Pressmud, the solid residue collected from sugar cane industry industry before the sugar crystallisation process [10], is a soft, spongy, amorphous and dark brown solid that containing sugar, fibre, and coagulated colloids including cane wax, albuminoids, inorganic salts, soil particles and mineral elements. Some experts claimed pressmud can be applied to stop soil erosion, soil pH adjustment, crusting and cracking, drainage improvement, soil conditioner, soil reclamation and promote normal bacterial and mirobial growth in soil [11].

Clay is a small particle that exists naturally on Earth surface, made up mainly of silica, alumina, water and weathered rock. Clay is often used as pollution barrier in waste storage sites due to their high impermeability characteristic [12]. The ability of landfill liner to adsorb heavy metal becomes a significant design issue in environmental aspect. However, after long-term cycles of drying-wetting or freezing-thawing, the clay liner can possible crack, thus resulting in an increment of leachate generation. Thus, this research focus on the potential of pressmud as sugar waste industry that to be combined with clay as the landfill liner. Generally, the aims of this study are to determine the characteristics of earthenware clay and pressmud mixtures, and their suitability in reducing heavy metals leachability from leachate based on batch equilibrium study and CEC test.

MATERIAL AND METHODS

Leachate Characterisation

Leachate was taken from a raw and untreated pond at Pulau Burung Sanitary Landfill (PBSL), Pulau Pinang and kept in High-Density Polyethylene (HDPE) bottle and stored at ±4°C chiller. This landfill is a level III sanitary landfill as according to [9] and was operated by Idaman Bersih Sdn. Bhd. (IBSB) beginning July 2001, but then PLB Terang Sdn Bhd took over in 2012 until present. Leachate was analysed for heavy metal content using Inductive Coupled Plasma Emission Spectrometry (ICP-OES).

Clay and pressmud characterisation

Earthenware clay was samnpled from Kuala Kangsar, Perak while sugar pressmud was collected from Malaysian Sugar Manufacturing (MSM) Sdn Bhd, Pulau Pinang. Pressmud and clay were analysed for pH, specific gravity, grain size, Atterberg limit, moisture content, cation exchange capacity (CEC) and heavy metal content. Both samples were air-dried under sunlight for three days before sieved to remove large and coarse pebbles. The mixture was prepared in ratio of pressmud: clay = 0:100, thus labelled as PM0. The same goes for other ratios and named as PM10, PM30, PM50, PM80 and PM100

Batch equilibrium study

4g of mixture was introduced into 40mL of leachate for 24 and 48 hours. The solution then centrifuged at 6000 rpm for 20 minutes to separate supernatant and soild. Next, supernatant was filtered using No.42 Whatman filter paper, before analysed using ICP-OES for heavy metal content. The heavy metal percentage removal was calculated usingthe following formula:

$$\text{Heavy metal \% removal} = \frac{C_0 - C_e}{C_0} \times 100$$

where
C_0 = initial concentration of the solution (mg/L)
C_e = concetration left in the solution (mg/L)

The chemical characteristic involved element content in clay and pressmud by using X-Ray Flourescence and cation exchange capacity (CEC).

RESULTS AND DISCUSSION

Leachate characterisation

Table 1 shows leachate characteristics. Leachate characteristics depend on the type of municipal solid waste being dumped, the degree of solid waste stabilisation, hydrology site, moisture content, seasonal weather variations, the landfill age and the decomposition stage in the landfill [13]. From Table 1, the BOD, COD, BOD/COD ratio of leachate were 182 mg/L, 3470 mg/L and 0.05, respectively. The BOD is a measure of the biodegradable organic mass of leachate and indicates the maturity of the landfill in which the value typically decreases with age of landfill. While COD shows the amount of oxygen required to fully oxidise the organic waste constituents chemically to the inorganic end product. The obtained result was closely similar to study conducted by [14] that showed the characteristics of old leachate (>10 years) are relatively low COD (<4000mg/L), slightly basic pH (>7.5) and low biodegradability ($BOD_5/COD < 0.1$). The value of BOD_5/COD is an indicator whether leachate is stabilised or not by a biodegradable process of waste. $BOD_5/COD \approx 0.1$ is an indicative of stabilised leachate while the range of 0.5-0.7 indicates a large amount of biodegradable organic matter [15]. As BOD_5/COD ratio and pH of PBSL leachate were below than 0.1 and greater than 7.5 respectively, it is deemed acceptable for stabilised leachate. Generally, the pH of stabilised leachate is higher than young leachate. The pH is low during young leachate due to the high volatile fatty acids concentration. This landfill leachate can be categorised as stabilised leachate according to a literature [16] because the pH falls from 7.5 to 9.0

The concentration of Ca, Mg and Fe were 119.067mg/L, 42.628mg/L and 1.832mg/L, respectively. While the other metals like As, Be, Cd, Co, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, V,

Zn were in insignificant concentrations (>1mg/L). Landfill leachate is complex wastewater and contains high organic and inorganic compound compared to industrial waste water. The composition of contaminants is influenced by many factors such as the type of waste deposited and landfill age [17].

TABLE 1. Characteristics and heavy metal content of leachate from PSL

Parameter	Value
COD	3470 mg/L
BOD	182 mg/L
BOD/COD	0.05
pH	7.65
TDS	2780 mg/L
TSS	420 mg/L
Electrical Conductivity	4.76 ms/cm
Heavy metal	Concentration (mg/L)
As	0.312
Be	0.102
Ca	118.067
Cd	0.152
Co	0.713
Cu	0.14
Fe	1.832
Li	0.137
Mg	2.628
Mn	0.805
Mo	0.26
Ni	0.268
Pb	0.136
Sb	0.132
Se	0.111
Sr	0.533
Ti	0.177
V	0396
Zn	0.061

Clay and pressmud characterisation

The characteristics of earthenware clay sample are shown in Table 2. Earthenware clay consists of 6.1% sand, 65.39% silt and 28.51% clay, which then can be classified as silty clay. When added to a clayey and silty soil, zeolites can improve workability to reduce weight and moderate water content while allowing for slower drying rate, which reduces soil cracking probability. The zeolite with silty and clay soil as a liner allowed diffusion process to occur [18]. This study suggests that silty clay has a potential to reduce the contamination of the leachate to flow into the groundwater. The previous study by researchers [19] stated that plasticity index, which is less than 10% (<10%) and liquid limit greater than 20% (≥ 20%) are suitable for the construction of compacted liners. Besides, high plasticity clays tend to desiccate easily, and

any cracks could increase the hydraulic conductivity [19]. The pressmud pH was almost neutral (6.9). The specific gravity of the pressmud was 1.94g, which is lower than clay and the moisture content was 63.2%. The condition of pressmud, which was in wet and compact may influence the higher moisture content. The cation exchange capacity value of pressmud was somehow lower than earthenware clay, which reflects the ability to adsorb less heavy metal ions.

TABLE 2. Characteristic of earthenware clay and pressmud

Characteristic	Earthenware clay	Pressmud
pH	4.86	6.9
Specific gravity (g)	2.13	1.94
Moisture content (%)	4.86	63.2
Grain size		
i. Gravel	0	0
ii. Sand	6.1	2
iii. Silt	65.39	95.98
iv. Clay	28.51	2.02
Atterberg Limit (%)		
i. Liquid limit	53.6	64.8
ii. Plastic limit	37.5	33.3
iii. Plasticity index	16.1	1.9
CEC (meq/100g)	36.35	10.95

The compound and metals content in the clay and pressmud were tabulated in Table 3. The concentration of metal contents in clay was obtained and obviously, Fe, Mg, Ca and Ti showed higher concentrations, which were 68.2591mg/L, 7.0682mg/L, 4.7439mg/L, and 3.2463mg/L respectively. The other metals contained in clay like As, Cr, Mn, Mo, Ni, Pb, Se, Ti and Zn were at very low concentrations (less than 1.0mg/L). The element SiO_2 and CaO showed higher concentrations in the pressmud, which were 14.89%, and 41.73% respectively. The other elements like Al_2O_3, Fe_2O_3, K_2O, TiO, MnO, MgO, Na_2O, P_2O were at lower concentrations in the pressmud which were less than 1.0 mg/L. Ca, Fe and Mg showed the high concentration in the pressmud which were 265.2mg/L, 5.5405 mg/L and 9.4529mg/L respectively. The other metals contained in the clay such as As, Mn, Mo, Se, Sr, Ti, V and Zn showed lesser concentrations in the pressmud which were less than 1.0 mg/L. Sugar industry wastes relatively have very high concentrations of nitrogen, calcium, magnesium and potassium and they are generally deficient in phosphorus, iron and zinc [20].

TABLE 3. Compound and heavy metal content in earthenware clay and pressmud

Element/ compound	Earthenware clay (mg/g)	Pressmud (mg/g)
SiO_2	54.04	14.89
TiO_2	0.47	0.04
Al_2O_3	26.1	0.37
Fe_2O_3	3.45	0.55
MnO	0.03	0.02
MgO	0.42	0.51
CaO	0.18	41.73
Na_2O	0.34	0.58
K_2O	1.78	0.03
P_2O_5	0.04	0.22
Metal content	(mg/L)	(mg/L)
As	0.0708	0.0113
Ca	4.739	265.2
Cr	0.0266	-
Fe	68.2591	5.5405
Mg	7.0682	9.4529
Mn	0.6171	0.2077
Mo	0.017	0.0333
Ni	0.0725	-
P	0.0854	-
Se	0.0394	0.1923
Sr	-	0.0812
Ti	3.2463	0.2153
V	-	0.058
Zn	0.3036	0.267

Table 4 shows the result of CEC for clay-pressmud. The value of the CEC depicts the negative charge in the samples. The charge characteristic of the adsorbent, as well as the metal properties of ionic charge and radius, may affect the efficiency of the metal ion adsorption by clay mineral [21]. Overall, the values of the CEC of the clay-pressmud mixture were increased when the percentage of the clay in the mixture was higher.

Table 4. CEC of clay-pressmud mixture

Sample	Value of CEC (meq/100g)
PM0	36.35
PM10	33.68
PM30	31.71
PM50	32.46
PM80	17.89
PM100	10.95

From batch equilibrium study, the percentage removal of the heavy metals was calculated. The heavy metals content in the leachate at Pulau Burung Sanitary Landfill were Cu, Cd, Mn, Ni, Pb, and Zn with initial concentrations of 0.1404mg/L, 0.152mg/L, 0.8051mg/L, 0.2685mg/L, 0.1364mg/L and 0.0615mg/L respectively. The different ratios of the clay-pressmud weight mixtures were studied on their ability to retain heavy metals at different contact times which were 24 hours and 48 hours. In this paper, only the removal trends of Cu, Mn, Ni,

Pb and Zn were discussed because of their significant removal.

PM0 (clay only), in both reaction time, was sufficient sufficient to remove Pb from the leachate solution. According to the analysis of variance (ANOVA), it showed that the mixture weight ratio and contact time with the removal of Pb were significant (p >0.05). All the ratios of the clay-pressmud mixtures have the potential to remove Pb at 24 hours and 48 hours contact times. The characteristic of the clay, which has higher CEC content, may increase the ability of the mixtures to adsorb heavy metals. It can be concluded from this study that clay alone is enough to remove the Pb from the leachate.
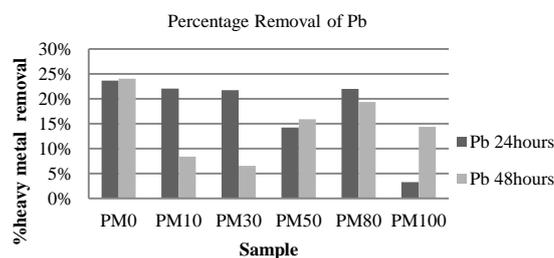
Figure 1. The percentage removal of Pb from leachate

From Figure 2, it can be seen that the equal mixture of the clay-presmud, PM50 removed almost 50% of Ni in the leachate solution. In the flasks of PM0, PM10, PM30 and PM50, the longer the contact times, the higher the percentage removal of Ni was observed. Based on ANOVA, it showed that the ratio and contact time significantly affects the removal of Ni (p>0.05). According to a literature [22], the optimum pH removal for Ni was in the range of 4.0-7.0. The removal of Ni in leachate solution was more obvious in longer contact time and at a higher ratio of clay content.
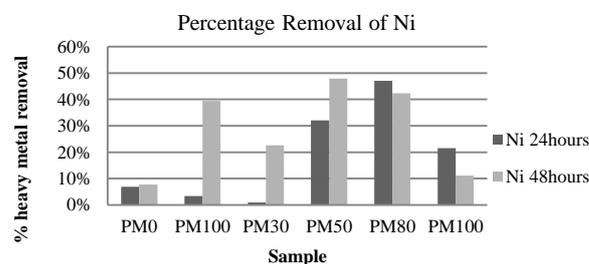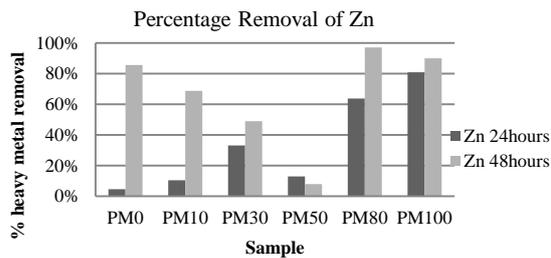

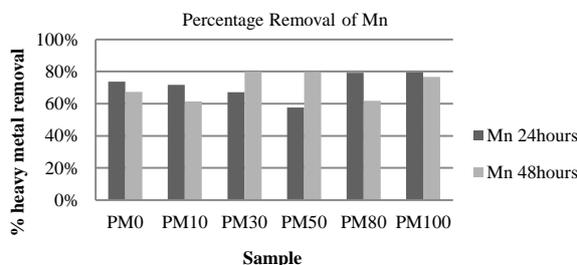**Figure 2**. The percentage removal of Ni from leachate

Figure 3 depicts the removal trend of Zn. In PM0, there was was a significant difference in removal of Zn after 24 hours and 48 hours. PM0 (100% clay) after 24 hours, only removed 4.5% of zinc while the same ratio removed 85% after 48 hours of contact time. Zinc removed more than 50% in PM80 and

PM100 both after 24 hours and 48 hours. Based on ANOVA, it showed that the relationship between ratio and time with percentage removal of Zn in leachate is significant (p >0.05). Therefore, to remove the Zn in the leachate, either 24 hours or 48 hours of contact times is applicable. It is noted that clay also contains some Zn and it may affect the removal of Zn. The pressmud mixtures have a tendency to remove Zn because the pH of the pressmud and leachate mixture was almost neutral. Based on the previous study by the researcher [23] many metal ions are relatively insoluble at neutral pH.

Figure 3. The percentage removal of Zn from leachate.

From Figure 4, the highest removal of manganese was by PM30 after 48 hoursof reaction time. No clear/ linear relationship can be seen between pressmud content and percentage removal, but this elemet can be easily removed from leachate at any given ratio pressmud-clay and contact time.

Figure 4. The percentage removal of Mn from leachate

CONCLUSION

The characteristics of leachate, clay and pressmud is the dominant factor affects the efficiency of heavy metals' removal. Every single species of heavy metal have their own tendency to be removed significantly either by the contact time or by clay-pressmud ratio. The clay-pressmud mixtures have the potential to be applied as a landfill liner but it is noteworthy to acknowledge that not all of the heavy metals in the leachate can be removed at the same rates and it depends on the mixtures' characteristics and parameters.

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Persian Abstract

چکیده

شیرابه از محل دفن زباله که نفوذ به سطوح می تواند آب های زیرزمینی و رودخانه را آلوده کند. از این رو، مواد لاینر باید به درستی انتخاب شوند تا آلاینده ها بتوانند تا حد ممکن در لاینر حفظ شوند و در نتیجه خطر آلودگی را کاهش دهند. در این مطالعه ویژگی های رس و سفالی سفالی و مناسب بودن آنها در کاهش میزان فلزات سنگین در شیرابه مورد مطالعه قرار گرفته است. سازگاری آنها با شرایط نامناسب برای چسب زباله های پلی اتیلن با استفاده از روش تعادلی دسته ای در زمان واکنش ۲۴ و ۴۸ ساعته آزمایش شد. مخلوط رس و پرسمود PM0، PM10، PM30، PM50، PM80 و PM100 براساس محتوای pressmud آنها برچسب گذاری شده اند. هر دو زمان واکنش، در هر مخلوط، منگنز به راحتی از سدیم خارج می شود. پس از ۴۸ ساعت واکنش، روی ٪۹۷ روی PM80 کاهش می یابد. هیچ آزمایش قابل توجهی برای سرب در PM0، PM50 و PM80 یافت نشد، اگرچه آزمایش از ۲۴ تا ۴۸ ساعت طولانی بود. به طور خلاصه، برای آلودگی های کلی، بیشتر زمان واکنش، درصد حذف بالاتر. مخلوط رس-پرسمود دارای توان بالقوه ای است که به عنوان یک خط کش تخمیر استفاده می شود، اما درصد حذف یون های فلزی بستگی به ویژگی فیزیکوشیمیایی مخلوط دارد.