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Characterization of Poultry Litter Ash in Environmental Point of View

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Abstract

In this study, a poultry litter ash (PLA) sample was characterized in environmental point of view and examined for its utilization potential as a raw material for P-based fertilizer. Within this scope, several characterization methods, such as ICP-MS, SEM and EDX analyses were conducted. In addition, TS EN 12457-4 leaching test was performed to evaluate leachability characteristics of heavy metals. According to the results, Ca, P and K were determined as the major elements in PLA with 29.54, 6.13 and 4.96%, respectively. Although the sample contains 2472 ppm Zn and 922 ppm Cu, their solubility determined by the leaching test is below the toxicity limit for hazardous waste. In particular, PLA is categorized as inert and non-hazardous waste for the respective solubility of Cu and Zn probably due to the high concentration of zinc. Despite its relatively much lower concentration compared to copper, solubility of Cr makes PLA non-hazardous because of high mobility of chromium, especially hexavalent state. In terms of the major elements, about 290 mg/l Ca was detected in the leachate, resulting in a pH value higher than 13. High Ca solubility makes PLA a highly alkaline waste, causing the major difficulty for its direct use as a fertilizer. P concentration in the leachate was found only 0.0092 mg/l, which also limits the use. Overall results have suggested that the poultry litter ash sample examined could have a utilization potential as a partial replacement material for the production of P-based fertilizers. However, its high alkalinity should be neutralized prior to its use.

Keywords: Characterization, Environmental effect, Poultry litter ash, P-based fertilizer.

1. INTRODUCTION

The global livestock industry has been largely expanding to meet the incessantly increasing demand for food. It accounts for 40-50% of worldwide agricultural gross domestic product and provides one-third of humanity's protein need [1], [2]. Global livestock production is expected to increase by 14% between 2020 and 2029, about half of which will belong to poultry mainly due to its short production cycle and relatively low price compared to other protein sources [2], [3]. In addition, according to the European Union, there will be 8.44% increase in poultry meat production from 2019 to 2027 [4]. Hence, a large quantity of poultry litter is generated, probably aggravating the management of this waste [2], [4].

Poultry litter is a mixture of bedding material, waste feed, dead birds, broken eggs and chicken feathers. Its generated amount varies in the range of 1.5-5.7 kg of litter/bird [2]. The annual production of dry chicken manure in the USA alone is around 12 billion pound [5]. The traditional recycling method of poultry litter is direct land application as a source of nutrients (N, K and P) for agricultural crops. However, intensive poultry

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farming dramatically changed this situation, resulting in various environmental issues including eutrophication of water bodies, spread of pathogens, production of phytotoxic substances, air pollution and greenhouse gases, mainly methane and nitrous oxide [2], [6], [7].

Although there are some alternative technologies such as compaction, composting, anaerobic digestion and solid-liquid separation, the most suitable management of poultry litter is considered as thermal processes including combustion, pyrolysis and gasification mainly due to its relatively low moisture content as well as recovery of energy and nutrients [2], [6]. From the thermal processes, the most desirable technology with commercial scale applications is by far combustion which is currently used in the USA, UK and Netherlands for the production of heat and electricity and recovery of poultry litter ash (PLA) [2].

The type of poultry, feeding properties, bedding materials and the incineration process conditions used determines the elemental composition of PLA. Typically, PLA contains 2-10% P, 12-32% Ca and 6-15% K in oxide forms, making it a potential raw material for P-based fertilizers. However, it also includes heavy metals such as Cu and Zn originating from poultry diet as a typical supplement and bedding materials. This may constitute a significant obstacle for direct use of PLA as a fertilizer depending on local legislation [2], [4], [7]–[9]. Since the reuse of waste and by-products is a fundamental principle of circular economy, accurate characterization of PLA especially for its heavy metal contents should be determined for its possible bulk utilization, which seems to be as a raw material for P-based fertilizers [4].

In this study, an ash sample resulted from combustion of chicken litter was characterized in environmental point of view and examined for its utilization potential as a fertilizer.

2. EXPERIMENTAL

2.1. Materials

The poultry litter ash sample was provided from Güres Power Plant (Turkey). The PLA sample used is generated as the underflow product of the cyclone in the biomass power plant. The sample was first dried for 24 h at 105°C prior to its use. The solid sample was digested with a mixture of hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acids for subsequent determination of elements based on the European standard EN 13656:2002 [8]. Distilled water was used throughout the experiments.

2.2. Methods

Elemental composition and heavy metal contents were determined by an Agilent 7800 inductively coupled plasma (ICP)-mass spectroscopy (MS) instrument after the complete digestion of the sample with microwave assisted operation. Within this scope, Ca, P, K, Mg and Na were analyzed as major elements while heavy metal contents were determined for seven elements including Cu and Zn. Leachability characteristics were also examined for the heavy metals in accordance with TS EN 12457-4 leaching test [10]. According to this test, suspension with liquid to solid ratio of 10 by mass was first prepared using distilled water and then continuously agitated for 24 h at 25°C. After filtration, the filtrate was then analyzed by ICP-MS. The regulation of hazardous waste in Turkish standard (Appendix 11-A) was used to evaluate the obtained heavy metal contents for their toxicity limits [10]. The pH measurements were also performed on the leachate using a calibrated Mettler Toledo pH-meter. Furthermore, microstructural characterization and point elemental contents were determined using a high-resolution Zeiss Sigma 300 scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer.

3. RESULTS AND DISCUSSION

3.1. Chemical Composition

Table 1 shows elemental composition of the PLA sample determined by ICP-MS analysis. As seen in Table 1, since Ca is the main supplement added as a calcium phosphate and Na, K and Mg are nutrients typically added as chlorides in the poultry diet, Ca was detected as the major component in the sample with 29.54% by weight, followed by P and K with 6.13 and 4.96%, respectively. On the other hand, Si, Fe and Al were found as minor elements, all of which have concentrations less than 1%. All of these results are in line with the literature studies conducted by Pandey et al. and Rivera et al. [2], [11].

Heavy metal concentrations of the sample are given in Table 2 for seven elements. As clearly seen in Table 2, concentrations of Zn and Cu are a way higher compared to the other elements examined. Specifically, concentrations of Zn and Cu were sequentially determined to be 2472 and 922 ppm whereas all of Ni, Cr, Pb, Cd and Co have a concentration less than 50 ppm. Similar results were also reported in the literature studies [11].

Table 1. Elemental composition of the PLA sample

Element	**Content (Wt. %)**
Ca	29.54
P	6.13
K	4.96
Mg	2.83
Na	1.15
Si	0.92
Fe	0.37
Al	0.18

Table 2. Heavy metal concentrations of the sample

Heavy metal	**Concentration (ppm)**
Zn	2472
Cu	922
Ni	35.36
Cr	30.17
Pb	27.82
Cd	13.04
Co	3.93

The leachability characteristics of seven heavy metals from PLA are exhibited in Table 3. According to Table 3, PLA is far from being considered as hazardous waste in terms of the leaching capacities of all the metals examined except Cr and Zn, which was determined in the region of non-hazardous waste. In addition, solubility of Cd, Co, Cu, Ni and Pb are even a way below the toxicity limits for non-hazardous waste. In particular, based on the TS EN 12457-4 leaching test, solubility of Cr and Zn were found as 0.4338 and 1.1950 mg/l, respectively. As seen in Table 2, although PLA contains much higher Cu concentration (922 ppm) than Cr (30.17 ppm), high solubility of chromium can be attributed to its extremely high mobility, particularly its hexavalent state.

Table 3. Leachability characteristics of heavy metals

Element	**Solubility (mg/l)**	**Toxicity limits (mg/l) (Appendix 11-A)**		
		IW[a]	**NHW[b]**	**HW[c]**
Cd	0.0009	≤ 0.004	0.004-0.1	< 0.1-0.5
Co	0.0001	NI[d]	NI[d]	NI[d]
Cr	*0.4338*	≤ 0.05	*0.05-1*	< 1-7
Cu	0.0033	≤ 0.2	0.2-5	< 5-10
Ni	0.0002	≤ 0.04	0.04-1	< 1-4
Pb	0.0014	≤ 0.05	0.05-1	< 1-5
Zn	*1.1950*	≤ 0.4	*0.4-5*	< 5-20

[a] Inert waste.
[b] Non-hazardous waste.
[c] Hazardous waste.
[d] Not included.

In addition to the heavy metals, the leachability characteristics of the two major elements, Ca and P, were also determined in accordance with the TS EN 12457-4 leaching test. According to the experimental results, concentrations of Ca and P in the leachate were found as 289.8102 and 0.0092 mg/l, respectively. Low water solubility of P was also reported in the literature [12]. Furthermore, pH of the leachate was measured as 13.12. Both low water solubility of P and highly alkaline properties constitute a significant obstacle for direct use of the PLA as a fertilizer, all of which are also well correlated with the literature [11].

3.2. Microstructural Characterization

Figure 1 illustrates the SEM images of PLA sample. General view of particles seen in Figure 1 (a) indicates that PLA is generally composed of coarse particles with average size of 40-50 µm. The SEM images with different magnifications can also be seen in Figure 1 (b)-(d). According to Figure 1 (c)-(d), PLA sample consists of particles with various sizes and irregular shapes and mainly two crystalline phases, hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and calcite ($CaCO_3$) [11].

Point elemental contents of PLA were examined using EDX analysis conducted during the SEM investigations. According to the EDX spectra shown in Figure 2, in line with the ICP-MS analysis, O, Ca, P and K constitute the main structure of the sample. Specifically, Ca, P and K contents were sequentially found as 36.40, 14.54 and 2.78% by weight as seen from the table in Figure 2.

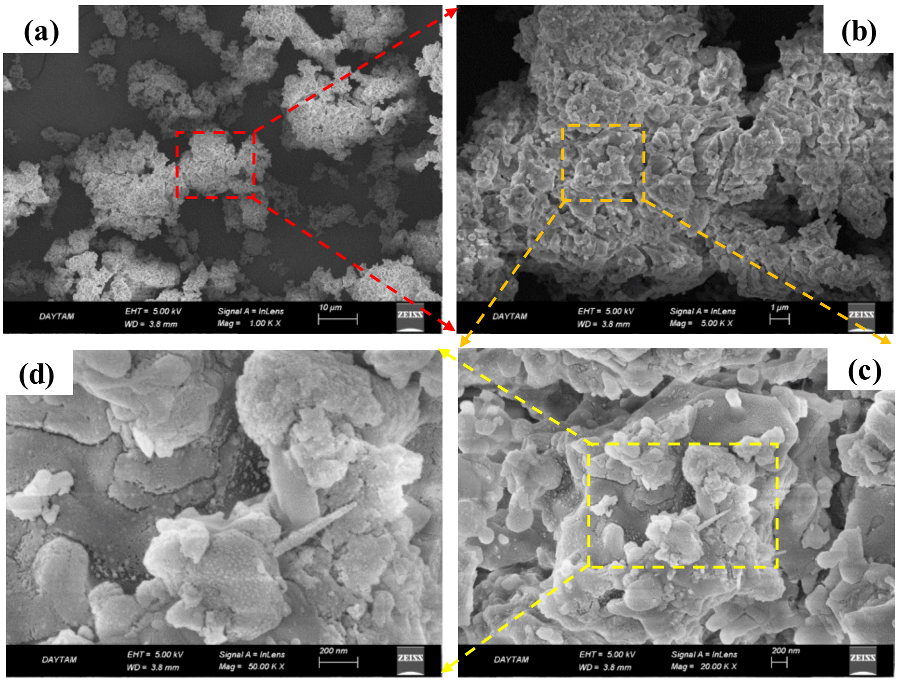

Figure 1. SEM images of PLA sample

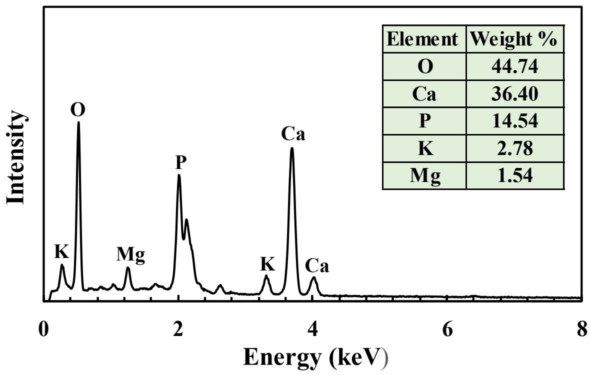

Figure 2. EDX spectra and elemental composition of the PLA sample

4. CONCLUSION

In this study, a poultry litter ash sample was characterized in environmental point of view. According to the experimental results, the sample is mainly constituted by oxide forms of Ca, P and K, which were found as the respective 29.54, 6.13 and 4.96% as a result of the poultry diet. Zn and Cu were determined as the major heavy metals with the concentrations of 2472 and 922 ppm, respectively. However, solubility of Cu with water is a way below the toxicity limit for non-hazardous waste while that of Cr and Zn were determined in the region of non-hazardous waste probably due to high mobility of chromium and high concentration of zinc in the sample. In terms of the major elements, Ca has high solubility with a concentration of about 290 mg/l in the leachate, making PLA a highly alkaline waste. This is the major difficulty for its direct use as a fertilizer which is also hindered by the low water solubility of P with 0.0092 mg/l. Overall results have shown that although PLA sample is not labeled as a hazardous waste, its direct application on land seems to be not possible mainly due to its very high alkalinity and low water solubility of P. On the other hand, PLA can be used as a partial replacement material for the production of P-based fertilizers after removing its highly alkaline conditions. If it is dumped as a waste in landfill, storage conditions should be carefully controlled.

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