# BATCH REMOVAL OF HEAVY METALS IN LANDFILL LEACHATE BY USING CLAY-PRESSMUD MIXTURES

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## ABSTRACT

*Leachate from the landfill that infiltrates the liner may contaminate nearby groundwater and river. Hence, the last barrier in a landfill site, the liner material must be chosen properly so that pollutants can be retained as much as possible. This study aims to study the characteristics of earthenware clay and pressmud, and their suitability in reducing heavy metals leachability from leachate. Their suitability as a candidate for a landfill liner was tested using batch equilibrium study at 24 and 48 hours contact times. The clay-pressmud were mixed in a ratio of 0%, 10%, 30%, 50%, 80% and 100% and, hence labelled as PM0 (for 100% earthenware clay), PM10 (10% pressmud and 90% earthenware clay) and as well for other ratios, respectively. Among the individual species, manganese (Mn) can easily be removed from leachate solution at any given contact time and mixture ratio. Zinc content was reduced by almost 97% from leachate at PM80 at 48 hours contact time. As for lead (Pb), there was no significant removal by PM0 mixture when the contact time was prolonged from 24 to 48 hours. The same pattern was observed in PM50 and PM80 mixtures. Generally, all contaminants portrayed that the longer the contact time, the higher percentage removal of heavy metals contents were observed. The clay-pressmud mixtures have the potential to be applied as a landfill liner, however, the removal of different heavy metals in the leachate varied with the mixture's physicochemical characteristics*

**Keywords**: Batch study; earthenware clay; heavy metal; pressmud.

## INTRODUCTION

The landfill is a common method used for municipal solid waste disposal in developing countries like Malaysia. Landfill waste is capable of contaminating the nearby water source via underflow groundwater or infiltration from precipitation. The solid waste normally releases its initial interstitial water and some of its by-products from decomposition process that get into water by moving through the waste deposit. Some of the leachate (liquid waste containing a lot of organic and inorganic compound) accumulates at the landfill bottom and percolates through the soil and affect the groundwater quality [10]. Areas nearby the landfill have a high potential for groundwater contamination sourced from leachate that has a high value of chemical oxygen demand (COD), biological oxygen demand (BOD), ammonia, halogenated hydrocarbon, heavy metal, strong colour and bad odour [12, 16]. Leachate stream can contaminate the nearby soil with heavy metals such as lead, copper, zinc, manganese, chromium and cadmium, and these heavy metals cannot be biodegraded and cause problems to nature [12]. This problem leads to considerable efforts to look for an effective method to remove heavy metal from landfill leachate. Several techniques were studied and applied to cope this problem like ion-exchange, reverse osmosis, chemical precipitation, solvent extraction, adsorption [12], cementation, membrane separation, electro deposition, and electro coagulation [11]. Among these processes, adsorption can be said an effective option for heavy metal removal from wastewater [12].

In recent years, one of the popular technique applied is sorption of metals on organic waste from forest industry, agro-industry, fermentation, sewage sludge and biomasses (bacteria, algae, fungi) which are cheaper and easily available [11]. The example of waste from agro-industry is pressmud, which is the solid residue collected from sugar cane industry before sugar crystallisation process [15]. The physical characteristic of pressmud is it is soft, spongy, amorphous and dark brown solid that contains sugar, fibre, and coagulated colloids including cane wax, albuminoids, inorganic salts, soil particles and mineral elements. Pressmud can be used to stop soil erosion, soil pH adjustment, crusting and cracking, drainage improvement, soil conditioner, soil reclamation and promote normal bacterial and microbial growth in soil [17].

Clay is a small particle that exists naturally on Earth surface, made up mainly of silica, alumina, water and weathered rock. Clay is given the attention as an option for effective adsorbent due to its ability to trace heavy metal ion present in solution [20]. Clay is often used as pollution barrier in waste storage sites due to their high impermeability characteristic [4]. The ability of liner landfill to adsorb heavy metal becomes a significant design issue in environmental aspect. However, the clay liner will crack after undergoing long-term drying-wetting or freezing-thawing cycles, and resulting increment of leachate generation. Thus, seeing the potential of the sugar waste industry, namely pressmud to be combined with clay to be applied as the landfill liner, initiated this study. 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.

## METHODOLOGY

Earthenware clay that is used to make a wide range of pottery product was sampled from Kuala Kangsar, Perak. The clay is originally dry and contains some heavy circular stone. While the pressmud was collected from Malaysian Sugar Manufacturing (MSM) Sdn. Bhd., located in Seberang Perai, Pulau Pinang. The original condition of the pressmud is wet and compact. Leachate was sampled from the first pond (raw and untreated leachate) at Pulau Burung Sanitary Landfill (PBSL) in Byram Forest, Nibong Tebal, Pulau Pinang and kept in High-Density Polyethylene (HDPE) bottle and preserved at approximately 4 $^{\circ}$C chiller. This landfill is categorised as level III sanitary landfill and was operated by Idaman Bersih Sdn. Bhd. (IBSB) beginning July 2001, but then PLB Terang Sdn Bhd took over in 2012 until present [9].

Pressmud and clay were analysed for their characteristics (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 two days before sieved to remove large and coarse pebbles. Leachate was analysed for heavy metal content using Inductive Coupled Plasma Emission Spectrometry (ICP-OES).

The mixture was prepared in ratio of PM0 (Pressmud 0%, clay 100%), 10%, 30%, 50%, 80% and PM100 (pressmud 100%, clay 0%). The batch test was performed by mixing 4g of sample mixture with 40mL of leachate. The samples were keptin the homogeneous state for 24 and 48 hours. Samples then centrifuged at 6000 rpm for 20 minutes, filtered using No.42 Whatman filter paper, and analysed for the heavy metal removal.

The heavy metal percentage removal was calculated using the following formula

$$Heavymetal\ \%\ removal = \frac{C_0 - C_e}{C_0} \times 100$$

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

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

**RESULT AND DISCUSSION**

Table 1 shows the leachate characteristics. The 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 [6]. From Table 1, the BOD, COD, BOD/COD ratio of leachate was 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 reflects the amount of oxygen required to completely oxidise the organic waste constituents chemically to the inorganic end product. The obtained result was closely similar to study conducted by [8] 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 ≈0.1 is an indicative of stabilised leachate while the range of 0.5-0.7 indicates a large amount of biodegradable organic matter [2]. 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 [13] because the pH falls from 7.5 to 9.0.

The concentration of Ca, Mg and Fe were 118.067mg/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 showed that the concentrations were lower than 1mg/L. Landfill leachate is complex wastewater and contains high organic and inorganic compound compared to industrial wastewater. The composition of contaminants is influenced by many factors such as the type of waste deposited and landfill age [3].

**Table 1.** Characteristicsand Heavy Metal content of leachate fromPBSL

| **Parameter** | **Value** |
|---|---|
| Biological Oxygen Demand, BOD | 182 mg/L |
| Chemical Oxygen Demand, COD | 3470 mg/L |
| BOD/COD | 0.05 |
| pH | 7.65 |
| Total Suspended Solid, TSS | 420 mg/L |
| Total Dissolved Solid, TDS | 2780 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 | 0.396 |
| Zn | 0.061 |

The characteristics of the earthenware clay sample are shown in Table 2. Earthenware clay consists of 6.1% sand, 65.39% silt and 28.51% clay. The type of clay 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 potential soil cracking. The zeolite with silty and clay soil as a liner allowed diffusion process to occur [19]. 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 [7] 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 [7]. The pressmud pH is almost neutral (6.9). The specific gravity ofthe pressmud was 1.94g, which is lower than clay and the moisture content is 63.2%. The condition of pressmud, which is 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.** Characteristics 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 |
| Cation Exchange Capacity, CEC (meq/100g) | 36.35 | 10.95 |

The compounds 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, 7.0682 mg/L, 4.7439 mg/L, and 3.2463 mg/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 1.0 mg/L). The element $SiO_2$ and CaO showed higher concentrations in the pressmud, which were14.89%, 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 are less than 1.0 mg/L. Ca, Fe and Mg showed the high concentration in the pressmud which were 265.2 mg/L, 5.5405 mg/L and 9.4529 mg/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 [18].

**Table 3.** Compound and Heavy Metal content in Earthenware Clay

| **Element/ compound** | **Earthenware clay (mg/g)** | **Pressmud (mg/g)** |
|---|---|---|
| Silicon oxide,$SiO_2$ | 54.04 | 14.89 |
| Titanium dioxide, $TiO_2$ | 0.47 | 0.04 |
| Aluminium oxide, $Al_2O_3$ | 26.1 | 0.37 |
| Ferric oxide, $Fe_2O_3$ | 3.45 | 0.55 |
| Manganese oxide, MnO | 0.03 | 0.02 |
| Magnesium oxide, MgO | 0.42 | 0.51 |
| Calcium oxide, CaO | 0.18 | 41.73 |
| Sodium oxide, $Na_2O$ | 0.34 | 0.58 |
| Potassium oxide, $K_2O$ | 1.78 | 0.03 |
| Phosphorus pentaoxide, $P_2O_5$ | 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 results of cation exchange capacity (CEC) for the clay-pressmud mixture. 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 [14]. Overall, the values of the CEC value of the clay-pressmud mixture were increased when the percentage of the clay in the mixture was higher.

**Table 4.** Cation Exchange Capacity (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 study equilibrium test, 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 contact times, was 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 that clay alone is enough to remove the Pb from the leachate.

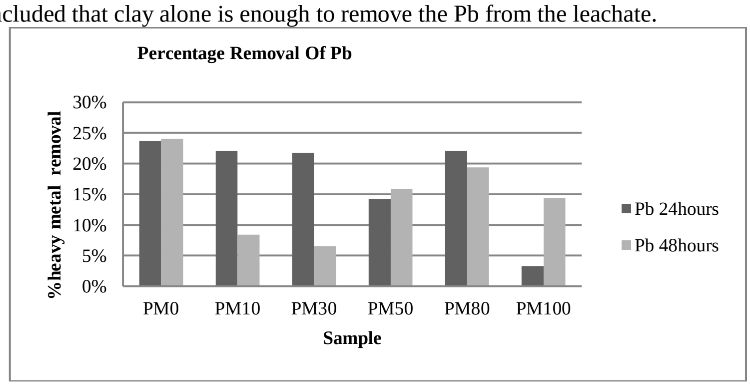


**Figure 1.** The percentage removal of Pb from leachate

From Figure 2, it can be seen that the equal mixture of the clay-pressmud, 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 [5], 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.

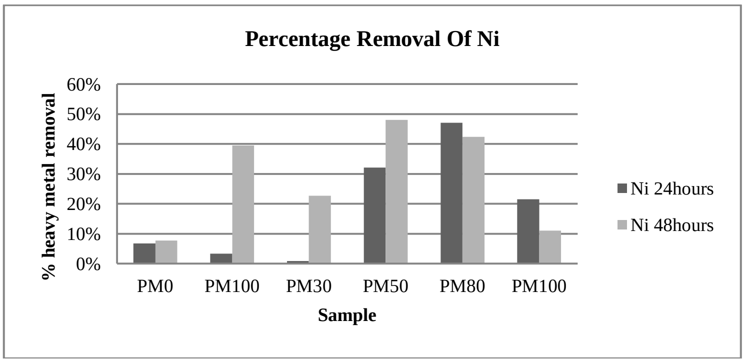


**Figure 2.** The percentage removal of Ni from leachate

Figure 3 depicts the removal trend of Zn. In PM0, there was 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 researchers [1] many metal ions are relatively insoluble at neutral pH.

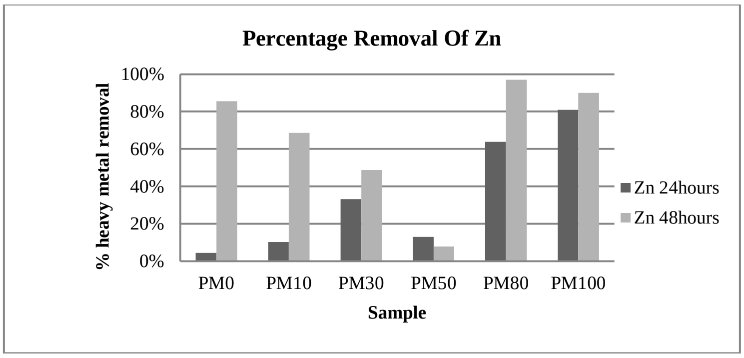


**Figure 3.** The percentage removal of Zn from leachate

From Figure 4, the highest removal of manganese was by PM30 after 48 hours of contact 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.

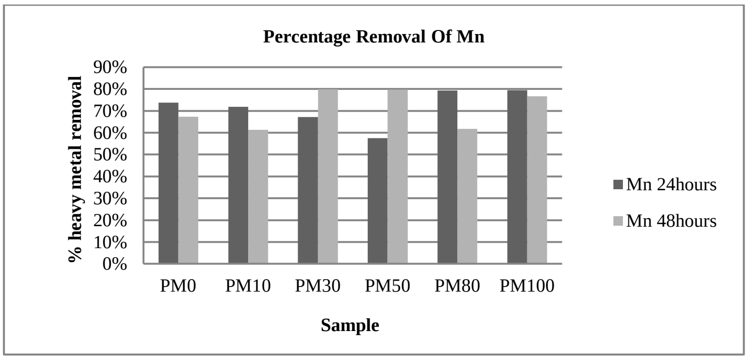


**Figure 4.** The percentage removal of Mn from leachate

## CONCLUSION

In conclusion, the characteristic of the 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 a ratio of the clay-pressmud mixtures. 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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## REFERENCES

[1] Amnani Abu Bakar, "Integrated Leachate Treatment by Sequencing Batch Reactor (SR) and Micro-Zeolite (MZ)" (Master's thesis, Universiti Tun Hussein Onn, 2015), 19.

[2] Bhatt, A. H., Altouqi, S., Karanjekar, R. V., Sahadat Hossain, M. D., Chen, V. P. & Sattler, M. S. (2016). Preliminary regression models for estimating first-order rate constants for removal of BOD and COD from landfill leachate. *Environmental Technology & Innovation, 5*, 188-198.

[3] Daud, Z., Awang, H., Latif, A. A., Nasir, N., Ridzuan, M. B. & Ahmad, Z. (2015). Suspended Solid, Color, COD and Oil and Grease Removal from Biodiesel Wastewater by Coagulation and Flocculation Processes. *Procedia - Social and Behavioral Sciences, 195*, 2407-2411.

[4] Ghorbel-Abid, I. & Trabelsi- Ayadi, M. (2015). Competitive adsorption of heavy metals on local landfill clay. *Arabian Journal of Chemistry, 8***,** 25-31.

[5] Ho, Y,S., John Wase, D.A. & Forster, C.F. (1995). Batch nickel removal from aqueous solution by sphagnum moss peat. *Water Research*, *29*(5), 1327-13332

[6] Kurniawan, T. A., Lo, W.-H. & Chan, G. Y. S. (2006). Physico-chemical treatments forremoval of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials, 129***,** 80-100.

[7] Li, L., Lin, C. & Zhang, Z. (n.d.). Utilization of shale-clay mixtures as a landfill liner material to retain heavy metals. *Materials & Design*.

[8] Li, W., Hua, T., Zhou, Q., Zhang, S. & Li, F. (2010). Treatment of stabilized landfill leachate by the combined process of coagulation/flocculation and powder activated carbon adsorption. *Desalination, 264***,** 56-62.

[9] Maheera, M., Harlina, A, Ismail, A., Kamarudin, S. & Norli, I. (2015). Minimization of heavy metals migration in landfill leachate by using amixture of laterite soil and pressmud (mud cake). *Advances in Environmental Biology*, *9*(16), 5-12

[10] Manikalai, B. & Vijayalakshmil, P. (2012). Analysis of leachate contamination potential of a municipal landfill using leachate pollution index. *Journal of Environmental Sciences, Toxicology and Food Technology* (IOSR-JESTFT), *2*(1), 16-39.

[11] Meunier, N., Blais, J.-F. & Tyagi, R. D. (2004). Removal of heavy metals from acid soil leachate using cocoa shells in a batch counter-current sorption process. *Hydrometallurgy, 73***,** 225-235.

[12] Mohan, S. & Gandhimathi, R. (2009). Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent. *Journal Hazardous Materials, 169***,** 351-359.

[13] Muhammad, U., Hamidi, A. A., & Mohd, S. Y. (2010). Variability of parameters involved in leachate pollution index and determination of LPI from four landfills in Malaysia," *International Journal of Chemical Engineering, 2010,* Article ID 747953, 6 pages, 2010. doi:10.1155/2010/747953.

[14] Musso, T. B., Parolo, M. E., Pettinari, G. & Francisca, F. M. (2014). Cu(II) and Zn(II) adsorption capacity of three different clay liner materials. *Journal of Environmental Management, 146***,** 50-58.

[15] Partha, N. & Sivasubramanian, V. (2006). Recovery of chemicals from pressmud - a sugar industry waste. *Indian Chemical Engineering Section A, 48*(3), 160-163.

[16] Raghab, S. M., Abd El Meguid, A. M. & Hegazi, H. A. (2013). Treatment of leachate from municipal solid waste landfill. *HBRC Journal, 9***,** 187-192.

[17] Saleh-E-In, M. M., Yeasmin, S., Paul, B. K., Ahsan, M., Rahman, M. Z. & Roy, S. K. (2012). Chemical Studies on Press Mud: A Sugar Industries Waste in Bangladesh. *Sugar Technology, 14***,** 109-118.

[18] Satisha, G. C. & Devarajan, L. (2007). Effect of amendments on windrow composting of sugar industry pressmud. *Waste Management, 27***,** 1083-1091.

[19] Silva, G. & Almanza, R. (2009). Use of clays as liners in solar ponds. *Solar Energy, 83***,** 905-919.

[20] Uddin, M. K. (2017). A review on the adsorption of heavy metals by clay minerals, with a special focus on the past decade. *Chemical Engineering Journal, 308***,** 438-462.