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Phytoremediation of Heavy Metal on Entisols and Plant Uptake Amended with Palm Oil Mill Effluent (POME) Sludge

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ABSTRACT

Palm oil mill effluent (POME) sludge was derived from about 50% of wastewater effluent of fresh fruit bunch (FFB) productions. The objective of this study is to determine the effect of contaminant status which was applied with POME sludge on Entisols and plant uptake of maize growth. POME sludge obtained from the Jengka 8 FELDA Palm Oil was used in this study. The maize (Zea mays) was used as a test crop and planted in Rasau series soil (Entisols). The soil, leaves and stem samples were air-dried, homogenized and sieved. Heavy metal analysis identified the existence of Cu, Cr, Cd, Zn, Pb, Ni and Mn elements by the sequential extraction procedure using optical emission spectrometry (ICP-OES). The physicochemical of POME sludge showed that most heavy metals in each treatment fulfilled the WHO/FAO standard and were safe for human consumption. After applying treatments on Entisols, a small amount of Cu, Cr, Zn, Pb, Ni and Mn was retrieved from the exchanges phase. Small amount of Cr, Ni and Mn were identified in the stems and leaves. Zn, Cd, Pb and Cr were not detected in the bioavailable forms, while Cu was only available in the mixing ponds sludge samples. The results showed that most heavy metal properties contained low residual fractions from the soil and plant uptake in stems and leaves. The application of POME sludge in agricultural practices might offer a sustainable utilization of waste materials in the oil palm plantation.

Keywords: Entisols, Phytoremediation, POME sludge amended.

1. INTRODUCTION

The palm oil industry is one of the most important commodity products, worth about 8% of total Malaysia's GDP in 2015 [1]. Malaysia planted nearly 4.70 million hectares and set up 416 mills across the country, which is expected to generate over 19.8 million tonnes of Empty Fruit Bunches (EFB, wet weight) and 60 million tonnes of palm oil mill effluent (POME) [2]. Hence, the majority of the oil palm production contributed significantly to the environmental problem which mainly derived from biomass waste such as palm oil mill effluent (POME). Palm oil mill effluent (POME) consists of suspended solids and dissolved solids left in the mills and discharged into the treatment ponds, commonly known as palm oil mill effluent sludge. Therefore, the amount of sludge was increased significantly due to the huge quantity of POME production each year [3]. POME sludge consists of high nutrient values [4]. Recent studies have shown that the treated

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POME sludge was suitable and in accordance with the WHO-ML standard of safety for human consumption in terms of heavy metal contents and microorganisms (Table 1). Mostly, oil palm waste is widely available and virtually free [5]. However, the sludge produced a bad odor and was considered a source of pollution. Therefore, the industry players were adopting a more cost-effective approach and sustainable technologies for disposing of the industrial sludge. According to Khairuddin et al. (2016) [3], recent studies showed that proper management and treatment processes of POME sludge in the ponds might utilize the abundant materials and turn them into beneficial organic matter for plant consumption. Hence, it is possible that in the upcoming years, adopting proper treatment techniques and methodologies, the abundant POME sludge issues will be resolved as it was possible to be processed and produced as an organic fertilizer. Comparison between POME sludge [3], final compost, POME mixing with empty fruit bunch [6] and WHO-ML Standard [7], identified that the heavy metal contents were insignificant difference.

Table 1 Comparison of heavy metals analysis of POME sludge.

Parameter	Cu (mg kg^{-1})	Cr (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})	Ni (mg kg^{-1})	Mg (mg kg^{-1})
POME Sludge (Khairuddin et al., 2016)	45.05 ± 2.87	27.86 ± 0.55	0.41 ± 0.01	130.11 ± 3.49	0.38 ± 0.10	10.77 ± 0.15	422.56 ± 12.04
Final compost (Wan Razali et al, 2010)	70.40 ± 21.60	9.30 ± 0.20	4.10 ± 0.50	90.70 ± 10.00	4.20 ± 1.60	n.d	250.40 ± 25.10
WHO-ML Standard (FAO/WHO, 2011)	75.00	150.00	1.90	140.00	0.30	67.00	500.00

1.1 Palm Oil Mill Effluent (POME) Sludge

Generally, the POME was found to have high heavy metal contents, nevertheless, in this study, heavy metal contents was important to determine the safety usage for human as an organic fertilizer. Furthermore, the heavy metals content in the treatment pond system was identified below the WHO-ML standard measurement [8]. Heavy metals such as cadmium, plumbum, mercury, chromium, nickel, and manganese were present in the POME. According to Bigdeli and Seilsepour (2008) [9], cadmium was a highly mobile metal, easily absorbed by the roots and moved into the wood tissue before it was transferred to the upper parts of the plants. The main source of cadmium in the air was found in the burning of fossil fuels such as coal or oil and similar to the incineration processes by municipal waste treatment [10]. The treated POME sludge consisted of heavy metals that were below the WHO-ML standard and suitable for fertilizer application [8].

1.2 Entisols

According to the Department of Agriculture Malaysia (2010) [11], the Rasau series soil consisted mainly of fine sandy clay loam and low organic matter content. In addition, cation exchange capacity was identified <5 cmol (+) per kilogram and low base saturation. Rasau Series soil showed low pH at 3.65 ± 0.15, low electrical conductivity at 2.21±0.12 dS/m, and availability of macronutrients such as phosphorus (P) and low magnesium (Mg) content. The amount of Potassium (K) was acceptable [12]. Table 1 shows the total phosphorus in the Rasau series soil at 6.55±1.27 mg/kg, indicating that the soil contained slightly higher P on the surface layer [12]. This amount was considered low compared to 3-10 mg/kg of soil P reported by the Department of Agriculture [11].

Table 2 Available nutrients and chemical properties of Rasau series soil [12].

Horizon	Depth (cm)	P (mg/kg)	Available K (cmol/kg)	Available Ca (cmol/kg)	Available Mg (cmol/kg)	CEC (cmol/kg)
A	0-8	7.96	0.08	0.09	0.09	3.12
AB	8-20	6.68	0.06	0.02	0.04	3.37
BA	20-80	6.26	0.05	0.01	0.03	2.75
B	>80	5.54	0.05	0.02	0.03	2.54
Average	0-20	6.55±1.27	0.06	0.035	0.047	

In this study, the maize (*Zea mays*) was used as a phytoremediation associated with soil to reduce the concentration effects of heavy metals. According to Ali et al. (2013) [13], plants generally handle heavy metal contaminants without affecting topsoil, thus conserving their utility and fertility. The objective of this study was to investigate the phytoremediation of Entisols and plant uptake (leaves and stem) amended with palm oil mill effluent sludge on heavy metal content. The information generated from this study was valuable to determine the soil status and understanding of the contamination assessment of POME sludge.

2. MATERIAL AND METHODS

The samples of POME sludge were collected from Jengka 8 Felda Palm Oil Mill, Bandar Tun Abdul Razak Jengka, Pahang. Each sample was taken from the different pond systems that were cooling, anaerobic, facultative, algae and dumping ponds based on the different hydraulic retention times (HRT) (Figure 1). The hydraulic retention time was used as the reference of the palm oil mill effluent maturity stage before it was released into the stream in accordance with the DOE (Department of Environment) standard. Overall, the current processing of the palm oil mill abiding the HRT of pond treatment was set above 100 days [14]. The sample was dried and sieved in fine texture before it was applied in the field.

The field trial was set up at Research Farm in Universiti Teknologi MARA Pahang campus, Jengka, Bandar Tun Abdul Razak, Pahang. The period of the experiment was from February 2015 until June 2016. Bandar Tun Abdul Razak Jengka, Pahang (3.7562 °N, 102.5611 °E) acquires a relative humidity of 70–90 %. The average farm temperature ranged between 31 and 35°C. Rasau series soil was used in this study due to its low fertility and left abundantly in the area. Based on the USDA standard of Rasau series soil was classified as Entisols. It was air-dried, homogenized and sieved using a 2 mm sieve.

The experiment consisted of 16 cm × 20 cm polybags filled with 10 kg of amended soils. The polybags were arranged in randomized completely block design (RCBD) with three replications. The maize plant (Zea may L.) variety Hibrimas was amended with POME sludge from mixing ponds (MP), anaerobic ponds (ANP), facultative ponds (FP), algae ponds (ALP), dumping ponds (DP) and untreated (control) which mixed homogenously in the polybag. The drip irrigation system was used for watering the maize based on plant-available water (PAW). The maize was harvested after 75 days of planting (DAP).

The soil samples amended with POME sludge from mixing ponds (MP), anaerobic ponds (ANP), facultative ponds (FP), algae ponds (ALP), dumping ponds (DP) and untreated (control) were taken for heavy metals analysis. In addition, the leaves and stem samples were also analyzed to determine the heavy metal content in each treatment of this study. The soil and plant samples were prepared as a digestion solution and analyzed using ICP-OES (Perkin Elmer - Optima 5300 DV, USA). Data were subjected to an Analysis of variance (ANOVA) using the SAS 9.4 statistical package [15] and the means separation of LSD test at $p < 0.05$.

(A) Cooling ponds (B) Mixing ponds (MP) (C) Anaerobic ponds (ANP)

(D) Dumping ponds (DP) (E) Algae ponds (ALP) (F) Facultative ponds (FP)

Figure 1: Different Treatment Ponds; Cooling Ponds (A) , Mixing Ponds (B) , Anaerobic Ponds (C) , Facultative Ponds (D), Al-Gae Ponds (E) And Dumping Ponds (F) In Felda Jengka 8 Palm Oil Mill.

3. RESULTS AND DISCUSSION

3.1 The heavy metal properties in different POME sludge

Approximation value was often used to determine the general chemical composition (elements of heavy metal) availability in the POME sludge. The heavy metals content in the POME sludge strongly influenced the characteristics and properties of wastewater. Research from Wan Razali et al. [6] and Rihani et al. [16] indicated that high concentrations of heavy metals could affect plant growth, including soil properties and microorganisms.

The heavy metal properties of POME sludge from different treatment systems were measured. Table 3 exhibits the influence of different treatment systems on POME sludge. POME sludge from facultative and algae ponds indicated the highest value of Cu (60.85 mg kg^{-1}), Ni (11.86 mg kg^{-1}), Cr (31.17 mg kg^{-1}) and Mn (473. 63 mg kg^{-1}). However, samples from the DP sludge had shown the lowest amount of Pb (0.29 mg kg^{-1}). Furthermore, the value of the heavy metal in each treatment pond system was observed below the WHO-ML standard. The element Cd was not detected in this study. Perhaps, the Cd level was below the standard (1.5 mg kg^{-1}). Bigdeli and Seilsepour [9] reported that Cd was quickly absorbed by the plants through roots and tissue mostly in the leaves. Accumulation of Cd toxicity in leaf plants could be due to the fact that plants easily take up this element [17]. Uptake of high Cd by humans can cause health problems.

Table 3: Effects of heavy metal element on treatments pond. (Means with the same letter are not significantly different at $p<0.05$).

	DP sludge	ALP sludge	FP sludge	ANP sludge	MP sludge	WHO-ML Standard
Cu ($mg\ kg^{-1}$)	49.26bc	46.97bc	60.85a	54.62ab	44.92	75.00
Cr ($mg\ kg^{-1}$)	26.91a	31.17a	28.68a	26.61a	31.29a	150.00
Cd ($mg\ kg^{-1}$)	n.d	n.d	n.d	n.d	n.d	1.90
Zn ($mg\ kg^{-1}$)	128.57a	125.08ab	123.62ab	119.71b	91.49c	140.00
Pb ($mg\ kg^{-1}$)	0.19a	0.14a	0.13a	0.27a	0.22a	0.30
Ni ($mg\ kg^{-1}$)	10.64bc	10.97ab	11.86a	7.97d	8.55cd	67.00
Mn ($mg\ kg^{-1}$)	434.73a	473.63a	452.37a	411.70a	459.47a	500.00

Note: MP sludge (Mixing ponds sludge), ANP sludge (Anaerobic ponds sludge), FP sludge (Facultative ponds sludge), ALP sludge (Algae ponds sludge) and DP sludge (Dumping ponds sludge).
n.d: Not detectable
WHO-ML; Codex Alimentarius Commission (FAO/WHO). Food additives and contaminants. Joint FAO/WHO Food.

3.2 Effect of heavy metal amended of different POME sludge on Entisols

Table 4 shows the changes in Cu content in the various treatments. There were significant differences ($p<0.05$) of Cu in the DP sludge (0.44 mg kg^{-1}), control (0.62 mg kg^{-1}) and MP sludge (0.79 mg kg^{-1}). Meanwhile, Cd showed no significant difference among the treatments. Pb and Ni content were significant ($p<0.05$) differences between the DP sludge and control. A report by Khairuddin et al (2016) [3] showed that the concentrations of Cu, Cd, Pb and Ni were in accordance with the WHO/FAO standard and safe for human intake. Heavy metals might affect growth, morphology and metabolism of microorganisms in bulk soils through functional disturbance, protein denaturation or the destruction of the integrity of cell membranes [18]. In addition, organic matter also supplied organic chemicals to the soil solution that could serve as chelates and metal availability to plants [19]. Heavy metal absorption onto soil constituents declined due to decreased organic matter content in the soils. The dissolved organic matter could increase the mobility and uptake of heavy metals in the plant roots. Zeng et al. [20] estimated that Cd, Pb and Zn contents were positively correlated with organic matter contents in soils.

Table 4 The composition of heavy metal in different treatment on Entisols. (Means with the same letter are not significantly different at p<0.05).

	Treatment						WHO-ML Standard
	DP sludge	ALP sludge	FP sludge	ANP sludge	MP sludge	Control	
Cu (mg kg^{-1})	0.44c	0.47c	0.43c	0.66b	0.79a	0.62b	75.00
Cr (mg kg^{-1})	0.0948a	0.3125a	0.092a	0.0948a	0.092a	0.0842a	150.00
Cd (mg kg^{-1})	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	1.90
Zn (mg kg^{-1})	0.134a	0.135a	0.138a	0.138a	0.147a	0.072b	140.00
Pb (mg kg^{-1})	0.13b	0.14b	0.09b	0.15b	0.11b	0.21a	0.30
Ni (mg kg^{-1})	0.18b	0.10b	0.17b	0.18b	0.18b	0.34a	67.00
Mn (mg kg^{-1})	0.814b	0.841b	0.857b	0855b	0.824b	1.032b	500.00

Note: MP sludge (Mixing ponds sludge), ANP sludge (Anaerobic ponds sludge), FP sludge (Facultative ponds sludge), ALP sludge (Algae ponds sludge) and DP sludge (Dumping ponds sludge); WHO-ML (2001); Codex Alimentarius Commission (FAO/WHO).

3.3 Effect of heavy metal amended of different POME sludge on plant uptake.

3.3.1 Accumulation of Cu, Cr, Zn, Pb, Mi, and Mn in leaves-stem

In Figure 2, the accumulations of Cu, Cr, Zn, Pb, Mi, and Mn were identified based on plant uptake of leaves and maize stem (*Zea mays*) in the different POME sludge. In contrast, the Cd concentration was not detected in this experiment. The existence of Cu, Cr, Zn, Pb, Mi, and Mn indicated that the result was significantly different p<0.05 in each element, respectively. Awokunmi et al. [21] revealed that heavy metals accumulated mostly in the plant's leaves and stem compared to the root.

The concentration of Cu in the leaves and stem are presented in Figure 2A. The plant leaves accumulated a significant amount of Cu in MP sludge (13.24 mg kg^{-1}) compared to the stem (7.384 mg kg^{-1}). According to Sheldon and Menzies (2005) [22], the effect of Cu toxicity was mostly on leaves and roots. In addition, the Cu had antagonistic effects with Zn and Cd, which accumulated at higher concentrations than Cu. A similar response was observed for the effects of heavy metals in dill, peppermint and basil plants, where Cd and Cu have antagonistic effects [23].

The patterns of Cr accumulation were similar, with the highest concentration of Cu found in MP sludge, leaves (33.61 mg kg^{-1}) and stem (17.33 mg kg^{-1}) (Figure 2B). Cu accumulation pattern of POME sludge was in sequence of ANP sludge>FP sludge>ALP sludge>DP sludge. The lowest concentration was observed in the control treatment: leaves (5.48 mg kg^{-1}) and stems (4.82 mg kg^{-1}). The result revealed Cr concentration in the leaves was increased to 28% compared to control and MP sludge. The effects of high Cr concentration can cause a significant decrease in water potential in the plants [24]. Furthermore, Cr was a highly toxic non-essential element for microorganisms and plants [25]. Rajkumar et al. [26] reported that a higher concentration of Cr inhibits the growth of most bacteria and was tolerated by a minority of organisms.

The results showed that Zn was detected in the highest leaf concentration for all six treatment samples (Figure 2C). The analysis also showed that Zn was highest in the ANP sludge for both plant part leaves (21.08 mg kg^{-1}) and stem (18.73 mg kg^{-1}). In contrast, the control revealed the lowest Zn content for leaves (1.27 mg kg^{-1}) and stems (0.17 mg kg^{-1}). The Zn accumulated in the plant uptake can be used as antagonistic effects; when Zn was applied, it reduced the plant uptake of Cd in a range of crop plants grown in the soils [27]. In this study, it was found that Cd was not detected in the leaves and stem parts. According to Hafeez et al. [28], Zn plays an important role in plant metabolism by influencing metabolism and growth performance.

The Pb metals in the leaves and stem parts under different POME sludge treatments are presented in Figure 2D. Pb in leaves and stem accumulation was in the trend MP sludge, ANP sludge, FP sludge, ALP sludge, DP sludge and control. The lowest value recorded was at stem grown on control (1.21 mg kg^{-1}). Pb was highest in the leaves and stem at MP sludge amendments, 57.13 mg kg^{-1} and 47.30 mg kg^{-1}, respectively. The readings in the leaves and stem varied significantly from each other ($p<0.05$). According to Yongsheng et al. (2011) [29], Pb can inhibit plant growth by decreasing biomass and plant tissue cells. The effect of Pb with high concentration can cause health problems with certain plants having a strong ability to transfer Pb from the soil to the tissue [29]. Therefore, a preliminary assessment was important in determining the potential contamination of Pb as soil amendments.

Enrichment factors of Ni were 0.22 mg kg^{-1}, 0.23 mg kg^{-1}, 0.23 mg kg^{-1}, 0.19 mg kg^{-1}, 0.76 mg kg^{-1} and 0.42 mg kg^{-1} for DP sludge, ALP sludge, FP sludge, ANP sludge, MP sludge and untreated (control) in leaves and 0.14 mg kg^{-1}, 0.16 mg kg^{-1}, 0.17 mg kg^{-1}, 0.16 mg kg^{-1}, 0.68 mg kg^{-1} and 0.34 mg kg^{-1} in the stem of the respective amendments (Figure 1E). A significant ($p<0.05$) effect of Ni was found on leaves and stem parts. Ni was found to have a role in phytoalexin synthesis and plant disease resistance [30]. However, the low level of Ni can benefit the plant growth performance [31]. However, high Ni concentrations may turn toxic to plants [32, 33].

The analyzed data showed that Mn in the leaves and stems responded differently to different POME sludge amendments (Figure 1F). There was a significant ($p<0.05$) increase in the leaves and stem at DP sludge; 0.27 mg kg^{-1} and 0.20 mg kg^{-1} compared to the control, 0.83 mg kg^{-1} and 0.97 mg kg^{-1}. The analyzed data showed Mn in the leaves and stem responded differently to different POME sludge amendments (Figure 1F). There was a significant ($p<0.05$) increase in the leaves and stem at DP sludge; 0.27 mg kg^{-1} and 0.20 mg kg^{-1} compared to the control, 0.83 mg kg^{-1} and 0.97 mg kg^{-1}. In plant growth, Mn was used in root development rather than leaves [32]. In addition, the total Mn toxicity content was low due to the contribution of the leaf [34].

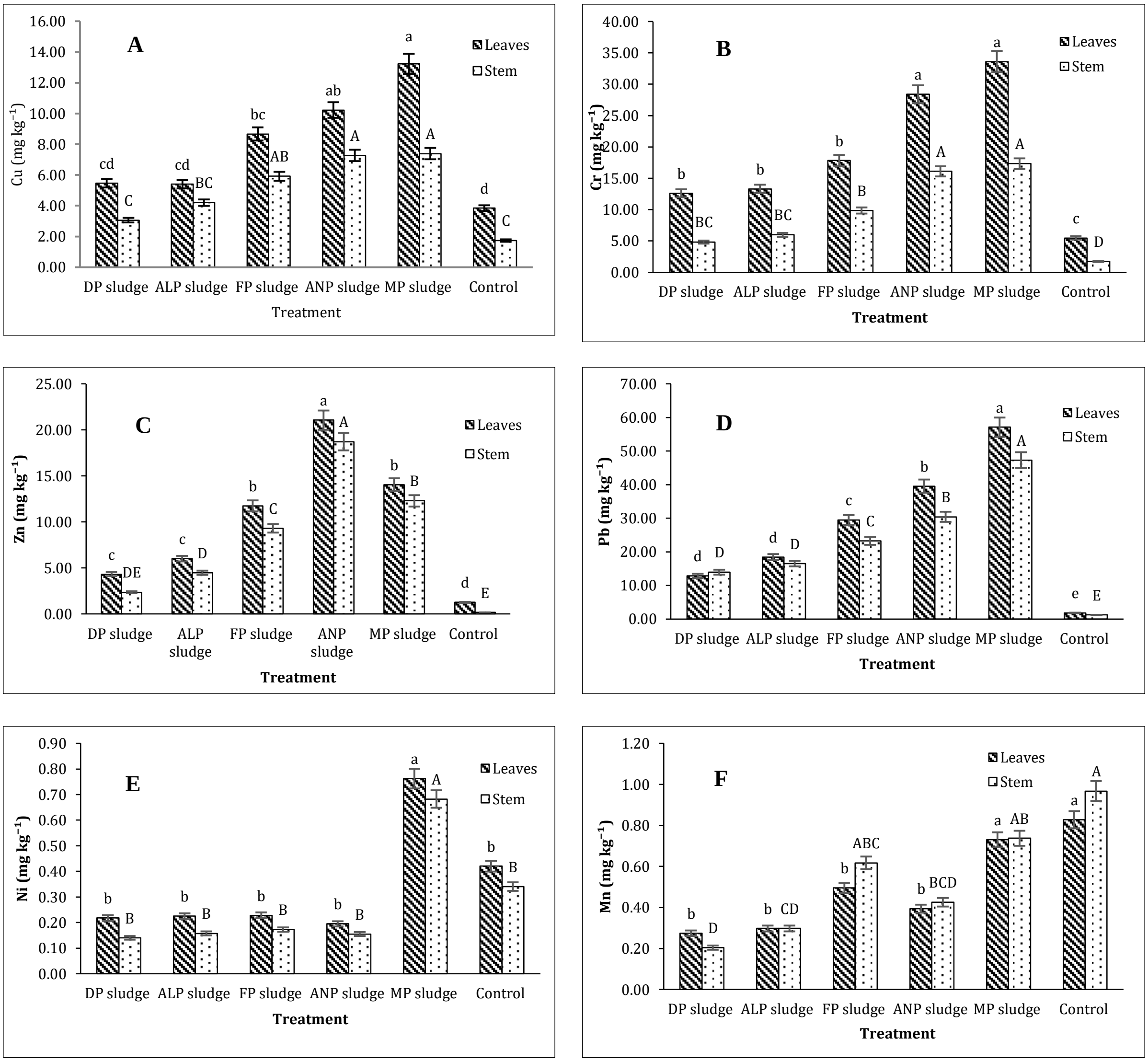

Figure 2: Accumulation of Cu (A), Cr (B), Zn (C), Pb (D), Mi (E) and Mn (F) in leaves-stem with different POME sludge treatment (Means with the same letter are not significantly different at $p<0.05$).

4. CONCLUSION

The results from this study showed that proper processing and technique applied might transform these abundant materials into organic fertilizer. The study revealed that heavy metal in soil and plant systems was available and unharmed for human consumption. In general, Entisols were identified as a low amount of heavy metals in each POME sludge treatment. Nevertheless, the Cu, Cr, Zn, Pb, Cd, Mi and Mn contents were in compliance with the WHO-ML standard. Furthermore, the maize (Zea mays) was able to become a phytoremediation due to high heavy metals levels in their leaves. Mixing pond sludge was identified as a pollutant of heavy metal (Cu, Cr, Pb and Ni) with the exception of anaerobic pond sludge (Zn) and control (Mn). It was important that the utilization of POME sludge might improve plant growth and food chain sustainability, whereby organic matter from the plant would return to the soil as an organic fertilizer.

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