Treatability of stabilize landfill leachate by using pressmud ash as an adsorbent

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Abstract. Leachate is a liquid produced from the landfill that contains high concentration of heavy metals, chemicals and nutrient loading. The treatability of these contaminants are complicated since the current treatment technology are costly and site specific. Therefore, this study was conducted to evaluate the treatability of stabilized landfill leachate by using waste (pressmud ash) as an absorbent. Pressmud ash was prepared by burning at different temperature from 100 to 700 degree Celsius and test at 24 hours shaking time, pH 8, and 4000 rpm. Leachate samples were collected from municipal solid waste (MSW) Pulau Burung Sanitary Landfill (PBSL) and were analyzed for heavy metal, COD, ammonia and colour. This study was performed in two phases i) leachate characteristic, ii) treatability assessment by using pressmud ash. Pressmud was sampled from the sugar mill, Malaysian Sugar Manufacturing (MSM) Sdn Bhd, Seberang Perai, Pulau Pinang. The pressmud with 400ºC are highly potential material with a low cost which can be a good adsorbent was capable reducing efficiencies of COD (60.76%), ammonia (64.37%) and colour (35.78%) from real wastewater leachate. Pressmud showed good sorption capability. Surface modification with burning greatly enhanced the reducing efficiency of sugar waste based adsorbent with adsorption efficiency.

1. Introduction
In Malaysia, population has been rising at a rate of 2.4% every year and the generation of municipal solid waste (MSW) also increase drastically. As a result, numerous types of MSW including agriculture, residential area, commercial, institutional by products and non-scheduled waste from industry are being disposed at the landfill over the years [1]. Landfilling are the common methods of organized waste disposal and the simple way to dispose the solid waste. Principally, landfill will receive the wastes from municipal that are near to a landfill. If the location of waste generated is far, the transfer station is the solution to reduce cost of waste transportation [2]. The liquid waste will leach out from the source known as leachate [3]. There are three classification of outputs for landfills based on case in point are gas, liquid (leachate) and inert solids. Production of liquid leachate is among the main problem at landfill sites [2]. Leachate pollution is one of the main issue in landfilling. Among the most problematic parameters in stabilized leachate are COD, ammonia, and colour. There are specific methods of treatment used to treat leachate generated from landfills such as the biological, physical and chemical treatments, combination
of physico-chemical treatment such as adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping and breakpoint chlorination [4]. Biological treatment processes are often used to treat young leachate because of its reliability, simplicity and cost effectiveness but less effective for treating matured leachate due to its unstable organic materials and difficult to biodegrade. However, physico-chemical methods such as adsorption using activated carbon found to be effective to remove almost 99.99% of organic pollutants including organic materials that are susceptible to biodegradation process [5]. However, despite its high effectiveness as an adsorbent, industrial activated carbon is very costly, subsequently, re-searchers are trying to find cheaper adsorbent to substitute industrial activated carbon [6]. The main objectives of this paper are to determine leachate characteristics and treatability assessment by using pressmud ash in order to control and minimize the contamination problem at PBLS.

1.1 Pressmud Characteristics
In sugar mills, sugar is produced through several processes and produce many solid waste in the production. The major by-products of the sugar industry are Bagasse, Molasses and Pressmud (Filter press cake) [7]. Pressmud is a by-product obtained from the clarification process of sugarcane juice, raw juice has non-sugar contaminants are removed using a mixture of chemical reactants such as sulfur and lime in which about 3.5 - 4% from crushed sugarcane ends up as press mud (6 - 40 kg of pressmud is obtained after 1000 kg of sugarcane crushing). The main chemical component of pressmud is CaO [8]. Pressmud is a very soft, spongy, amorphous and dark brown material containing sugar, fibre and coagulated colloids including soil particles. It consists of 80% water and 5-15% sugar, organic matter, nitrogen, phosphorus, potassium, calcium, sulphur, coagulated colloids and other materials in varying amounts [9]. Basic characteristics of pressmud are shown in Table 1. Organic materials such as sugar industry wastes, municipal bio solids, animal manures and agriculture are of utmost importance in maintaining the tilth, fertility and productivity of agricultural soils. They also protect the soils from wind and water erosion, thus preventing nutrient losses through runoff and leaching. Pressmud or filter cake is one of the important organic wastes capable of supplying sufficient amount of plant nutrients to soil. Due to its favourable effects on physical condition of soil, the water holding capacity and aeration of the soil is improved. Thousands of tonnes of pressmud produced annually cause great disposal problems for the sugar industry and environment. Recently, its use as fertilizer in agriculture has been started. Limited research on the use of pressmud has shown positive effects on improving crop yield. Pressmud also improve input use efficiency when used in combination with organic fertilizer [10].

| Pressmud characteristics | Heavy metal content (background) (mg/L) |
|--------------------------|----------------------------------------|
| Colour (PtCo)            | 326                                    |
| Odour                    | Unpleasant                             |
| Temperature (°C)         | 28.7                                   |
| pH                       | 8.12                                   |
| Total suspended solid (mg/L) | 3                                 |
| Total dissolved solid (mg/L) | 0.131                             |
| Chemical oxygen demand (mg/L) | 74                                  |
| Dissolved oxygen (mg/L)  | 4.23                                   |
|                          | Manganese, Mn                         |
|                          | Zinc, Zn                              |
|                          | Lithium, Li                           |
|                          | Titanium, Ti                          |
|                          | Strontium, Sr                         |
|                          | Iron, Fe                              |
|                          | Nickel, Ni                            |
|                          | Calcium, Ca                           |
|                          | Magnesium, Mg                         |
2. Material and method

2.1 Leachate Sampling

Pulau Burung Sanitary Landfill (PBSL) is located at Byram reserves, Nibong Tebal, Penang. It has an area of 624000 square meter (m²) of which 330000 square meter (m²) are currently operational receiving about 1800000 kg of municipal and non-hazardous industrial solid waste daily. Approximately, about 600000 kg of incoming MSW are from Penang Island and the remaining from the mainland. This site has a natural marine clay liner because of the landfill is located near to seashore. In the first 10 years of operation from early 1980s until 1990, the waste was disposed without proper management and no leachate control. In 1991, PBSL started operation as a semi-aerobic system complying with level II sanitary landfill standard by establishing a controlled tipping technique. In 2001, PBLS was enhance to level III sanitary landfill by employing controlled tipping with leachate recirculation. In 2012, the operation of PBSL has been awarded to private company to ensure smooth and effectiveness of daily operation and management at the landfill [1]. Figure 1 showed the location of PBSL.

![Figure 1. Location of Pulau Burung Sanitary Landfill (PBSL) Nibong Tebal, Pulau Pinang.](image)

Sampling for leachate was collected from Pulau Burung Sanitary landfill (PBSL) Nibong Tebal Pulau Pinang located near Byram Reserve Forest (5°24’ N, 100°24’ E) in Penang. Leachate samples were collected from an active reservoir containing leachate over 5 years, transferred into a 20 L plastic container and stored at 4°C in the laboratory. Pressmud was sampled from the sugar mill, Malaysian Sugar Manufacturing (MSM) Sdn Bhd, Seberang Perai, Pulau Pinang.

2.2 Characterization Study of Pressmud

Leachate and pressmud were investigated for their physical and chemical properties. The physical properties tested includes temperature, pH, colour, odour, ammonia, COD, dissolved oxygen, total suspended solid and total dissolve solid. The surface physical morphology of the local pressmud was observed by using a Field Emission Scanning Electron Microscope (FESEM). The surface functional group was performed by Fourier Transform Infra-Red Spectroscopy (FTIR).

2.3 Sample Preparation of pressmud ash (Burning process)

The original pressmud that has been collected directly from Malaysian Sugar Manufacturing (MSM) Sdn Bhd, Seberang Perai, Pulau Pinang has large particles. Hence in order to be used as material in the production of ash (adsorbent), the original pressmud was dried in oven at temperature 105 ± 5 °C for 24 hours and then sieved passing through 300 µm to remove the large particles by sieved it. The following step was to heated again in furnace at temperature 500±5 °C for 90 minute to remove unburned carbon and the colour of modified pressmud was turned from light brown to grayish after the unburned residue was removed [11]. In this study, the same method was practice where there are only differ in heat treatment temperature (100°C to 700°C) of ash. The steps where the pressmud was dried in oven at temperature 105 ± 5 °C for 24 hours and sieved (300 µm) passing through sieve were the same as above
and proceed to burn with different temperature. Ash has proved to be a suitable material for its use as landfill liners [12].

2.4 Analytical method
The test was performed by using 5±0.02 g of press mud ash as an adsorbent with varied temperature (100°C to 700°C) was weighed and mix with 100 ml of leachate in 250 mL erlenmeyer conical flasks respectively, as shown at [Figure 2]. The samples were agitated using a horizontal shaker at a speed of 180 rpm for 24 hours at room temperature. The samples were centrifuged at 4,000 rpm for 20 minutes to separate the liquid and solid portions. Next, the supernatant fluid was filtered with Whatman filter paper (No. 601) and then analysed physical and chemical properties after treatment [13].

![Figure 2. Sample of leachate with adsorbents (pressmud).](image)

2.5 Calculation
From the analysis, the percentage reducing of the selected parameter that remained in the filtrate was used to calculate the amount of absorbed by the pressmud. The removal percentage from initial concentration (C\textsubscript{i}) and final concentration (C\textsubscript{f}) in the leachate was calculated from [Equation 1] [14]. Adsorption capacity and percent reducing were then used to optimize the material conditions. The formula applied to calculate the percentage of COD, colour and ammonia removal efficiency is as per equation 1:

\[
\% P = \frac{C_i - C_f}{C_i} \times 100
\] (1)

where P = percentage removal of impurity (%); \(C_i\) = initial concentration of impurity (mg/L or Pt-Co), and \(C_f\) = final Concentration of impurity (mg/L or Pt-Co).

3. Results and discussion
The characteristics of landfill leachate can be represented in terms of temperature, pH, colour, ammonia, turbidity, BOD\textsubscript{5}, COD, conductivity, salinity, dissolved oxygen, suspended solid and total dissolve solid. Table 2 shows the leachate characteristics at PBSL based on extracted from environmental quality (sewage) Regulation 2009 (PU(A) 432) Second Schedule (Regulation 7).

| NO. | PARAMETER            | AVERAGE VALUE | STANDARD       |
|-----|----------------------|---------------|----------------|
| 1.  | Temperature (°C)     | 31.21         | 40.00          |
| 2.  | pH                   | 8.41          | 5.5 - 9.0      |
| 3.  | Colour (Pt-Co)       | 3022.78       | ~              |
| 4.  | Ammonia (mg/l)       | 536.00        | 5.00           |
| 5.  | Turbidity (NTU)      | 192.00        | ~              |
| 6.  | BOD\textsubscript{5} (mg/l) | 188         | 50.00          |
| 7.  | COD (mg/l)           | 2062.33       | 200.00         |
| 8.  | Conductivity (µs/m)  | 21547.00      | ~              |
Leachate is known as a liquid that passes through the waste refuse and water generated within the landfill site. The produced liquid contains suspended solids. Soluble elements of the waste and products from the degradation of the waste by various microorganism’s activities. Leachate also contain different types of pollutants depending upon the categories of waste disposed into a landfill. During the first few years (<5 years), the landfill is in acidogenic phase and the leachate produced is commonly referred to as “young leachate”. Landfills older than 10 years are normally in the methanogenic phase and the leachate produced is referred to as “old leachate” [15]. Since PBSL has been in operation for more than 20 years, the leachate produces are categorized as old or stabilized leachate. The leachate permissible discharge limit must be complied with extracted from environmental quality (sewage) Regulation 2009 (PU(A) 432) Second Schedule (Regulation 7) prior to be discharge to waterways [16]. Production of liquid leachate is among the main issues at landfill sites [4]. Leachate pollution is one of the main issue in landfilling. Among the most problematic parameters in stabilized leachate are COD, ammonia, and colour. The treatment technology that can be used may contrast based on the type of leachate produced. Even after treatment, the effluent characteristics are always hard to comply with the discharge standard [17]. Frequently, leachates may contain organic contaminants in large amounts and can be measured as Chemical Oxygen Demand (COD), pH, ammonia, and colour [2]. Therefore, these gives a major health hazard in most countries especially in term of solid waste problem. The ability of activated carbon to minimize ammonia by change its surface as ion exchanger and the determination of the capabilities of modified activated carbon to remove ammonia from leachate using fixed bed column [4].

3.1 Field Emission Scanning Electron Microscope (FESEM) Of Pressmud
Field Emission Scanning Electron Microscope (FESEM) are functioning to observe the surface morphology, which is, pores of different sizes and shapes can be observed. In this study showed the particles of pressmud in 8000 and 20000 times magnification. Since sample was non-conducting, it was coated with gold in the presence argon, as inert gas. After the completion of coating process, the sample was analysed in FESEM. The resulting micrographs of pressmud analysis by FESEM are shown in Figure 3 (a) and (b). Microspores are very important in attracting and binding heavy metals ion from the contaminant. They are responsible for water holding capacity of soil. Some particles were trapped in the pores and could possibly block the entry of pores to some extent. Pressmud observed to have granular textured; the texture and surface became uneven and enclosed with a few pores. The physical properties studied includes surface physical morphology it was estimated that its surface contains various ions such as calcium, magnesium and silicon oxide [18].
3.2 The Fourier Transform Infrared Spectroscopy (FTIR) Spectra of Pressmud

The Fourier Transform Infrared Spectroscopy (FTIR) Spectroscopy of pressmud as shown in Figure 4 are the chemical structure of the adsorbent is of vital importance in understanding the adsorption process that present the percentage transmission for various wave numbers given by the FTIR spectrum of the pressmud. The bands were identified in the spectra and the assignments to the corresponding functional groups in the pressmud. The FTIR technique is an important tool to identify the characteristic functional groups. The FTIR spectra of the pressmud is shown in [Figure 4]. The absorption bands and peaks provide evidence for the present of some surface functional groups such as carbonyl, hydroxyl and silica that are capable of adsorbing. The broad and decline band at 3692-3416 cm\(^{-1}\) could be assigned as hydroxyl group which was probably attributed in adsorbing water. The 2959-2515 cm\(^{-1}\) is stretching vibration of C-H. The broad and strong band observed at 1084-1141 cm\(^{-1}\) was assigned as Si-O-C or Si-O-Si (silica group) a structure that was associated with the pronounced concentration of silicon in the materials [19]. Wave number of 1797 for pressmud indicates the presence of carbonyl group on the pressmud surface. The trough which was observed at 713 cm\(^{-1}\) indicates the presence of C-H groups. The high content of organic carbon in pressmud can also enhance the capability of this material in adsorbing.
3.3 Removal test

Adsorption showed the effectiveness process of reducing pollutants from wastewater due to simplicity methodology design, low cost and easiness to operate which is batch adsorption experiment in this study (Table 3). The application of press mud ash as an adsorbent with varied temperature form 100°C – 700°C in wastewater was done with 100 ml leachate, 24 hours shaking time (180 rpm), centrifuge (4000 rpm) (20 minute) and filtering process. It showed that, the best treatability optimization effect of adsorption based on temperature are at 400°C. Showed that, removal on COD (60.76%), ammonia (64.37%), and similar trend for colour (35.78%) percentage of removal. This suggested that colour in landfill leachate was mainly contributed by organic matters with some insoluble forms that exhibited turbidity and suspended solids readings. Adsorption with a suitable adsorbent that can be a simple but effective technique for reducing reading of parameter and removing pollutant from wastewater [13]. This paper presents the recent advance in the utilization of sugar industry wastes as adsorbents and their performance in the reducing of physicochemical parameters. The study revealed that surface modification with burning greatly enhanced the reducing efficiency of sugar waste based adsorbent with adsorption efficiency [20]. Fly ash can be used as an efficient absorbent for the adsorption in landfill leachate [21]. The quality of ash depends on different heating conditions like temperature, heating rate and burn time. Rapid heating does not allow the oxidation of carbon before the surface melting occurs. The addition of a carbon source may have been an additional factor CO$_2$ evolution rates from pressmud treatments [22]. The majority of previous researches have indicated that the process of ash production occurs when the raw materials are burned at a temperature of 800-1000°C, without reference to the required time for burning and exact desired temperature [23]. Temperature has significant effect according to the combustion processes. Practically no literature is available on the exclusive use of pressmud. This study was aimed to determine the temperature of production pressmud ash in order to treat the stabilize landfill leachate taking into consideration the physical, chemical properties.

The study was carried out to evaluate the effect of combining pressmud ash and leachate in reducing efficiencies of physicochemical parameters in real wastewater. The result showed that the reducing efficiency with the addition of press mud ash [Table 3]. Press mud alone was able to reduce ammonia and colour. This reveals the presence of several functional groups in pressmud help for absorption process such as carbonyl, hydroxyl and silica that are capable of adsorbing. Amongst main contributing factor to the excellent performance is due to the high organic and fibre content present in pressmud.

Table 3. Physicochemical parameters of leachate Pulau Burung Sanitary Landfill (PBSL) after treatment based on temperature.

| Parameter                                          | COD   | Ammonia | Colour |
|----------------------------------------------------|-------|---------|--------|
| Raw (leachate)                                     | 10965 | 140.36  | 953    |
| Control (pressmud + deionized water)               | 25553 | 0.38    | 14     |
| Pressmud (original) + leachate                     | 8903  | 84.27   | 744    |
| 100°C                                              | 8735  | 78.92   | 746    |
| (18.81%)                                           | (39.96%) | (21.93%)|
| 200°C                                              | 7550  | 77.70   | 754    |
| (20.34%)                                           | (43.77%) | (21.72%)|
| 300°C                                              | 6471  | 65.45   | 709    |
| (31.14%)                                           | (53.37%) | (20.88%)|
| 400°C                                              | 4303  | 50.01   | 612    |
| (40.98%)                                           | (64.37%) | (25.60%)|
| 500°C                                              | 5989  | 57.83   | 687    |
| (45.38%)                                           | (58.80%) | (27.91%)|
| 600°C                                              | 7584  | 60.83   | 727    |
| (31.16%)                                           | (56.66%) | (23.71%)|
| 700°C                                              | 7023  | 72.96   | 709    |
| (35.95%)                                           | (48.02%) | (25.60%)|
4. Conclusion

Based on the treatment results, the following conclusions can be made. Pressmud showed good sorption capability. The burning of pressmud (ash) showed better in reducing efficiencies of physicochemical parameters in real wastewater (leachate). Pressmud with 400°C are highly potential material with a low cost which can be a good adsorbent substitute due to capability reducing efficiencies of physicochemical parameters in real wastewater. Moreover, found that the pressmud modified (burning) was capable of removing COD (60.76%), ammonia (64.37%) and colour (35.78%) from leachate more effectively. The high content of organic carbon in pressmud can also enhance the capability of this material in adsorbing.

The surface modified pressmud showed high percentage of removal and maximum adsorption capacity.

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