Utilization of Zeolite-Feldspar as an Potential Adsorbent for the Adsorption of COD and Ammonical Nitrogen in Stabilized Landfill Leachate

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Abstract. The robust combination of landfill waste recognized as a potential source of hazards. Landfills is one relatively distinctive issue associated with leachate. Generally, zeolite is considered a known adsorbent however relatively very high in cost. Meanwhile, Feldspar is the world’s most common mineral groups which making up as much as about 60 percent of the crust of the eath. Its quality and availability makes the feldspar become relatively low price material. The mixture of feldspar-zeolite are believe to produces effective and inexpensive composite for the treatment of leachate wastewater. The batch experiment was conducted in an Erlenmeyer flask, 250 mL volume with varying the volume of composite mixture ratio and then shaking for 5 hrs with 200 rpm at pH7. The optimum mixing ratio of feldspar-zeolite is chosen 1:1. The optimum removal of COD and ammonical nitrogen i is 55% and 50% respectively. The availability of low-cost materials such as feldspar in the composite has helped to minimize the cost of treatment and has helped to increase the potential capacity for adsorption.

1. Introduction
Nowadays, the population growth is leading to contribute to increase in industrial and commercial development in the most of the countries. The growth has been influenced by the rise of municipal solid waste (MSW) generation. MSW is a diversity at waste, derived from various origins (i.e., residential,
agriculture, municipal services, commercial sources), where each is heterogeneous in itself [1]. The percentage of solid waste composition is varies for each areas and currently about 95% of MSW generated waste is dump in landfills [2]. Landfilling has become one of prominent options for disposal and management of solid waste because this alternative offer dumping high quantities of MSW at economical cost compared to other disposal method [3]. However, the production of highly contaminated leachate is a major drawback of this method [4]. Leachate wastewater identified as one of the potential sources of ground and surface water pollution source. Landfill leachate is the dangerous and highly contaminated wastewater that is produced at landfill site through percolates the rainwater and moisture content. Leachate from landfill contains higher level of organic matter, higher level of ammonical nitrogen, inorganic salt, heavy metals and chlorinated organic [5,6].

The untreated contamination leachate wastewater from landfills is a significantly the main sources of pollution (i.e., ground and surface water, soil) in particularly also effect the environment. The treatment of leachate wastewater is very complicated, expensive and generally requires multiple process [2]. In the last 20 years (1983-2005), various research study were conducted for the treatment of leachate wastewater worldwide by utilizing different types of processes like individual or combine treatment technologies such as Physicochemical and biological combined and/or physico-chemical [4]. In recent years, physico-chemical treatment in landfill leachate has gained great interest. Several treatment techniques (i.e., reverse osmosis, chemical precipitations, membrane filtration, ions exchange, air stripping, oxidations and adsorption are applied in the treatment of leachate wastewater [2]. However, there are few materials available in the nature which seem have less and/or no utilization. The usage of those materials as low-cost adsorbent for the wastewater treatment. Recently available several low cost and indigenous material such as palm ash [7], zeolite [8] and limestone [9] in the treatment of wastewater, especially as adsorbent seems to have gain great interest [10]. Geological available materials like clay, sandstone and minerals are used a low cost adsorbent for the treatment of water and wastewater because of its locally availability and environmentally sound material. Among this mineral, feldspar is the world’s most common mineral groups which making up as much as about 60 percent of the crust of the earth. In most countries, this occurs in igneous, metamorphism and sedimentary deposit [11]. Because of the characteristics and potential absorption capacity of the feldspar, feldspars are used in inexpensive and environmentally friendly process and in particularly in the removal of ionic contaminants from water and wastewater [12].

Previous study on felspar as adsorbent show feldspar can remove heavy metal and color in water and wastewater treatment [11]. Besides, zeolite naturally hydrated mineral aluminosilicate, which belongs to the “tectosilicates” minerals class. Zeolite, alkali or alkaline earth cation earth cation frame structure is reversibly fix with in cavities and can also be easily exchange nearby positive ions such as Ca2+, K+, Mg2+, Na+ [13]. In contrast to the aluminium and silicone structure atoms, which are mutually bound by chemical (covalent) bonds over common oxygen atoms, cations are bound by the aluminosilicate structure mainly by weaker electrostatic bonds, which cause their mobility and capability of being exchanged with solution cations [14]. It make zeolite a material that can remove heavy metals and ammonium ions [16]. Author [17] has stated that a composite material is developed to improve adsorption properties. This study has combined two types of minerals to improve the adsorption properties and reduce costs by replacing part of zeolite with feldspar. The effect of zeolite and feldspar ratio toward COD and NH3-N removal is investigated through this study.
2. Materials and Methods

2.1. Leachate Characteristics
A raw leachate sample was taken manually from SRLS in Johor and stored according to the Standard Methods for the Examination of Water and Wastewater [16]. Leachate samples were taken from landfill sites and placed in clean airtight HDPE (“high density polyethylene”) container. Once the samples of leachate wastewater have arrived in the laboratory and stored in a cold room at 4°C prior to experimental use to minimize chemical and biological reaction. All chemical analysis was performed within 48h.

2.2. Media
Feldspar and natural zeolite used in this study were purchased from CCS Corporation and PT. Anugerah Alam Sdn. Bhd respectively. Both feldspar and zeolite were sieved to obtained 1.18-2.36 mm particle size. Then, both media were rinsed and oven dried at 105°C for 24h. Prior to the experiment, chemical composition of Feldspar and Zeolite were determined by X-Ray Fluorescence (XRF) instrument. Table 1 shows the properties of Feldspar and Zeolite respectively.

| Properties  | Feldspar | Zeolite     |
|-------------|----------|-------------|
| pH          | 8.62-9.07 | 7.33-8.48  |
| SiO₂        | 53.9%    | 65.06%     |
| C           | 11.0%    | 12.1%      |
| AL₂O₃       | 15.6%    | 10.23%     |
| K₂O         | 10.12%   | 4.18%      |
| CaO         | 0.45%    | 2.77%      |
| Fe₂O₃       | 0.96%    | 1.34%      |
| Na₂O        | 2.84%    | 0.74%      |
| MgO         | 0.19%    | 0.61%      |
| Cr₂O₃       | 0.19%    | -          |
| SrO         | -        | 1.9%       |
| Particle size (mm) | 1.16-2.36 | 1.16-2.36 |

2.3. Optimum ratio
The best optimal removal ratio determine between the feldspar-zeolite are depend on removal of COD and ammoniacal nitrogen. The batch experiment was conducted in an Erlenmeyer flask, 250 mL volume with varying the volume of composite media mixture ratio (measured by volume, 40 cm³) as shown in table 3. Erlenmeyer flask is to be add with 100 mL of leachate wastewater and then shaken for 5h at 200 rpm at pH7 [18]. The best optimum removal ratio for COD and ammoniacal nitrogen, which achieve maximum removal.
Table 3. Zeolite and feldspar ratio.

| Sample no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|------------|---|---|---|---|---|---|---|---|---|
| Feldspar (cm$^3$) | 40 | 35 | 30 | 25 | 20 | 15 | 10 | 5 | 0 |
| Zeolite (cm$^3$) | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 |

2.4. Analytical method
COD analyses are performed in accordance to the standard methods described [17] with the use of DR5000 spectrophotometer. Meanwhile ammoniacal nitrogen was determined by Nessler’s method, using HACH spectrophotometer, DR5000.

3. Results and Discussions

3.1. Leachate characteristic analysis
The determination of leachate characteristic acted as indicator to determine the level of leachate wastewater stability, which is important in deciding the most appropriate treatment methods. Table 4 shows the characteristics of Simpang Renggam Landfill site (SRLS) raw leachate sample. The characteristic of landfill leachate from the SRL site indicates and average COD value is 9811 mg/L and the average value of BOD is 937 mg/L respectively. Thus, biodegradable ratio is 0.095, which is less than 0.1. Meanwhile, the ammoniacal nitrogen show high value [18]. Thus, it is indicate that the leachate is a stabilize leachate. Thus, physico-chemical treatment like adsorption is suitable method to applied [19].

Table 4. Simpang Renggam Landfill Site leachate characteristic.

| Parameter          | Average | Regulation 2009 (Pu(A) 433) |
|--------------------|---------|-----------------------------|
| pH                 | 8.65    | 6-9                         |
| Temperature        | 24      | 40                          |
| Suspended Solid (mg/L) | 658   | 50                          |
| Ammonical nitrogen (mg/L) | 1808 | 5                           |
| COD (mg/L)         | 9811    | 400                         |
| BOD$\text{$_5$}$   | 937     | 20                          |
| BOD$\text{$_5$}$/COD | 0.095 | -                           |
| Iron (mg/L)        | 15.82   | 5.0                         |

3.2. Optimum ratio of composite
The determinations of adsorption media composition were depend on highest COD and ammoniacal nitrogen removal. The ratio of feldspar and zeolite that give best percentage removal for COD and NH$_3$-N is 20:20. Whereas, optimum percentage of COD removal is 55% and NH$_3$-N removal is 49% respectively. Figure 1 and 2 show the result of the effect of different ratio of media towards adsorption properties. Natural zeolite is known as highly porous material that contributed to adsorption capacity. It also has a natural negative charge or specifically alkali or alkaline earth cations that are easily exchanged
by surrounding positive ion which gives it the remove cations like ammonium (NH$_{4}^{+}$) as ion exchanger [20,21]. Fortunately, feldspar also has almost similar properties make it a suitable substitute.

Figure 1. The optimum ratio of Feldspar-Zeolite for COD removal at shaking speed 5 hrs with 200 rpm at pH7.

Figure 2. The optimum ratio of Feldspar-Zeolite for NH$_3$-N removal at shaking speed 5 hrs with 200 rpm at pH7.

4. Conclusion
A composite material is developed using the feldspar-zeolite with feldspar used as an alternative adsorbent to reducing costs by replacing part of zeolite with feldspar. The optimal removal ratio of feldspar-zeolite obtained 20:20. With this ratio, the composite managed to remove 55% of COD and 50% of NH$_3$-N, which is higher compared to other ratios but almost as good as zeolite without feldspar. Furthermore, the cost for feldspar is more than cheaper than zeolite. Therefore, with replacing 50%
(based on 20:20 ratio) of zeolite, it can reduce more than 50% treatment cost and indirectly produce effective but inexpensive adsorbent.

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