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Research Article

Utilization potential of poultry litter ash as phosphorus-based fertilizer

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ABSTRACT

A large quantity of poultry litter is globally generated as a result of expanding poultry industry. From several alternative technologies, one of the most feasible management for this waste is combustion, which exhausts poultry litter ash (PLA) as the main by-product. In this study, a PLA sample was examined for its utilization potential as a raw material for phosphorus-based fertilizer. According to the experimental results, Ca, P and K were determined as the major elements in the PLA sample 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 terms of the major elements, about 290 mg/l Ca was detected in the leachate, resulting in a pH value higher than 13, whereas P concentration was found only 0.0092 mg/l. These two crucial results constitute the major difficulties for direct use of the PLA as a fertilizer. On the other hand, a usable P-rich product with low heavy metal contents and neutral pH can be obtained through acidification, heavy metal removal and neutralization processes. However, in this case, the feasibility of processes to be used should be carefully considered in economic point of view. In conclusion, direct application of the PLA sample examined as P-based fertilizer is not possible without any pre-treatments mainly due to its very high alkalinity and the low water solubility of P.

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INTRODUCTION

The substantial increases in global human population and the resultant incessant demand for food have resulted in an increased need for fertilizers. Therefore, sustainable fertilizer production, especially phosphorus-based (P) mainly met by non-renewable mineral sources has a vital importance. Although the worldwide phosphate rock is far from exhaustion with the estimated reserve more than 300 billion tons, its non-renewable characteristic, decrease in the amount of high-quality phosphate rock, the continuously increasing prices of P-based fertilizers and the need to keep the sustainability of agricultural systems have motivated researchers to look for lower-cost and renewable alternative phosphorus sources [1–3]. One promising solution can be the use of animal processing wastes for this purpose [1–4].

Poultry litter (PL) consists of a mixture of bedding material, waste feed, dead birds, broken eggs and chicken feathers. Expanding poultry industry generates high amount of poultry litter varying in the range of 1.5–5.7 kg of litter/bird [5–7]. Around 12 billion pounds of dry chicken manure is annually generated in the USA alone while this value is estimated more than 2 billion tons in Europe [8, 9]. Direct land spreading is accepted as the traditional method for the disposal of PL due to its high nutrient inclusion (N, K and P) for agricultural crops. However, intensive poultry farming causes some deleterious environmental impacts such as eutrophication of water bodies, spread of pathogens, production of phytotoxic substances, air pollution and greenhouse gases [5, 10–12].

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From various alternative technologies, thermal processes such as pyrolysis, gasification and especially combustion are considered as one of the most suitable management approaches of poultry litter mainly because of their technical, economic and environmental feasibilities. These feasible properties are suitability of poultry litter for thermal processes attributed to its relatively low moisture content as well as recovery of energy and nutrients attained as a result of the processes [5, 10]. In particular, combustion is accepted as the most widely used thermal process with commercial scale applications primarily due to its economic outcomes. In the USA, UK and Netherlands, combustion is currently and conventionally used for the production of heat and electricity. The main by-product or waste generated as a result of the process is poultry litter ash (PLA) including high nutrient contents [5, 13].

Chemically, as expected from a combustion by-product, PLA mainly consists of oxide forms of Ca, P and K in high amounts. In elemental basis, it generally contains 12–32% Ca, 6–15% K and 2–10% P, which is mainly determined by the poultry type, feeding properties, bedding materials and combustion conditions used. Relatively high K and P contents make PLA a potential raw material for fertilizers. Nevertheless, heavy metal contents of PLA especially Cu and Zn resulted from the respective poultry diet and bedding materials limit significantly its direct use depending on local legislation [5, 11, 14–16]. Since the reuse of waste is the main principle of economic and environmental sustainability, utilization potential of PLA as a phosphorus source should be studied in detail [14, 15].

In this study, a PLA sample resulted from the combustion of chicken litter was examined as a raw material for phosphorus-based fertilizer. Within this scope, several characterization analyses such as ICP-MS, SEM and EDX and a leaching test were conducted to determine its chemical composition, microstructural properties and leachability characteristics.

EXPERIMENTAL

Materials

The poultry litter ash (PLA) sample used is underflow product of cyclone in a biomass power plant. Prior to its utilization in the experimental stage, the PLA sample was first dried for 24 h at 105 °C. Analytical grade hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acids were used for the sample digestion. Distilled water was used throughout the experiments.

Methods

Inductively coupled plasma (ICP)-mass spectroscopy (MS) analysis, conducted by an Agilent 7800 instrument, was used to determine the elemental composition of the PLA sample as well as its heavy metal contents after the microwave assisted-acid digestion (MW-AD) based on the European standard EN 13656:2002 [16]. Leachability characteristics of major elements and heavy metals were investigated using distilled water to PLA ratio of 10 by mass in accordance with TS EN 12457-4 leaching test [17]. Similarly, the filtrate was analyzed by ICP-MS after the leaching test. Toxicity limits of heavy metals were determined through the regulation of hazardous waste in Turkish standard (Appendix 11-A) [17]. pH of the leachate was measured by a calibrated Mettler Toledo pH-meter. A high-resolution Zeiss Sigma 300 scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer was used to examine the microstructural properties and to determine the point elemental contents.

Table 1. Elemental inclusion of the 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 contents in the PLA sample

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

RESULTS AND DISCUSSION

Chemical Composition of the Sample

Elemental composition of the PLA sample is exhibited in Table 1. In accordance with the literature studies, since dicalcium phosphate is the main supplement in the poultry diet, Ca was detected as the highest-content element with 29.54% by weight as expected [13]. The other major elements were P and K with the respective contents of 6.13 and 4.96% resulted from the nutrients of Na, K and Mg typically added as chlorides. On the other hand, Si, Fe and Al were determined as minor elements with the concentrations less than 1%. All of these results are in line with the literature investigations conducted by Pandey et al., and Rivera et al., [5, 18].

Table 2 shows heavy metal contents in the sample. According to Table 2, concentrations of Zn and Cu are a way higher compared to the other elements examined with the respective 2472 and 922 ppm. All of the others, Ni, Cr, Pb, Cd and Co have a concentration less than 50 ppm. Similar results were also reported in the literature studies [15, 18].

Table 3. Solubility of the heavy metals and their toxicity limits

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.

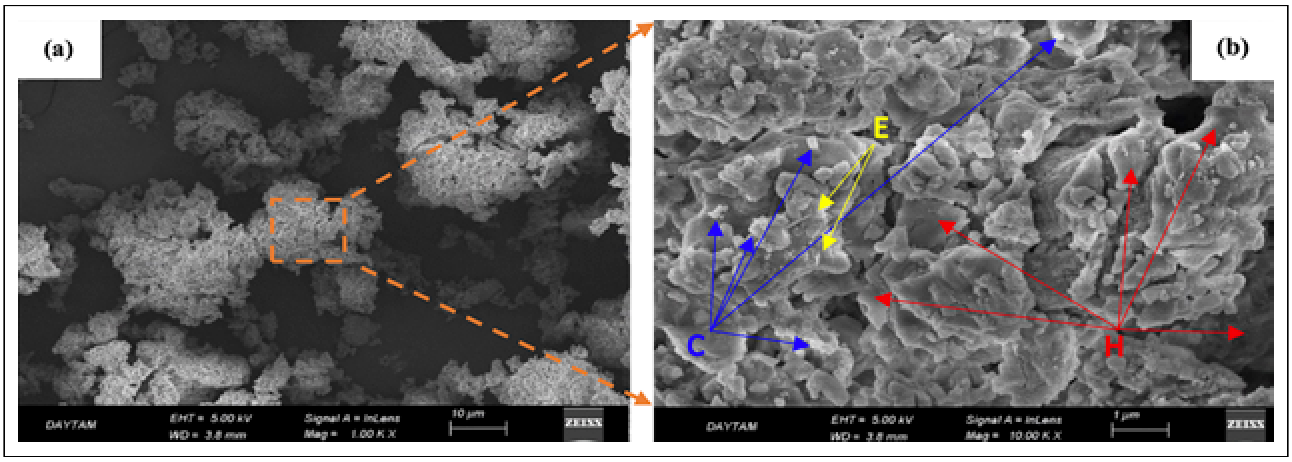

Figure 1. SEM images of the PLA sample. (H: Hydroxyapatite, C: Calcite and E: Ettringite).

Leaching Test Results of the PLA sample

Table 3 shows the leachability characteristics of the heavy metals from the PLA sample. As seen in Table 3, the PLA sample is clearly far from being considered as hazardous waste in terms of the solubility of all the metals examined except Cr and Zn, which were placed in non-hazardous waste region. Furthermore, leaching capacities of Cd, Co, Cu, Ni and Pb are even a way below the toxicity limits for non-hazardous waste. In other words, the sample can be labeled as an inert waste in terms of the solubility of these metals based on Appendix 11-A. Specifically, the solubility of Cr and Zn were determined to be 0.4338 and 1.1950 mg/l, respectively. Although the sample contains much higher copper (922 ppm) than chromium (30.17 ppm) which is indicated in Table 2, the higher solubility of chromium, 0.4338 mg/l, with respect to that of copper, 0.0033 mg/l, can be mainly attributed to its extremely high mobility, particularly its hexavalent state [19].

The leachability characteristics of Ca and P were also determined based on the leaching test conducted. The experimental results indicated that Ca and P concentrations in the leachate were determined as 289.8102 and 0.0092 mg/l, respectively. Low water solubility of phosphorus was also reported in the related literature which also indicates that phosphorus in waste materials has a low bioavailability, i.e., poorly available form to plants [3, 20, 21]. Therefore, prior to its use as a fertilizer, mainly acid treatment with chemical and biological methods must be used to form dissolved phosphates [3, 22]. In addition, pH of the leachate was measured as 13.12, which is certainly attributed to high water solubility of calcium. The general leaching test results show that direct use of the PLA as a fertilizer seems to be not possible mainly due to its low water-soluble phosphorus content and highly alkaline properties. All of these results are also well correlated with the literature studies [15, 18].

Microstructural Characterization

Figure 1 illustrates the SEM images of PLA sample. General view seen in Figure 1a indicates that PLA is generally composed of irregularly-shaped particles with an average size in the range of 60–70 μm. In addition, as seen in Figure 1b, particles tend to be more rounded as particle size decreases. Figure 1b also demonstrates that PLA sample mainly consists of two crystalline phases, hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and calcite ($CaCO_3$), and also includes low amount of needle-shaped ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) crystals. Moreover, according to the related literature, it may also contain other Ca-bearing compounds such as lime (CaO) and portlandite ($Ca(OH)_2$), and amorphous Ca-phosphate phase. Furthermore, potassium sulfate compounds can also be found as aphthitalite ($K_{2.25}Na_{1.75}(SO_4)_2$) and arcanite ($K_2SO_4$) [11, 15, 18].

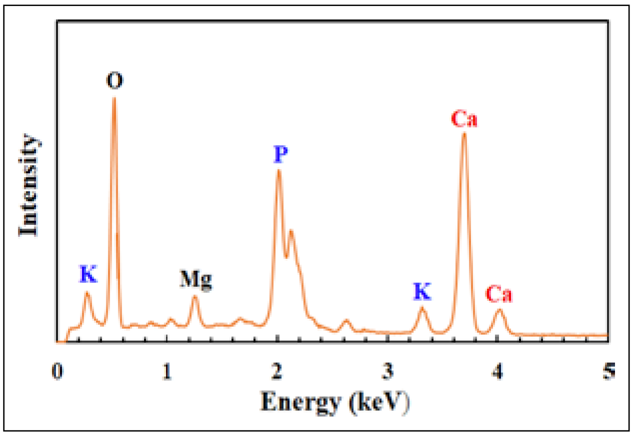

Figure 2. EDX spectra of the PLA sample.

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. Table 4 exhibits the point elemental contents based on the EDX measurements. As seen in Table 4, Ca, P and K contents were sequentially found as 36.40, 14.54 and 2.78% by weight. Compared to the ICP-MS results, lower K and higher Ca values were detected with EDX while much higher P content were obtained. This can be attributed to the nature of EDX, representing only the point where the measurement is taken not the whole sample. Similar differences were also reported in the related literature [15].

FINAL DISCUSSION

The ICP-MS analysis and TS EN 12457-4 leaching test conducted through the experimental stage have indicated that though its high P inclusion, 6.13%, the PLA sample examined has a very low water soluble-P content, which is determined to be only 0.0092 mg/l. This is the primary obstacle for its direct use as a P-based fertilizer. In order to increase the content of bioavailable phosphorus, various processes such as chemical and biological treatment methods must be used [3, 22]. In addition, high heavy metal contents of the sample constitute another limitation for its direct use due to strict local legislation. According to the Poultry Litter Protocol in the UK and Ireland, the upper acceptable concentrations of heavy metals for the use of poultry litter ash as agriculture fertilizer are given in Table 5.

As seen in Table 5, the PLA sample exceeds the upper acceptable limits in terms of Zn, Cu, Ni and Cd inclusions. This means that although the PLA is not labeled as a hazardous waste based on the TS EN 12457-4 leaching test exhibited in Table 3, its direct utilization as a fertilizer is not recommended due to potential threat to human health or the environment. A heavy metal removal process like ion exchange can be used to meet the limits [22, 23]. Furthermore, high alkalinity resulted from high water solubility of Ca also limits the direct use of the sample. For this reason, the leachate should be neutralized prior to its utilization [22].

Table 4. EDX point elemental contents

Element	Content (Wt. %)
O	44.74
Ca	36.40
P	14.54
K	2.78
Mg	1.54

Table 5. Upper acceptable limits of heavy metals within poultry litter ash used as a fertilizer

Heavy metal	Concentration within PLA sample the (ppm)	Upper limit in the UK and Ireland (mg/kg) [23]
Zn	2472	2063
Cu	922	596
Ni	35.36	24
Cr	30.17	31
Pb	27.82	244
Cd	13.04	3
Co	3.93	11
As	ND[a]	17
Hg	ND[a]	0.5
Mn	ND[a]	3500
Mo	ND[a]	45
Se	ND[a]	11
V	ND[a]	20

a: Not determined.

CONCLUSION

Overall results have suggested that although the poultry litter ash sample examined contains high amount of P (6.13%), its direct application as phosphorus-based fertilizer seems to be not possible mainly due to its very high alkalinity (pH 13.12) and the low water solubility of P (0.0092 mg/l). However, a soluble-P-rich product with a utilization potential as direct or partial replacement material can be obtained through few treatment steps, which are acidification, heavy metal removal and neutralization processes. Since P extraction by acid leaching is much more important than the other two processes, acid requirement is vital in this case for the economic feasibility of final product to be used as P-based fertilizer. Although the ash sample is not labeled as a hazardous waste in terms of the leachability characteristics of the heavy metals examined, its direct application on land is not considered as an environmentally friendly approach because of its highly-alkaline nature.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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