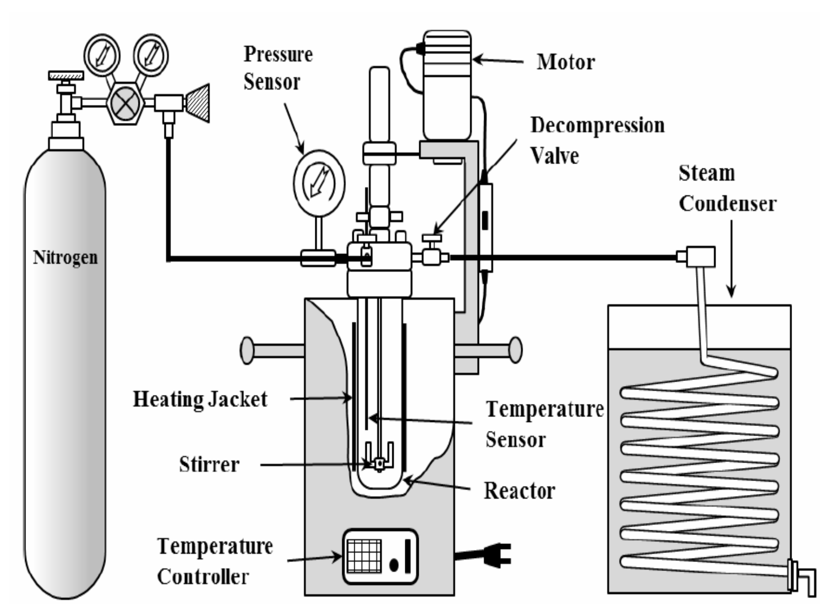

Fig. 2. HTT apparatus [17]

The liquid part of the wet solid residue was collected through filter units (Nalgene, USA), with a membrane (What man GF/A 4.7 cm, UK) of 1.6 µm pore size before analysis it. The separated solid part was dried at 105ºC for 24 hours in the oven. Approximately 400 ml of liquid amount was collected at each experiment. The total N (TN) and NH^{+}_{4} - N were determined in the raw and the treated solid and liquid using Kjeldahl method. It involved acid digestion followed by steam distillation and determined the released ammonia. The released NH_3, trapped in the boric acid (Cat. No-021-02195, WAKO Chemical, Japan) was determined using titration method. Kjeldahl steam distillation method was used for determining NH^{+}_{4} - N, where NaOH was replaced with MgO (Cat. No-135-00285, WAKO Chemical, Japan). The Kjeldahl method was used to determine the total N, the organic N and NH^{+}_{4} - N in the all raw and treated solid and liquid samples.

In addition to all forms of N in the solid and liquid samples, macro and micro nutrients and heavy metals were measured in the raw and treated solid and liquid samples using inductively coupled plasma emission spectrometer (ICPS - 8100, Shimadzu, Japan). A standard sample preparation is necessary prior to the measurement using this equipment. Acid digestion using nitric acid (Cat. No-143-01326, WAKO Chemical, Japan) and perchloric acid (Cat. No-162-00715, WAKO Chemical, Japan) are conducted. The digestion is finished within 2-4 days depending on the solubility of the sample. Filtration of digested sample was also conducted to prevent clogging in the ICPS. A standard solution was prepared by diluting with commercially available NIST traceable standard solutions.

Moreover, C, N, macro nutrients, micro nutrients and heavy metals were measured for the treated solid and liquid samples. Finally, pH values of all the liquid samples were measured to verify the applicability of the liquid sample as fertilizer. In order to express the result of the remaining solid fraction and the solubilization ratio of chemical elements after the HTT was defined as:

Solubilization ratio = [(Contentin initial sample - Content in treated sample) ×100]/Content in initial sample

3. RESULTS AND DISCUSSION

As shown in Table 1, BCM contained more moisture compared with LCM, while the N percentage is much higher in BCM than in LCM according to the elemental analysis results of raw samples. The both raw materials show high nitrogen content. Therefore two chicken manures can be considered to be appropriate for extracting nutrients by HTT.

3.1 Solid Solubilization

The solid solubilization is very important for liquid organic fertilizer production from biomass waste by utilizing HTT. The higher the solubilization ratio, more the nutrients are dissolved in to the liquid. The influence of the HT temperature on the solid solubilization ratio is shown in Fig. 3, which indicates that the solid solubilization ratio increased with the increase of HTT temperature and that no significant increase of the solubilization ratio could be observed by increasing the temperature nfrom 180ºC to 200ºC for both types of chicken manure [16].

3.2 Total Nitrogen Solubilization

Nitrogen is one of the major macro nutrients essential for the plant growth. The solubilization of TN in to the liquid is very important for the fertilizer production. Therefore, the influence of HTT on the solubilization of TN is very essential. The percentage of the total N moved from the raw material to liquid was shown in Fig. 4. In all three HTT temperatures, more than 50% of N was moved from solid to liquid and the rest remained in the solid. This indicates that these materials can be utilized to extract nutrients and produce liquid fertilizer. As shown in Fig. 4, the amount of N moved from solid to liquid decreased with the increase of the HTT temperature for both types of chicken manure. The difference between the amount of N moved from solid to liquid at 160ºC and 180ºC is very low. It is known that under the high HT reaction temperature part of ammonical nitrogen can react with the lignin and forms `aminated` lignin or aminophenol [19]. In our experiment both chicken manures contained notable amount of rice husk and probably part of N moved into reaction with lignin and consequently became stable, resulting in slight "loss" of N. On the other hand, 100% decomposition of organic N in to NH_3 by utilizing the Kjeldahl digestion is not possible [20]. According to previous research, nitrogenous compounds containing aromatic heterocycles during the Kjeldahl digestion are difficult to decompose completely or show a reduced nitrogen recovery [21]. This could be the second possible reason that N percentage was higher in the liquid extracted at higher HTT temperatures.

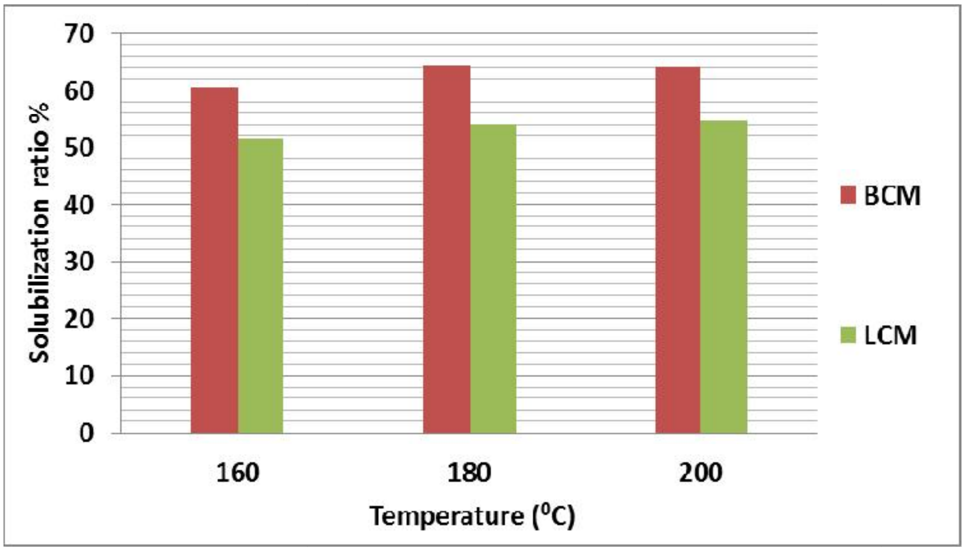

Fig. 3. Solubilization ratio as a function of reaction temperature

Moreover, NH_3 dissolved in the boric acid was measured using the Kjeldahl method in order to find out the loss of N as NH_3 during HTT. The released NH_3 was measured by steam distillation. According to the results, N was not lost as NH_3 during HTT.

3.3 Nitrogen Distribution in the Liquid

The forms of N are very essential to determine N release after application. On the other hand, the availability of N for the plant growth is one of the key factors to be considered in the liquid fertilizer. There were two forms of N found in the fertilizer: organic N and inorganic N. The organic N is slowly available to plants while the inorganic N is immediately available to plants [22]. The percentages of the organic N and the inorganic N (NH_4^+- N) were determined in the treated liquid samples. The results were shown in Figs. 5 and 6. It is obvious that N in the liquid samples is in two forms. It is very hard to determine the N availability and the N release to the plants from organic N [23,24]. In order to release N from organic forms, it should be first mineralized into inorganic forms by microorganisms [24]. The rate of organic N conversion in to inorganic N is not constant throughout the year due to different environmental and management factors [24]. Organic N will be mineralized slowly in years and months [24]. The inorganic N percentage at the HTT temperature of 200ºC was approximately 9% and 13% for the cases of BCM and LCM respectively. Inorganic N percentage was determined in undigested liquid sample by Kjeldahl steam distillation using mixture of MgO and Devarda`s alloy (Cat. No-043-25335, WAKO Chemical, Japan) [25]. After the distillation with MgO and Devarda`s alloy, strong alkaline was added. Then, 6% and 9% of more NH_3 was collected from the liquid obtained from the BCM and LCM respectively [25]. The 6% and 9% of organic N converted to NH_3 in the BCM and LCM, respectively, by adding strong alkaline solution could be more quickly available to plants than the rest of the organic N. The liquid samples obtained from both types of chicken manure have organic N content higher than 80%, which indicates that this liquid can be used as organic fertilizer. However, it could be more attractive among farmers, if the organic N to the inorganic N ratio is in the range from 1:1 to 2:1, as farmers tend to expect prompt effects of the fertilizer. Therefore, some amount of urea needs to be added in order to maintain this ratio in the target range and in order to compete with existing commercial fertilizers.

3.4 pH Value

The pH value is considered as an essential factor because it can affect to quality and suitability of the fertilizer [15]. The fertilizer with low pH value could be harmful to plants [15]. The favorable pH range is between 6-7.5 [12]. Therefore, the pH value was measured in all liquid samples after HTT. The results are shown in Fig. 7. According to this figure, the liquid obtained from both types of chicken manure were weak alkali at HTT temperature of 160ºC. The pH of the liquids decreased with the increase of the temperature. Chicken manures samples have high Ca content so alkaline liquids were obtained. Calcium is an alkali material and it made the liquid obtained from the chicken manures also alkali after HTT with a lower temperature. On the other hand, both liquids extracted from two types of chicken manure after HTT with the temperature of 180ºC were very close to neutral (pH 7). Moreover, at a higher HTT temperature, more organic acid was formed due to decomposition of proteins, fat, and lignin, which neutralized the alkaline Ca and made the liquids acidic as shown in Fig. 7. These results suggest that at HTT temperature of 180ºC, the liquid extracted from chicken manure seems the most suitable as fertilizer because the pH is close to neutral (pH 7).

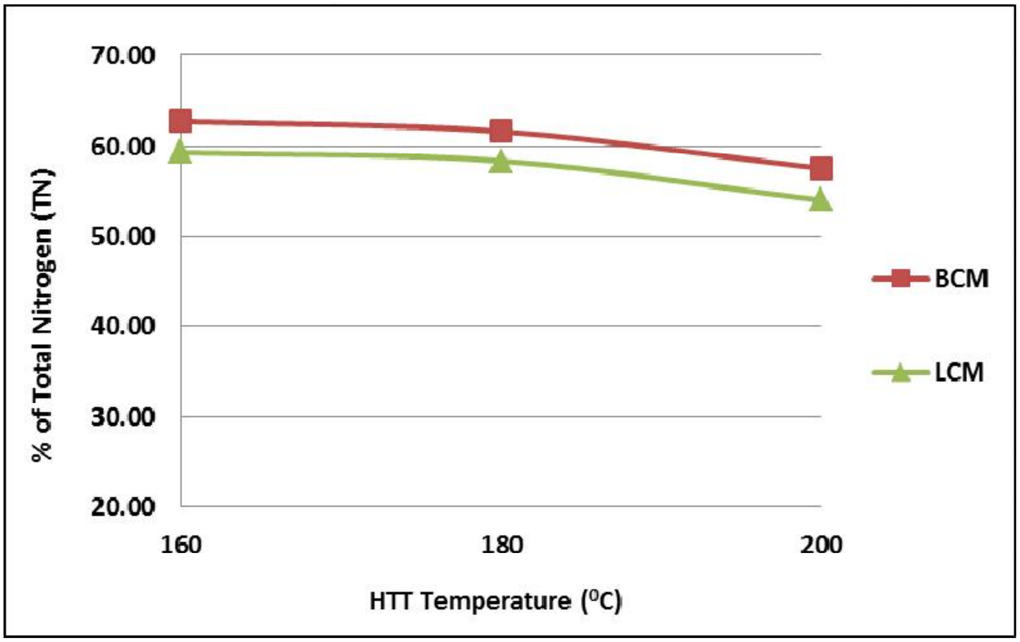

Fig. 4. Percentage of N moved to liquid

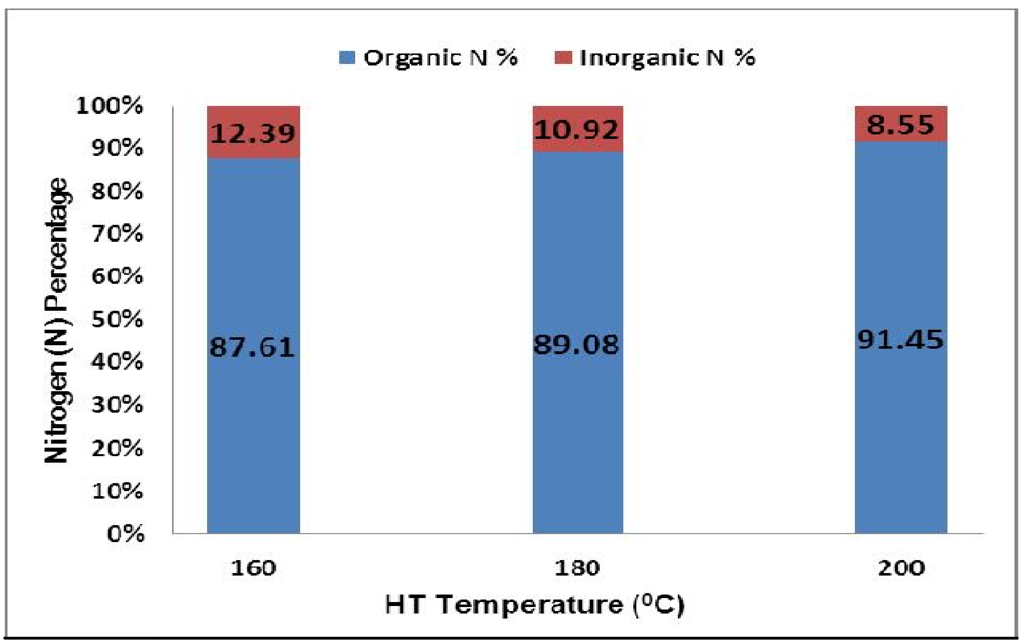

Fig. 5. N distribution in liquid from BCM

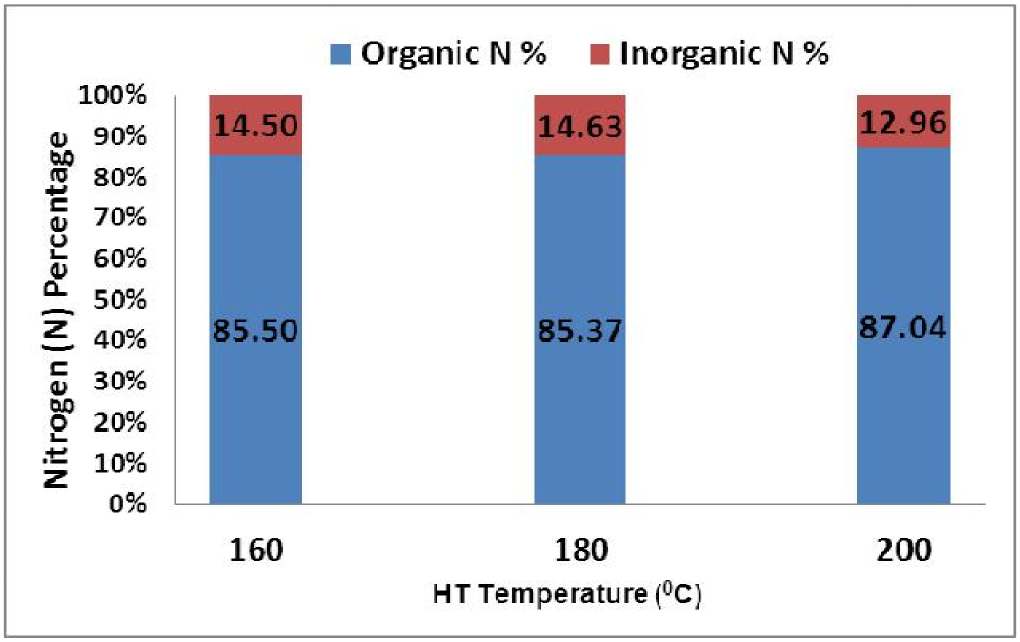

Fig. 6. N distribution in the liquid obtained from LCM

3.5 Macro/micro Nutrients and Heavy Metals in Solid and Liquid

Macro and micro nutrients are essential for the plant growth while heavy metals are very toxic to environment and living beings. Therefore, it is very important to analyze the macro/micro nutrients and heavy metals in the liquid fertilizer before application. By analyzing macro/micro nutrients and heavy metals in the raw and treated chicken manure by using energy dispersive X-ray fluorescence spectrometer, few important trends were found. According to the analytical results shown in Table 2, the heavy metal contents in the raw BCM and LCM were not detected. BCM and LCM were rich in P, K and Ca. In addition to P, K and Ca, other micro nutrients such as Mn were detected in both types of chicken manure. Moreover, Mg and S were detected only in LCM, while Zn was detected in BCM. The amounts of P and Ca are much higher in the laying hen chicken manure than the broiler chicken manure. Moreover, the trend of macro and micro nutrients in the solid fraction before and after HTT suggests that some part of macro and micro nutrients were dissolved into the liquid fraction.

This idea was reconfirmed by the liquid sample analytical results. According to the analytical result shown in Table 3, N and P contents are higher in the liquid extracted from BCM when compared to the liquid extracted from LCM. Moreover K concentrations are high in the liquids extracted from both types of chicken manure. Magnesium was also detected in both types of chicken manure and the amount of Mg in BCM is much higher than LCM. In addition, 400 ml of pure water was used to recover the treated material from the reactor tube in order to make the material balance which dilutes the concentrations of all the nutrients. The minimum amount of water to be used to recover the treated material from the reactor tube is 100 ml. The maximum and minimum concentrations are shown in Table 3.

3.6 C:N Ratio of Solid and Liquid

The C:N ratio is an essential parameter that affects to N immobilization and N release [15]. The acceptable limit of C:N ratio is less than 25 [15]. If it is 15 or even less, it is more preferable [15]. Therefore, it is very important to analyze the C:N ratio variation in both solid and liquid samples. According to the results shown in Figs. 8 and 9, the C:N ratio in solids increased after HTT while the C:N ratio in liquids decreased after HTT, which suggests that more N has moved to the liquid fraction after HTT. The solid fractions of both types of chicken manure after HTT had low N contents and high C:N ratios. Nevertheless, the C:N ratio of solid fraction was high, ratio was less than 25. Therefore, solid fraction could be utilized as solid fertilizer.

Table 2. Macro/Micro nutrients of solids

Sample Name	HTT Temperature	N	P	K	Mg	Ca	Cu	Mn	Co	Mo	Zn	S	Cr	Ni	Cd	Pb
		mg/g	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Broiler chicken manure	Raw	35.3	21.5	68.4	ND	100.9	ND	4.0	ND	ND	3.4	ND	ND	ND	ND	ND
	160	19.7	21.8	ND	ND	168.1	ND	4.5	ND	ND	0.8	ND	ND	ND	ND	ND
	180	20.6	ND	ND	ND	117.9	ND	8.0	ND	ND	19.9	ND	ND	ND	ND	ND
	200	22.6	37.9	22.2	ND	120.3	ND	3.8	ND	ND	4.2	ND	ND	ND	ND	ND
Laying hen chicken manure	Raw	24.1	29.8	14.5	13.1	318.9	ND	3.1	ND	ND	ND	8.6	ND	ND	ND	ND
	160	11.3	33.3	14.6	ND	0.00	ND	3.5	ND	ND	ND	5.0	ND	ND	ND	ND
	180	11.2	44.9	25.6	ND	386.0	ND	4.5	ND	ND	ND	6.8	ND	ND	ND	ND
	200	14.7	52.8	12.1	21.5	378.0	ND	4.9	ND	ND	ND	8.7	ND	ND	ND	ND

ND – Not detected

Table 3. Macro/Micro nutrients in liquid

Sample name	HTT Temperature	N		P		K		Mg		Co		Mo		Zn	
		Max mg/L	Min mg/L	Max mg/L	Min mg/L	Max mg/L	Min mg/L	Max mg/L	Min mg/L	Max mg/L	Min mg/L	Max mg/L	Min mg/L	Max mg/L	Min mg/L
Broiler chicken manure	180	4480.0	1120.0	324.7	81.2	4074.3	1018.6	472.3	118.1	ND	ND	0.3	0.1	2.9	0.7
	200	3808.0	952.0	172.3	43.1	4074.3	1018.6	622.9	155.7	ND	ND	0.2	0.1	ND	ND
Laying hen chicken manure	180	2856.0	714.0	169.4	42.4	4260.5	1065.1	46.1	11.5	ND	ND	0.2	0.1	ND	ND
	200	2772.0	693.0	102.0	25.5	4679.9	1170.0	140.9	35.2	ND	ND	0.1	0.0	ND	ND

ND – Not detected

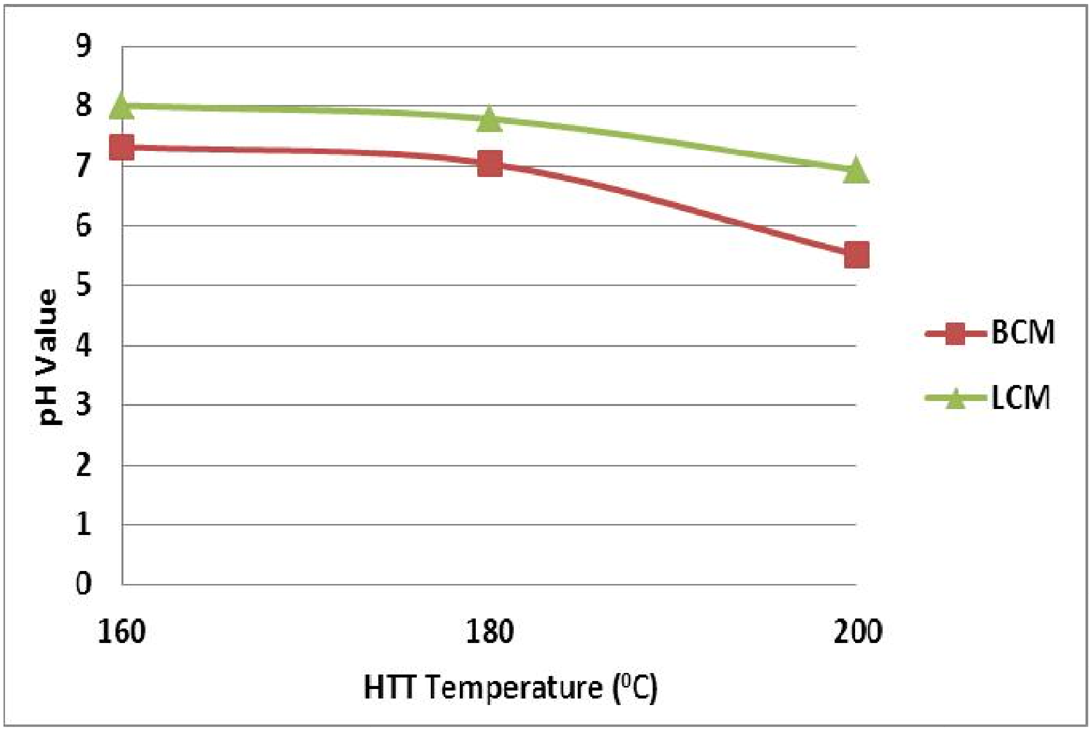

Fig. 7. pH of the liquid obtained from chicken manure

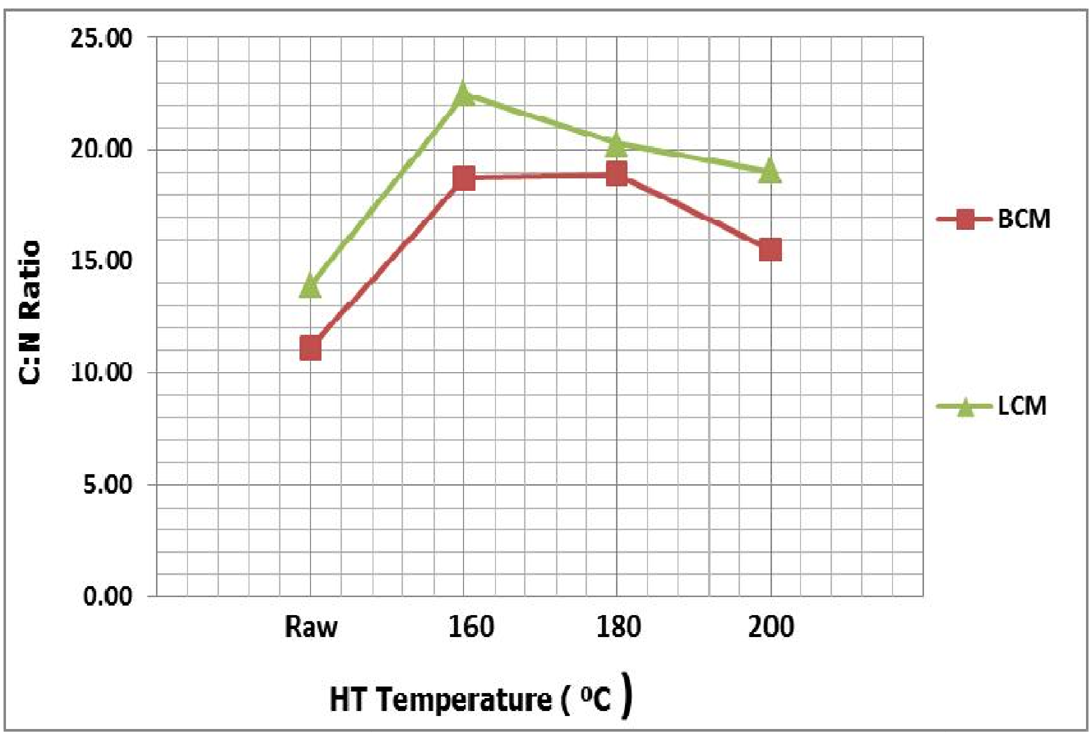

Fig. 8. C: N ratio of solid

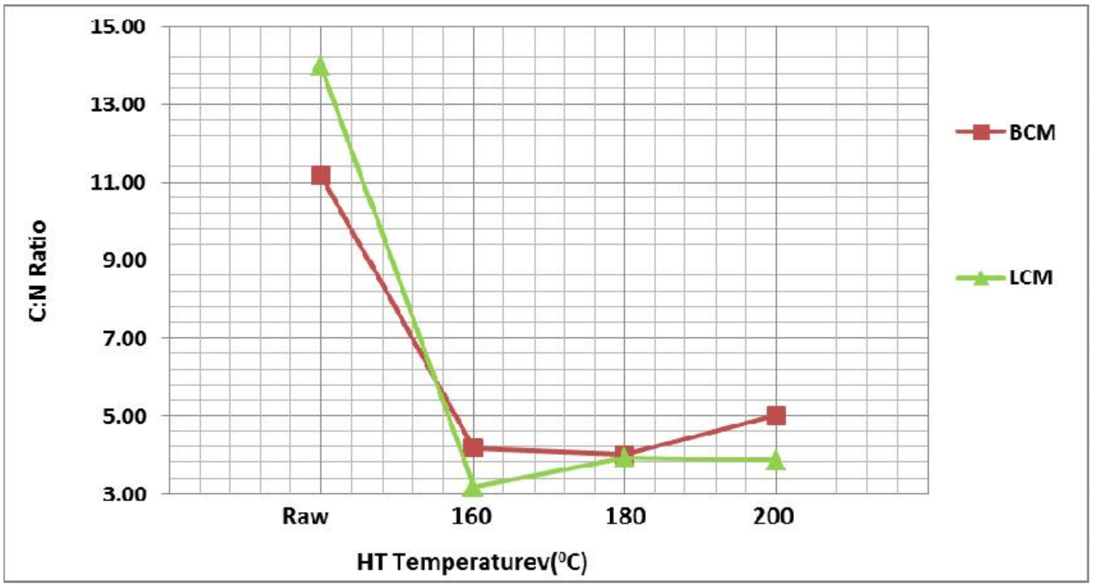

Fig. 9. C:N ratio of liquid

4. CONCLUSION

By considering all the data and results, we can conclude that more than 50% of N can be extracted from solid to liquid after HTT in the BCM and LCM. Moreover, the organic N content was more than 80% in all liquid samples. It is preferred to add urea and control the organic N to the inorganic N ratio in the range from 1:1 to 2:1. According to all the results, 180ºC is the optimum HTT temperature for both types of chicken manures because the liquids extracted at this HTT temperature were close to neutral (pH 7) in both chicken manures. The heavy metal contents in the liquids obtained from the broiler chicken manure and the laying hen chicken manure were not detected, which suggests that the liquid extracted from chicken manure has no risk of environmental pollution caused by heavy metals. It is shown that macro and micro nutrients were dissolved in liquid after HTT. N and P contents were high in the liquid extracted from the broiler chicken manure when compared to the laying hen chicken manure. Moreover K concentration was high in the liquids extracted from both chicken manures. The C:N ratio in solids increased after HTT while the C:N ratio in liquids decreased after HTT, which suggests that more nitrogen has moved to liquid after HTT.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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