Removal of ammonia from municipal solid waste (MSW) landfill using hydrated lime

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Abstract. Leachate is known as a vigorous wastewater in terms of its organic matter and ammonia content. It is a major problem for municipal solid waste (MSW) landfill. It posed threat to surface water and groundwater. This study focusing on the removal of ammonia-nitrogen (NH₃-N) by coagulation on a raw leachate sample taken from Rimba Mas municipal solid waste (MSW) landfill. The landfill leachate is tested for COD, colour and NH₃-N. Morphological features of calcium oxide are studied using XRF and SEM. Optimum dosage of coagulant for ammonia nitrogen removal from MSW leachate is investigated. The method used in this research was coagulant-flocculation treatment: jar test apparatus. The coagulant was conducted using hydrated lime, Ca(OH)₂ with varying amount of coagulant to find the optimum dosage for ammonia nitrogen removal. A raw leachate sample taken from Rimba Mas landfill was treated with a different amount of hydrated lime (2, 4, 6, 8, 10 g/L) and 0 as a control to investigate the removal of ammonia nitrogen. The results showed that the pH of leachate (9.09) after treated with hydrated lime is increased when the dosage of hydrated lime is increased. Results showed that the best value of removal efficiency from leachate of colour, COD and NH₃-N were 54.70%, 56.22% and 85.25% respectively. We can conclude that as the optimum dosage increases, removal efficiency is increases.

1. Introduction
Malaysia is experiencing expeditious industrialization and urbanization bring the negative effects on the environment from the rising of waste generated [1]. Presently, the people were summarized to be living in the urban is about 28.5 million and more than 70 %. This fast development will cause a huge amount of municipal solid wastes generated [2]. In consequences, landfill leachate will be produced in great amount as the municipal solid waste increases. Landfill leachate possibly polluting liquor which collects underneath a landfill site resulting from the groundwater, runoff, infiltration and percolation of rainfall, or flood water into and through a current or dumped landfill site of solid waste [3]. Leachate can be migrated to soil and sub-soils which might cause serious damage to eco-system of land and be receiving water, if not treated well and safely disposed [4]. Commonly, leachate is defined by large amounts of pH, chemical oxygen demand (COD), heavy metals, and ammonia nitrogen. It also contains a heavy colour and smelly. Notwithstanding, composition, volume and condition of biodegradable matter will alter the characteristics of leachate. Equally, the several of sources of leachate produce will affect the different amount of compositions and quantities [5]. Leachate generation of municipal solid waste (MSW) landfills has a significant problem that will lead to a major threat to both surface water and groundwater. The landfill leachate has different in characteristics, for
instance, a large concentration of ammoniacal nitrogen (NH$_3$ and NH$_4^+$), large value of COD, less potential for biological degradation and the presence of metals and other organic and inorganic substances that confer a large toxicity to this type of waste and obstruct the treatment of leachate. The main contributor to the toxicity of the leachate is ammonia nitrogen in its non-ionized form (NH$_3$) [6]. This study was performed using jar test experiments to investigate optimum dosage of calcium hydroxide used in removing ammonia nitrogen (NH$_3$-N) from MSW landfill. Ca(OH)$_2$ is mainly produced by hydration of calcium oxide (CaO), a product of the thermal decomposition of calcium carbonate (CaCO$_3$) from sources such as limestone [7].

2. Materials and methods

2.1 Leachate sampling and analysis
Landfill leachate samples were collected from Rimba Mas landfill located in Chuping, Perlis, Malaysia. It has a capacity to handle 150 tonnes of dry and wet waste in a day. The major constituents of the municipal solid waste are food wastes, papers, plastics, rubbers and so on. Besides, the facility is equipped with a raw leachate holding pond. The leachate samples were collected from the collection point in a 25 L container and stored it in the refrigerator at 4°C. The leachate sample was removed out of the refrigerator and for approximately 3 hours to reach ambient temperature for each experiment. Leachate sampling, preservation and analytical methods followed the Standard Methods for the Examination of Water and Wastewater [8]. The leachate sample were characterized especially pH, COD, BOD, colour, ammonia nitrogen and total suspended solids.

2.2 Landfill leachate characterization

2.2.1 pH. All the pH measurements were carried out by using a pH meter - HI 2211 pH/ORP Meter. The pH meter calibration was executed before the beginning of prior to each measurement for severe precision if necessary. Calibration was performed with two buffers which is pH 4.0 and pH 7.0. Precautions were taken to make sure the buffers were fresh. In addition, calibration was performed every time before taking pH measurements [9].

2.2.2 Colour. Colour was measured as a true colour using the spectrophotometric method - Platinum-Cobalt standard method (Method 8025) as adapted from HACH DR 2800. At first for the measurements, the leachate sample was filtered through filter crucibles for analysed, 455 nm using a DR 2800 HACH spectrophotometer. Platinum Cobalt (Pt-Co) are the units used for colour [10].

2.2.3 Chemical oxygen demand (COD). Chemical oxygen demand measures the overall amount of oxygen required for oxidising materials in a sample. COD measured colourimetrically. This method makes use of a COD high range digestion solution such as potassium dichromate and sulphuric acid reagent. A standard curve was created on this program using average absorbance values from different standards as a COD test guide. The spectrophotometer measures to a range of 1500 mg/L of COD concentration which indicates a high range of COD [11].

2.2.4 Ammoniacal nitrogen (NH$_3$-N). In this study, Nessler method was used to determination of ammonia concentration. Nessler method was conducted according to Method 8038. This method measures a very low concentration of ammonia within a range of 0.02 to 2.50 mg/L of NH$_3$-N [12].

2.3. Production of hydrated lime
The procedure of mixing water with quicklime to produce hydrated lime is indicated as hydration process or lime slaking. Firstly, dried the limestone overnight in an oven at 105 °C after the limestone is washed with distilled water as to remove dust and impurities. The acquired limestone or commercial CaCO$_3$ were crushed using mortar and pestle and sieved with sieve tray and calcined at 900°C and 1000 °C for 1 hour and 30 minutes or 90 minutes where it decomposes calcination into calcium oxide and carbon dioxide in furnace. Quicklime reactivity is influenced by many factors that can affect the
quality of the quicklime and the slaking process [13]. Then, the CaO samples was placed in desiccator for cold down. Lastly, the dry calcium oxide is slaked (hydrated) with water at temperatures of 30 to 50 °C, producing a calcium hydroxide slurry.

Production of Quicklime (heat in 900-1000°C, 90 minutes),

\[
\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g) \quad \text{(1)}
\]

(Limestone) \hspace{6cm} \text{(Quicklime)} \hspace{6cm} \text{(Carbon Dioxide)}

Slaking of lime,

\[
\text{CaO} (s) + \text{H}_2\text{O} (l) \rightarrow \text{Ca(OH)}_2 (aq) \quad \text{(2)}
\]

(Quicklime) \hspace{6cm} \text{(Water)} \hspace{6cm} \text{(Hydrated Lime)}

2.4. Characteristic of calcium oxide

2.4.1. X-ray fluorescence (XRF). The chemical composition of limestone was analyzed using x-ray fluorescence spectrometer, XRF. The composition of calcium oxide was analyzed by a brand of PAN analytical PW4030 and model MiniPAL4 to define the chemical composition and determine the element and substance not present in the samples [14].

2.4.2. Scanning Electron Microscopy (SEM). The surface morphology of calcium oxide was analysed by JEOL JSM-6460LA analytical scanning electron microscopy (SEM) to examine the surface morphology of the catalysts. The samples were placed on double-sided coated tape. Microstructure variation for each sample was observed under magnifications of 2000x with 10 kV of acceleration voltage. The samples were prepared dry frequently [15].

2.4.3. Coagulation-flocculation (jar test apparatus). This research was determined using a jar test apparatus, with 6 impellers equipped with 6 beakers of 500 mL. A 100 mL of the leachate sample was filled in each beaker and dosed with 0g (as control), 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g of Ca(OH)₂, which represents the lime concentration of 2, 4, 6, 8 and 10 g/L respectively. Initially, a rapid mixing of 80 rpm was used for first 5 minutes. Then, slow mixing of 30 rpm for 30 minutes and the settling period for 30 minutes [16]. Lastly, the supernatant was withdrawn from the beaker using a pipette for further analysis.

3. Results and discussion

3.1 Relationships between hydrated lime with pH, colour, COD and ammonia nitrogen

3.1.1 Effect of pH. pH is a vital parameter to the receiving environment as it will influences the chemical reactions. It is evident from the results that pH ranged around 8.2. The pH values for the leachate as sampled on control were 8.285, 8.228, 8.276 and 8.226 respectively. The pH of leachate in Rimba Mas landfill were more than 8, which is alkaline. As observed, by treated with hydrated lime, pH of leachate were increased as the amount of hydrated lime increased. Sample 1 showed the effect of pH against amount of hydrated lime was the highest compared with S2, S3 and S4 which had the pH value of 9.093. Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters [17]. From the graph below it can be noticed that most of the trend was almost increment. Thus, it shows that the 10g/L of hydrated lime had the biggest effect on the pH level of leachate. We can conclude that it can be observed that low temperature and small particle size of calcium oxide with water that was used to activate the coagulant increase, it tends to stabilize the value of the pH on although the variation of the coagulant dosages, this observation can also be confirmed on the following graph in Figure 1.
3.1.2 Removal of colour. In Figure 2, the leachate sample’s colour was dark brown and the measured values were 2,689 Pt/Co, 2,668 Pt/Co, 2,616 Pt/Co and 2,463 Pt/Co respectively. Generally, stabilised leachate consists of high organic matter (humic and fulvic compounds) that bring about the dark brown colour of the leachate. Generally, stabilised leachate consists of high organic matter (humic and fulvic compounds) that bring about the dark brown colour of the leachate. S1 had the highest percentage of removal of colour with 54.70%. The lowest removal of colour was S3 which had only 20.07%. Beside, as the colour removal increased with a rise of amount of hydrated lime. The trend for S1 is increment as the removal of colour is higher in 2g/L of hydrated lime at the beginning which had 22.80%. However, the percentage of removal of colour for S2, S3 and S4 are not more than 10%.
3.1.3 Removal of COD

In Figure 3, chemical oxygen demand (COD) indicates the mass of oxygen consumed per litre of solution to determine the amount of organic pollutants found in wastewater. The COD values measured from the leachate were 667 mg/L, 681 mg/L, 655 mg/L, and 649 mg/L respectively. COD is a measure of the total oxygen needed to oxidise all the organic waste to inorganic products such as carbon dioxide and water. Figure 3 below shows that the removal of COD of S1 had the highest removal efficiency compared to others which achieved 56.22% at the optimum dosage of 10g/L of hydrated lime while S4 shows that the lowest removal of COD at optimum of 10 g/L of hydrated lime. In this study, the optimum dosage of hydrated lime increase, the removal of COD will also increase. However, the reading of removal efficiency of COD were inconsistent. This was probably due to the complex characteristics of the raw leachate itself, which may need advanced treatment strategies.
3.1.4 Removal of ammonia nitrogen

In figure 4, the NH₃-N concentrations measured from the leachate were 190 mg/L, 182 mg/L, 183 mg/L, and 189 mg/L respectively. S1 had the highest removal of ammonia nitrogen with 85.25% by adding of hydrated lime which is 10 g/L of hydrated lime. As the ammonium nitrogen removal increased with a rise of amount of hydrated lime. This leachate is rich in ammonia and, moreover, ammonia is an inorganic component that causes serious concern in leachate. High concentrations of ammonia negatively impact the wastewater treatment processes and reduce the quality of the effluent, preventing it from meeting discharge standards. Furthermore, an ammonia concentration higher than 100 mg/L is said to be very toxic to aquatic life.

Figure 3. Graph of removal of COD against hydrated lime.

Figure 4. Graph of removal of ammonium nitrogen against hydrated lime.
3.2 Characterization of calcium oxide

3.2.1 XRF analysis. The XRF diffraction pattern was used to determine the percentages of chemical compositions. CaO was heated at 900 °C with different size of particle which is 75 µm and 150 µm. According to results of calcium, Ca elemental analysis has shown the percentage of concentration of calcium in calcium oxide using XRF in table 1. The result of XRF shows that limestone in powder form contains 92.51 % of calcium. After the calcination process, the limestone is sieved to particle size 75 µm and 150 µm and heated in the furnace at 900 °C in 90 minutes to become calcium oxide. The result XRF shows that calcium oxide in 150 µm contains 93.03 % of calcium which slightly higher than the calcium oxide in 75 µm which contain 92.17 % of calcium. Calcination temperature in the furnace impacts the size of the hydrated lime particles slaked from this lime and thus surface area of particles of hydrated lime. The larger the surface area in particles of hydrate the more efficiency of neutralization, this hydrated lime will have [18].

| Compound   | Particle Size (µm) | Ca (%)  |
|------------|--------------------|---------|
| CaCO₃      | -                  | 92.51   |
| CaO        | 75                 | 92.17   |
|            | 150                | 93.03   |

3.2.2 Scanning electron microscopy (SEM) analysis. There were SEM images of CaO with a different parameter of particle size and temperature. These results show that spherical calcium oxide obtained with particle size 75 µm and 150 µm using the thermal-decomposition method. The calcined of limestone were irregular in shape, and some of them bonded together as aggregates. The large size and the well-defined shape of the crystals are a consequence of a great crystal growth process that needs a long period to take place [19]. The structure of calcium oxide at 900°C with 75µm in figure 5 (a) showed a granular solid and more uniform in shape. In figure 5 (b) and figure 5 (d), the sample are conformed by small crystals with an epitaxial growth. In figure 5 (c), surface morphology of CaO at 900 °C with 150 µm particle size was unevenly distributed on the surface of CaO. The morphologies of calcium oxide decomposed at 900 °C and 1000 °C showed slightly differences in size and structure.
Figure 5. SEM images of calcium oxide at different temperature (a) CaO at 900°C 75μm. (b) CaO at 1000°C 75μm. (c) CaO at 900°C 150μm. (d) CaO at 1000°C 150μm.

4. Conclusion
Malaysia is a South East Asia country where landfill is important and the standard of waste management needs to be monitored and improved. A combination of pollutants (BOD₅, COD, ammonia, inorganic salts, etc.) in higher concentrations renders landfill leachate as a potential source of contamination both to ground and surface waters, hence necessitates its treatment prior to discharge to water resources. The management of leachate is among the most important factors to be considered in planning, designing, operation, and long term management of an MSW landfill. It is important for leachate monitoring to establish specific leachate chemistry and contaminants and to ensure these contaminants are included in the groundwater and surface water monitoring.

The main objective of this study is to investigate optimum dosage of coagulant for ammonia nitrogen removal from MSW leachate. This study explored the treatment of ammonia nitrogen from landfill leachate by using coagulation–flocculation. In this work, the coagulation-flocculation process with various dosages of hydrated lime (Ca(OH)₂) ranging from 0g/L to 10g/L was applied for the treatment of MSW leachate using jar test apparatus. The pH, colour, ammonia-nitrogen (NH₃-N) and chemical oxygen demand (COD) removal efficiency were investigated. This is essential that leachate monitoring is needed to create site-specific leachate chemistry and contaminants and to make sure these contaminants are included in the groundwater and surface water controlling. The hydrated lime has good potential of removing ammonia nitrogen and can be practised as natural source product. As the hydrated lime is produced from limestone which considers a cheap material that is significant to the renewable and sustainable product as well as environmentally friendly.

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