A PRELIMINARY STUDY ON REMOVAL OF HEAVY METALS FROM LANDFILL LEACHATE USING NATURAL SOIL AND AGRICULTURAL WASTES

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ABSTRACT: *This batch study focuses on suitability of natural soil-pressmud-EFB (Empty Fruit Bunch) as the daily soil cover of landfill. The natural soil samples were mixed with agricultural wastes which are pressmud and EFB. Pressmud is a rejected waste produced from sugar refinery process whereas EFB is a major by-product from the oil palm industry. These waste will be mixed with a natural soil at different percentages of weight ratio (50S:40P:10E, 50S:30P:20E, 50S:25P:25E, 50S:10P:40E and 50S:20P:30E). The batch equilibrium tests were carried out and they showed that the natural soil-pressmud-EFB mixtures have the capability to remove more than 73.1% (minimum) and 97.5% (maximum) of Arsenic (As^{2+}), (Cd^{2+}), (Cr^{2+}), (Cu^{2+}), (Fe^{2+}), (Ni^{2+}) and (Zn^{2+}) concentrations from the solution. Meanwhile, the removal efficiency of heavy metals from the solution in the natural soil alone was lower than 65.7% of As^{2+} and less than 33% for the rest of heavy metals stated previously. A raw sample of pressmud and EFB however showed the highest percentage which were 99% and 87% removal respectively. The natural soil-pressmud-EFB mixtures, significantly have a great potential as daily soil cover in minimizing heavy metals migration into landfill leachate.*

Keywords: Removal, soil, pressmud, EFB, heavy metals and daily cover

1. INTRODUCTION

Landfill leachate could be a main factor of water contamination, if not treated and disposed safely, due to its ability to percolate through soil and subsoil. Thus, before releasing, the treatment of hazardous leachate components has been made a legitimate obligation to avoid pollution of water resources and to elude both acute and chronic toxicities [1]. A variety of heavy metals are frequently found in landfill leachate including iron, zinc, copper, cadmium, lead, nickel, chromium and mercury [2,3]. A possible treatment to minimize the migration of pollutants in the leachate plume is by enhancing the natural or engineered landfill daily soil cover. The application to enhance the natural of daily soil cover by mixing pressmud and EFB into the soil matrix can reduce the amount of the pollutant materials through adsorption activity. By amending the soil pressmud and EFB with certain ratio, it could improve the potentiality of heavy metals sorption, as pressmud and EFB are high in organic matter content, high with cation exchange capacity. Therefore, the abundant waste of pressmud and EFB can be reduced by utilizing it as an admixture in landfill daily soil cover. In choosing the materials as potential daily soil cover, characterizations of the materials need to be evaluated and the specification must meet the standard requirements. This study introduced pressmud and EFB acting as a new admixtures material in daily soil cover at landfill to minimize the migration of heavy metals in landfill leachate.

2. EXPERIMENTAL DETAILS

Local soil which is used as daily cover in landfill was sampled in Changkat, Penang area and leachate was collected from Pulau Burung landfill of Peninsular Malaysia as in Figure 1, while pressmud was sampled from the sugar mill Malayan Sugar Manufacturing (MSM) Sdn. Bhd., Seberang Perai, Penang of Peninsular Malaysia. Empty Fruit Bunches (EFB) of oil palm was obtained from a local mill, United Oil Palm Industries Sdn. Bhd. situated in Nibong Tebal, Penang. The raw material, EFB, was washed several times with distilled water, dried at 100 °C for 24 hours in an oven to remove moisture until constant weight. The dried EFB was then ground and sieved to a particle size of <1mm and preserved at room temperature (28±°C). The basic characteristics of this sample were obtained.

Figure 1: Location of Pulau Burung Landfill

The local soil samples pressmud and EFB were then dried and analyzed for their characteristics. Raw leachate was collected from Pulau Burung Landfill. All leachate samples collected were kept in High Density Polyethylene (HDPE) bottles and preserved at approximately 4°C temperature in a refrigerator. The leachate was then analyzed for its heavy metal concentrations by using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Model Perkin-Elmer Optima 7000).

Basic characterizations of this sample such as pH, specific gravity and moisture content were analyzed. The 50% of soil samples were mixed with the pressmud and EFB with the percentages of 40% pressmud and 10% EFB (50S:40P:10E), 50% soil mixed with 30% pressmud and 20% EFB (50S:30P:20E), 50% soil mixed with 25% pressmud and 25% EFB (50S:25P:25E), 50% soil mixed with 10% pressmud and

40% EFB (50S:10P:40E) and 50% soil mixed with 20% pressmud and 30% EFB (50S:20P:30E) in weight, respectively. The samples were then ground in the rotary blender in order to obtain a homogeneous mixture. After mixing, all the samples were kept in sealed plastic bags for further analysis.

Batch Equilibrium Test (BET) was performed in order to evaluate the removal efficiency of heavy metals such as As^{2+}, Cd^{2+}, Cr^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+} and Zn^{2+} concentration using soil, pressmud and EFB alone and sample of soil-pressmud-EFB mixtures. In this experiment, synthetic solution with initial concentrations of heavy metals were mixed with the materials (soil, presmud, EFB alone and soil-pressmud-EFB mixtures) at ratio 10:1 (10 mL solution and 1 g of sample) and shaken in a tube for 24 hours in accordance with standard method [4]. The horizontal shaker was used to shake the samples. After reaching equilibrium, the tubes were centrifuged at 5,000 rpm for 25 minutes to separate the liquid and solid form. The supernatant was filtered with Whatman filter paper (No. 42) and then analyzed by ICP-OES. The removal percentage of heavy metals from initial concentration C_o in leachate was calculated from the following equation (Shaw, 2001). Adsorption capacity and percent removal were used to optimize the material conditions:

$$\%\, Removal = \{Co - Ce\}/Co$$

Where,
Co = initial concentration of the solution (mg/L)
Ce = the equilibrium concentration left in the solution (mg/L)

3. RESULTS AND DISCUSSION

Concentration of Heavy Metals in Pulau Burung Landfill Leachate

Table 1 shows the range of concentration of heavy metals content in leachate from Pulau Burung Landfill. From the results, Fe^{2+} showed the highest concentration which was 4.50-6.00 mg/L (ppm). Concentration of Cu^{2+}, Cr^{2+}, Mn^{2+}, Mo, Ni^{2+}, Sr, V and Zn^{2+} showed 0.48-0.9 mg/L, 0.55-0.70 mg/L, 0.19-0.62 mg/L, 0.11-0.20 mg/L, 0.17-0.54 mg/L, 0.27-0.47 mg/L. 0.41-0.57 mg/L and 0.69-3.49 mg/L respectively. Some of heavy metals concentrations such as Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} were exceeded the maximum permissible concentration (MPC) limits. Landfill leachate is a complex wastewater and its composition and concentration of contaminants is influenced by many factors such as the type of waste deposited and the age of landfill [5,6].

Table 1: Heavy metals concentration in Pulau Burung Landfill leachate

Heavy Metals	Concentration of Heavy Metals in mg/L (ppm)
Copper, Cu^{2+}	0.48-0.90
Chromium, Cr^{2+}	0.55-0.70
Iron, Fe^{2+}	4.50-6.00
Manganese, Mn^{2+}	0.19-0.62
Molybdenum, Mo	0.11-0.20
Nickle, Ni^{2+}	0.17-0.54
Strontium, Sr	0.27-0.47
Vanadium, V	0.41-0.57
Zinc, Zn^{2+}	0.69-3.49

Characteristics of Soil, Pressmud and EFB

According to the British Standard Method [7], basic properties of the soil, pressmud and EFB samples are shown in Table 2-4. The pH value shows 4.45 which was acidic and can be considered as strongly acidic condition. From previous studies, most of this type of soil in Malaysian landfills considered as strongly acidic at pH 4.4 [8]. This common scenario in the wet tropical regions has resulted soil becoming so weathered and leached [9] whereby base cations are leached by H^+ and Al^{3+} ions that caused the high acidity in the soil [10]. pH value for pressmud and EFB showed 8.07 and 8.6 respectively, which were indicated slightly alkaline condition. Specific gravity of EFB was 0.87 lower than soil and pressmud while the moisture content of pressmud showed 32.9% which was higher than soil and EFB. All the basic properties for soil, pressmud and EFB were in ranges as previous studies except specific gravity for EFB. According to [11] the basic soil properties and the other materials which will be used as an admixture normally monitored as a part of quality control during construction of soil liners.

Table 2: Basic properties of soil

Properties	Soil	Reference
pH value	4.45	3.5-5.5 [12]
Specific Gravity	2.33	2.24 [13]
Moisture Content, %	11.6	18.4 [13]

Table 3: Basic Properties of pressmud

Properties	Pressmud	Reference
pH value	8.07	8.06 [13]
Specific Gravity	1.92	1.76 [13]
Moisture Content, %	32.9	31.4 [13]

Table 4: Basic properties of EFB

Properties	EFB	Reference
Moisture Content, %	8.6	8.48 [14]
Specific Gravity	0.87	No reference for this properties from previous study
Moisture Content, %	13	14 [14]

Removal Efficiency of Heavy Metals

In this study, initial concentration of several heavy metals in synthetic solution was 4 ppm. The removal efficiency of local soil, pressmud, EFB and 5 of ratio of soil mixtures were investigated. Figures 3 to 9 showed the results of the removal efficiency of the samples. Figure 3 depicts the removal percentage of Arsenic (As^{2+}) in leachate. From the figure, it can be clearly seen that soil alone could only remove 65.7% of As^{2+}. The addition of pressmud and EFB to the soil clearly improves the removal efficiency. The removal efficiency of As^{2+} for the ratio of 50S:40P:10E, 50S:30P:20E, 50S:25P:25E, 50S:10P:40E and 50S:20P:30E were 93.6%, 95.2%. 91.4%, 89.2% and 86.75% respectively. However, pressmud alone could remove 98.1% but the value was higher than that of soil alone, whereas EFB removed 14.5% of As^{2+}. From an analysis of variance (ANOVA), it was proved that the addition of these agricultural wastes namely pressmud and EFB as admixture materials in the soil significantly removed As^{2+} from the solution ($p<0.05$). Pressmud, EFB and soil-pressmud-EFB mixture has a tendency to remove more than 98% of As^{2+} in the removal efficiency test due to the characteristics of pressmud that become sticky when it is drenched and the porosity of the soil-pressmud-EFB mixtures is enhanced. Its also influenced by the rich of fiber in the EFB that could help in improving the removal of As^{2+} from the solution.

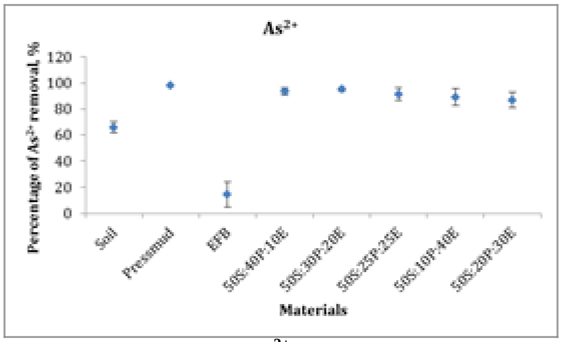

Figure 3: Percentage of As^{2+} removal from the solution

Figure 4 shows the percentage of Cadmium (Cd^{2+}) removal in leachate. From the figure, soil alone could only remove 4.1% of Cd^{2+}. The removal efficiency of Cd^{2+} for 50S:40P:10E, 50S:30P:20E, 50S:25P:25E, 50S:10P:40E and 50S:20P:30E were 94.5%, 94.9%. 94.0%, 92.0% and 89.4% respectively. Pressmud alone could only remove 99.7% much higher than that of the soil alone and EFB removed 34.7% of Cd^{2+}. ANOVA analysis proved that the addition of pressmud and EFB as admixture in soil significantly reduced Cd^{2+} in the filtrate ($p<0.05$). Apart from the characteristic of pressmud alone which easily turns sticky, the higher of CEC value of pressmud and EFB also increased the capability to adsorb heavy metals. It can be said that the addition of pressmud and EFB in soil removes higher concentration of Cd^{2+} from the solution.

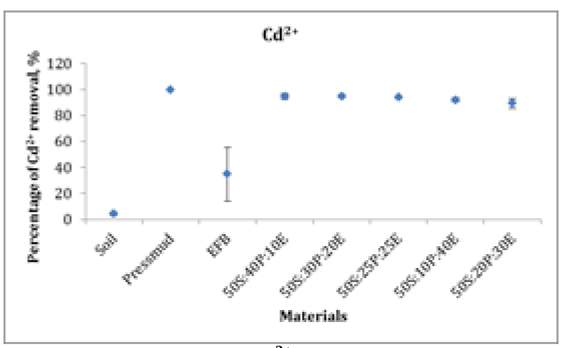

Figure 4: Percentage of Cd^{2+} removal from the solution

Figure 5 depicts the removal percentage of Cr^{2+} from the solution. From the figure, it can be seen that soil alone only removed 33.8% of Cr^{2+} whereas pressmud removed 97.8%. It is clearly shown that the value of pressmud was higher than that of soil alone. The removal efficiency of Cr^{2+} for 50S:40P:10E, 50S:30P:20E, 50S:25P:25E, 50S:10P:40E and 50S:20P:30E were 93.2%, 95.6%. 91.1%, 89.9% and 94.2% respectively. The efficiency was also improved by increasing the pressmud ratio in the soil. Based on ANOVA analysis, it was proven that the addition of pressmud and EFB as admixture in soil significantly improved leachate quality in terms of Cr^{2+} concentration ($p<0.05$). The results was very similar to [15]. They used lime as an admixture in daily soil cover in landfill to remove Mn^{2+} and Zn^{2+} and they found that the addition of lime in the soil significantly improved the sorption capacity of the soil where no desorption of Mn seemed to occur.

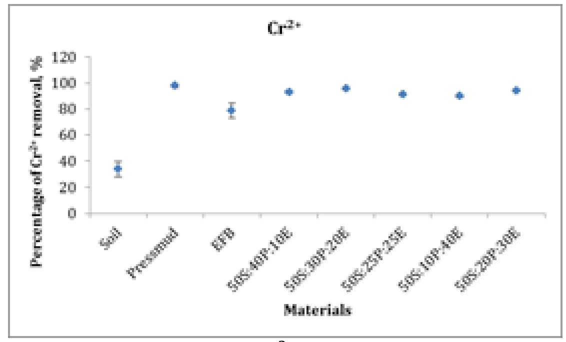

Figure 5: Percentage of Cr^{2+} removal from the solution

Figure 6 shows the removal percentage of Cu^{2+} from the solution. From the figure, it is clearly shown that soil alone could only remove 8.9% of Cu^{2+}. Addition of pressmud and EFB into the soil clearly improved the removal efficiency. The removal percentage of Cu^{2+} for 50S:40P:10E, 50S:30P:20E, 50S:25P:25E, 50S:10P:40E and 50S:20P:30E were 95.8%, 96.1%. 95.7%, 95.6% and 97.5% respectively. Pressmud and EFB alone removed 94.9% and 87.2% respectively, but it was still higher than that of the soil alone. From ANOVA analysis, it was proved that the addition of pressmud and EFB as admixture in soil significantly improved leachate quality ($p<0.05$). The presence of carboxyl groups in soil-pressmud-EFB mixture is believed to be responsible for the sorption of metal ions. There are positive correlations between the removal efficiency and characterization of soils and soil-pressmud-EFB mixture especially, cation exchange capacity (CEC) of that materials. The higher the CEC value of the materials, the higher the percentage removal of the heavy metals observed.

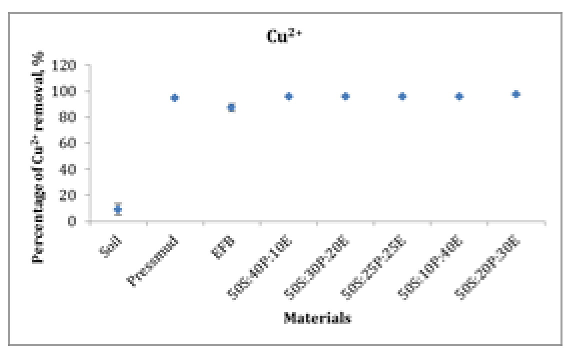

Figure 6: Percentage of Cu^{2+} removal from the solution

Figure 7 shows the percentage of Fe^{2+} removal from the solution. From the results, the removal percentage of Fe^{2+} for 50S:40P:10E, 50S:30P:20E, 50S:25P:25E, 50S:10P:40E and

50S:20P:30E were 85.2%, 90.5%. 77.2%, 73.1% and 75.0% respectively. All the mixtures indicated more than 73.0% removal while soil showed the least removal which was at 41.8%. Pressmud alone was capable in removing 91.2% of Fe^{2+}. From the figure, it can be said that the mixture of soil and higher pressmud content resulted in higher removal of Fe^{2+} in leachate. Addition of pressmud and EFB as admixture in soil significantly decreased the mobility of Fe^{2+} from the solution ($p<0.05$) in ANOVA analysis.

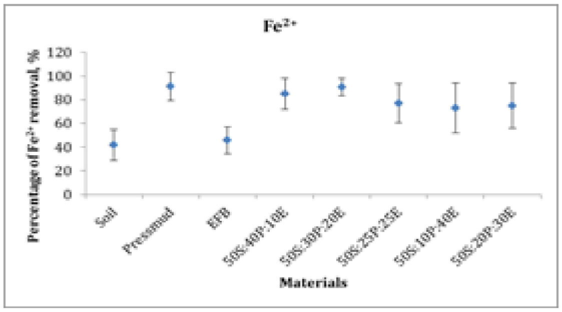

Figure 7: Percentage of Fe^{2+} removal from the solution

Figure 8 shows the removal of Ni^{2+} for soil-pressmud-EFB mixtures i.e. 50S:40P:10E, 50S:30P:20E, 50S:25P:25E, 50S:10P:40E and 50S:20P:30E was detected more than 79% while the soil was capable in removing 7.7% of Ni^{2+} only from the solution. The percentage removal of the pressmud and EFB was 63.6% and 70.1% respectively. However, the percentage was increased with the soil-pressmud-EFB mixtures, where the Ni^{2+} removal was obtained more than 79% as shown in Figure 8. ANOVA analysis also proved that the soil-pressmud-EFB mixtures increased the percentage removal of Ni^{2+} from the solution where $p<0.05$.

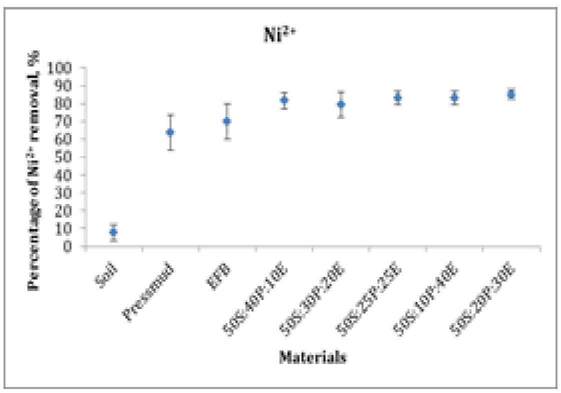

Figure 8: Percentage of Ni^{2+} removal from the solution

Figure 9 shows the percentage removal of Zn^{2+} for soil alone was 4.6%. Meanwhile, the percentage removal of Zn^{2+} for soil-pressmud-EFB mixtures ranges from 97.5%, 96.8%, 96.1%, 95.9% and 95.5% respectively. Pressmud alone can remove approximately 98.6%, it indicates that it is capable of removing nearly 100% of Zn^{2+}. About 41.7% of Zn^{2+} can be removed by using EFB. ANOVA analysis proved that the soil mixtures significantly removed Zn^{2+} from the solution where $p<0.05$.

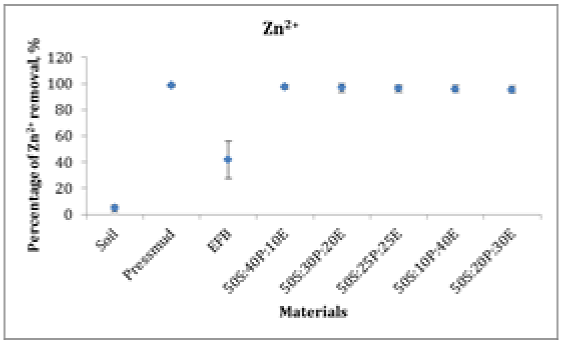

Figure 9: Percentage of Zn^{2+} removal from the solution

Summary of the heavy metals removal with several materials is tabulated in Table 5. Based on the data, the soil-pressmud-EFB mixtures seem to be more effective to remove most of the heavy metals from the solution and have a good potential to be utilized as filled daily soil cover material.

Table 5: Summary of the percentage removal of heavy metals from the solution

Materials	Percentage of removal, %						
	As^{2+}	Cd^{2+}	Cr^{2+}	Cu^{2+}	Fe^{2+}	Ni^{2+}	Zn^{2+}
Soil	65.7	4.1	33.8	8.9	41.8	7.7	4.6
Pressmud	98.1	99.7	97.8	94.9	91.2	63.6	98.6
EFB	14.5	34.7	78.8	87.2	45.7	70.1	41.7
50S:40P:10E	93.6	94.5	93.2	95.8	85.2	81.5	97.5
50S:30P:20E	95.1	94.9	95.6	96.1	90.5	79.3	96.8
50S:25P:25E	91.4	94.0	91.1	95.7	77.2	83.3	96.1
50S:10P:40E	89.2	91.9	89.9	95.6	73.1	83.2	95.9
50S:20P:30E	86.8	89.4	94.2	97.5	75.0	85.2	95.5

Batch equilibrium test glaringly showed that the soil-pressmud-EFB mixtures have the capability to remove more than 86.8% (minimum) for As^{2+}, 89.4% for Cd^{2+}, 89.9% for Cr^{2+}, 95.6% for Cu^{2+}, 73.1% for Fe^{2+}, 79.3% for Ni^{2+} and 95.5% for Zn^{2+} of heavy metals removed from the solution. Meanwhile, the removal efficiency of heavy metals from the solution in the soil alone was below than 65.7% for As^{2+} and 33.8% for Cd^{2+}, Cr^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+} and Zn^{2+}. Pressmud alone however showed more than 99.7% removal whereas EFB was 87% (maximum). It can be concluded that, the present of pressmud and EFB in the soil enhanced the capability to remove heavy metals from the solution.

4. CONCLUSIONS

As a conclusion, the soil-pressmud-EFB mixtures has a good potential to be used as a filled daily cover materials in order to reduce the migration of pollutant from the landfill site. The addition of pressmud and EFB as admixture materials into the soil improved chemical characteristics of the mixture to minimize heavy metals.

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