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Degradation of Organic Matter from Stabilized Leachate by Using Zinc Sulphate as Coagulant Agent

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Abstract. Stabilized landfill leachate often contains higher organic fractions than the young one. The organics require several sequential treatments to render the leachate parameters concentrations to permissible discharge limits before being discharged to receiving water. This study focused on the application of Zinc Sulphate ($ZnSO_4$) as coagulant agent followed with microfiltration of 0.45 µm pore size under different condition of landfill leachates. The results indicated that the sludge volume index (SVI), soluble COD and turbidity concentrations were inter-related to each other when compared under different $ZnSO_4$ dosages. However, that was not the case when correlation between stabilized and young leachate were compared side by side. To conform the finding, one-way analysis of variance (ANOVA) was conducted and the results were further explained by the adequacy and significant of confidence interval. Finally, it was proven that, soluble and particulate COD had significant CI of 95% applicable for stabilized leachate alone.

1. Introduction

Leachate is generated when water or moisture inherent within the waste percolates through the landfill [1]. Leachate is considered highly complex and contaminated wastewater by high concentrations of literally wide ranges of compounds present in waste including organic and inorganic compounds both in dissolved and suspended forms [2]. Among many discharge limit criteria's set, chemical oxygen demand (COD) is one of the major parameters to ensure safe discharge of wastewater [3]. COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. COD test uses a strong chemical oxidant (potassium dichromate), acid, and heat to oxidize organic carbon to carbon dioxide and water [4]. COD is the main parameter analyzed to determine the quality of a wastewater. The dichromate reflux method is preferred over procedures using other oxidants (potassium permanganate) because of its superior oxidizing ability, applicability to a wide variety of samples and ease of manipulation. Oxidation of most organic compounds is 95-100% of the theoretical value [5]. However, there is no documented nor published COD fractionation of Pulau Burung Sanitary Landfill (PBSL) leachate has been done. Thus, in order to establish appropriate behavioral mechanisms, COD fractionation was carried out in this study to compare the stabilized and young landfill leachate collected from the same landfill. Coagulation and flocculation method using $ZnSO_4$ as coagulant was applied and coded as Method 1 followed by filtration using 0.45 µm filter paper. Another method, which was a modified from Method 1 in determining the effect of coagulant amount, coded as Method 2. A simple mathematical formula was used in finding particulate COD value.

2. Materials and methods

Leachate was collected through from an oxidation pond which retains 'stabilized leachate' whereas the leachate produced from the active phase of the landfill which was defined as 'young leachate'. The leachate from PBSL is classified as standard B that refers to discharges outside catchment area Environmental Quality Control of Pollution from Solid Waste Transfer Station and Landfill Regulations (2009). Samples were collected by using polyethylene bottles. The bottles were washed and rinsed using distilled water before sample collection. Samples were kept in a cold room (4ºC) to avoid any changes. The following parameters were systematically monitored; COD, BOD_5, ratio of BOD_5/COD, ammonia (NH_3), iron (Fe^{3+}), conductivity, suspended solid (SS), pH, colour and turbidity.

2.1. Analytical

Soluble COD (SCOD) is one of the main fractions in total COD. Soluble COD contains readily biodegradable COD and unbiodegradable soluble COD. Determination of soluble COD is important in determining the other fractions. In this research, determination for SCOD is carried out using $ZnSO_4$ coagulation and flocculation process. Coagulation is the destabilization of colloid impurities and transfer small particles into larger aggregates by neutralizing the forces that keep them apart. Cationic coagulant provides positive electric charges to reduce the negative charge of the colloid to form larger particles [6]. Coagulation process is using as a main method in this analysis. Different volume of ZnSO4 was used in determine the optimum dosage for this process. The filtration process using 0.45 µm filter paper was applied in all methods. Fig. 1 shows the references for the methods.

2.2. Description of method

Method 1. 1 mL of a 0.6 M $ZnSO_4$ solution was added to each of the three 200 mL beaker containing 100 mL of sample. Sample was mixed for 1 min at 200 rpm followed by slow mixing (30 rpm) for 5 min. Samples were then allowed to settle for an hour and supernatant was withdrawn at the end of settling period. The supernatant were filtered using a pre-rinsed 0.45 µm mixed cellulose ester membrane filter (Milipore, MA). The aliquots of the filtrate was taken and measured for COD, turbidity and SVI value in triplicate samples. pH was adjusted to 10.5±0.3 using 6M NaOH.

Method 2. All the procedures were repeated from Method 1 in different volume of $ZnSO_4$ until the graph of $ZnSO_4$ volume verses COD value is constant. The constant graph shows the optimum dosage of ZnSO4 in both leachate samples. The maximum removal of COD, turbidity and SVI also related with optimum dosage of coagulant. SVI (sludge volume index) can be calculated using Equation. 1.

$$SVI = \frac{1000\ x\ sludge\ volume\ (SV)}{Suspended\ solids\ (SS)} \quad (1)$$

3. Results and discussions

3.1. Leachate characteristics

COD. Based on Table 1, young leachate (3100-3310mg/l) shows higher value in terms of COD as compared to stabilized leachate (2610-2830 mg/L). The COD value was due to degradation organic matters that contain in solid wastes and then contribute to leachate formation [7]. In the methanogenic phase in stabilized leachate, the production of methane achieved maximum concentrations and slowly decreased. Thus, the degradation of organic matters in the leachate also reduced. At this point, the oxygen demand was also decreased. However, young landfill leachate undergo acid phase contributed to the higher concentrations in organic matters [8]. COD oxidized all organic matters using strong oxidation agents in absence of oxygen. However, stabilized leachate exerts high molecular weight and became difficult to breakdown. As comparison, young leachate is a fresh leachate which is has a high level of O_2. The O_2 is used in oxidized organic matters in this leachate and increase the oxygen demand in COD value.

BOD_5/COD ratio. The BOD_5/COD ratio represents the proportion of biodegradable organics in landfill leachate. Some information on the wastewater biodegradability can be gained where a high ratio of BOD_5/COD showed that the wastewater is relatively biodegradable whereas a low ratio indicates that the wastewater slower to be biodegraded. In this research, the ratio of BOD_5/COD in young leachate (0.102-0.105) was higher than stabilized leachate (0.086-0.090) indicated that young leachate was more biodegradable than stabilized leachate. Thus, the suitable treatment was suggested to be flocculation and coagulation. Stabilized leachate shows the lower ratio in BOD_5/COD. This value indicated that this landfill had reached a stable status and probably were not suitable for biological treatment processes [9]. Results from BOD5/COD ratio in this experiment evaluated that the leachate from PBSL in different ages contain low percentage in biodegradable fraction of COD.

Table 1. Leachate characteristics.

	Stabilized leachate		**Young leachate**	
Parameter	**Range**	**Mean**	**Range**	**Mean**
COD(mg/l)	2610-2830	2744	3100-3310	3195
BOD_5(mg/l)	239-250	243	324-336	329.333
BOD_5/COD(mg/l)	0.086-0.090	0.089	0.102-0.105	0.103
Fe(mg/l)	1.4-1.6	1.5	2.13-2.33	2.259
Conductivity(mS/cm)	22.2-23.2	22.7	13.3-13.9	13.7
Ammonia(mg/l)	2190-2270	2227.5	1220-1280	1240
Suspended solid(mg/l)	87.4-95.9	93	231-249	240
Colour(PtCo)	2450-2740	2526	1480-1630	1559
Turbidity(NTU)	55.6-59.2	57.567	95.3-99.3	97.625
pH	8.16-8.27	8.22	7.43-7.65	7.57

3.2. Soluble COD and particulate COD.

Particulate organic commonly feature as a large particle size which could not pass through cell wall and needed to undergo extracellular hydrolysis prior to adsorption [10]. Both of soluble and particulate COD contain biodegradable and unbiodegradable matter. In this research, SCOD values determined by after the determination of soluble COD, the particulate COD can be calculated as shown in Equation 2*:*

$$Particulate\ COD\ (PCOD) = COD_{Total} - COD_{soluble} \tag{2}$$

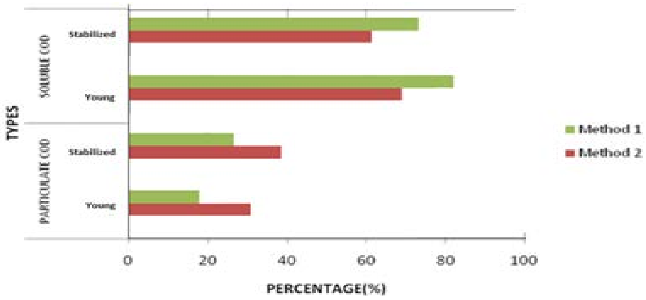


Figure 1. The correlation between PCOD and SCOD for two methods.

Method 1 utilized 5ml/l of zinc sulphate to coagulate and flocculate all the particulate matter in both leachate before filtered the sample was filtered with 0.45µm filter paper. The experimental results in Figure 1 indicated that Method 1 exhibited the highest percentage of soluble COD (stabilized leachate = 72.28%; young leachate = 82.19%) compared with Method 2. However, analysis on COD removal based on Figure 2 shows that Method 1 able to removed 27.50% of COD from stabilized leachate sample whereas young leachate showed smaller percentage of COD removal which is 19.70%. The analysis from Method 1 identified that the COD value in particles size 0.45µm contains more in young leachate compare in stabilized leachate.

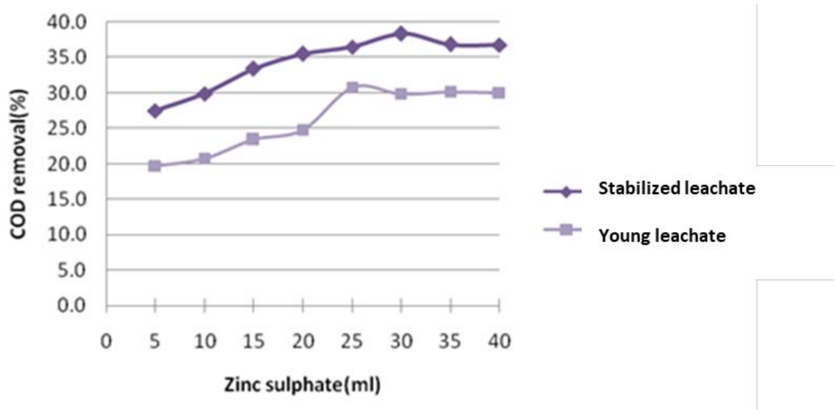
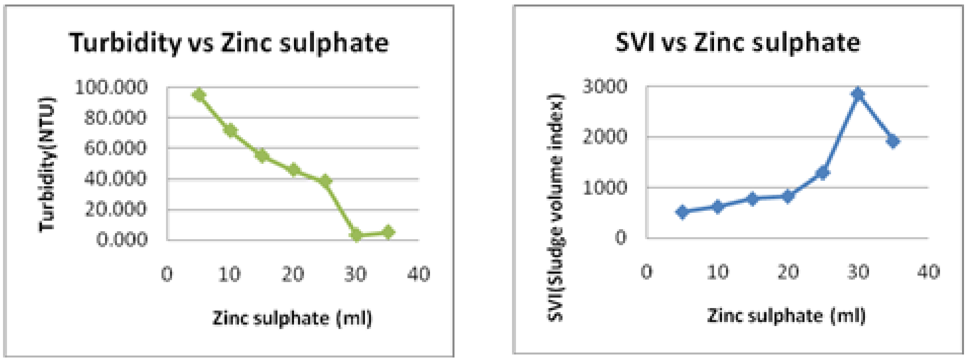


Figure 2. Correlation between COD removal and amount of Zinc sulphate.

As seen in Figure 2, the graph shows the correlation between COD removal percentage and dosage of zinc sulphate in flocculation and coagulation process. The graph also implied that the COD removal increased with increasing of zinc sulphate dosage until the point of maximum removal (stabilized leachate = 38.4%; young leachate = 30.8%), at about 30ml/l of coagulant in stabilized leachate and 25 ml/l in young leachate. The graph started to be constant after the optimum dosage was achieved. At the optimum dosage, the coagulant had no significant effect on the increasing dosage of coagulant [11]. The COD removal percentage in both leachate in Figure 2 was reduced after optimum dosage because of the destabilization of particulates. Zinc sulphate shows the effectiveness in remove more COD in stabilized leachate compare in young leachate. This result might have been caused by different molecular weight of leachate. Based on previous study, the stabilized leachate contains high molecular weight (humics like substances) whereas young leachate contains low molecular weight [12]. Therefore, the coagulation and flocculation process in this method could remove the organic materials including humics like substances that contains more in stabilized leachate. Consequently, the removal of COD in stabilized leachate is higher than young leachat**e.**

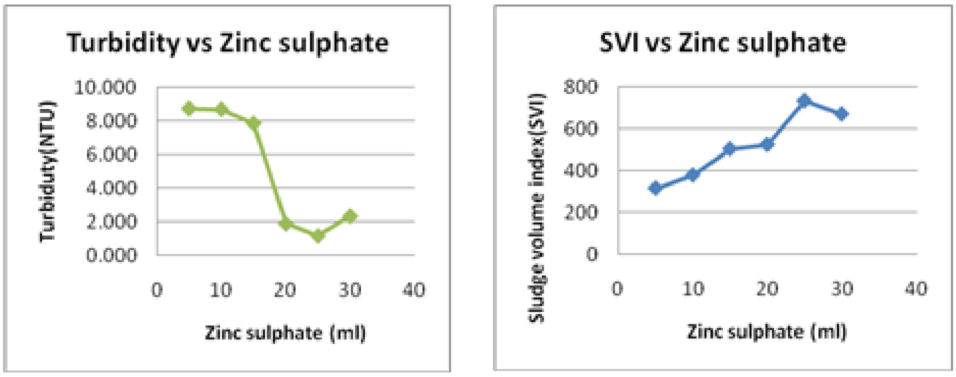
Figures 3 (a) and Figure 4 (a) show the effect of turbidity in stabilized and young leachate by increasing the dosage of zinc sulphate. The turbidity data for stabilized leachate was decreased when the volume of zinc sulphate was increased. It implied that the value of turbidity reduced from 38.336 NTU to 3.085 NTU when the dosage of zinc suphate was increased from 25 ml/l to 30 ml/l. Leachate from young leachate showed similar pattern; when the dosage of zinc sulphate was increased to 25 ml/l, the turbidity of leachate was decreased. At this stage, the volume of zinc sulphate was already optimum for the sample.

The sludge volume index (SVI) was calculated by using simple formulation. From Figures 3(b) and 4 (b), the results revealed that the highest SVI value was achieved by using 30 ml/l of zinc sulphate in stabilized leachate and 25 ml/l in young leachate. Determination of optimum dosage of zinc sulphate as coagulant was defined by analyzing the turbidity and SVI data. The research found that the optimum dosage for coagulant (zinc sulphate) in coagulation and flocculation process is 30ml/l in stabilized leachate and 25ml/l in young leachate.



(a) (b)

Figure 3. (a) Correlation between turbidity and amount of Zinc Sulphate; (b) Correlation between SVI and amount of Zinc Sulphate.



(a) (b)

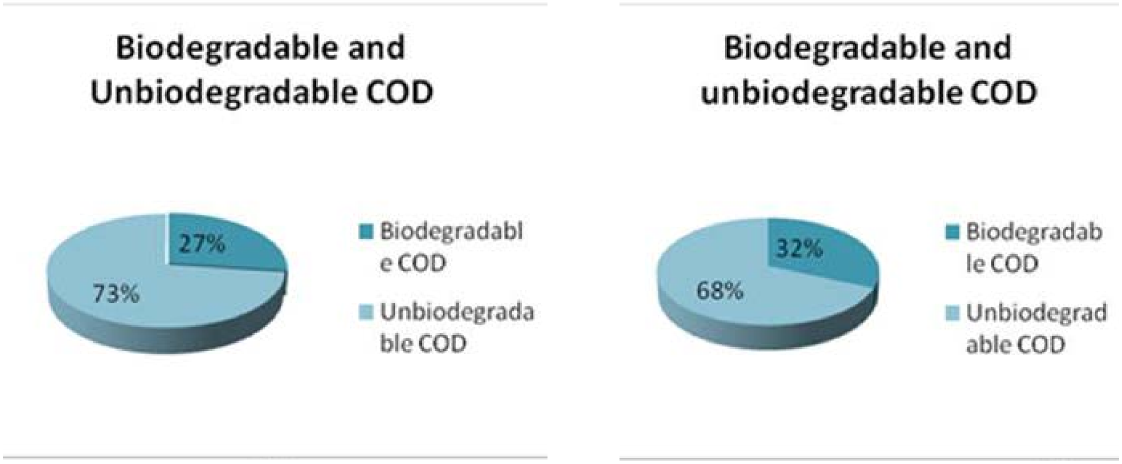
Figure 4. (a) Correlation between turbidity and amount of Zinc Sulphate; (b) Correlation between SVI and amount of Zinc Sulphate.

The optimum dosage of coagulant in stabilized leachate indicated the higher value compare to young leachate due to the characteristics of leachate. The results may affected by colour content. Colour usually related to COD and turbidity of sample. Stabilized leachate contains high value of colour (2526.667 Pt-Co) while young leachate contains lower value (1559.667 Pt-Co) of colour. Therefore, stabilized leachate need more coagulant in coagulated and flocculated all the organic materials (humic like substance) that cause the contamination of colour [13].

3.3. Biodegradable and Unbiodegradable COD

The biodegradable COD in both leachate sample from PBSL show a small value as compared to unbiodegradable COD. The results for stabilized and young leachate samples came out with same pattern in both leachates. Figure 5 (a) implied that stabilized leachate contains only 27% of biodegradable COD compare to 73% of unbiodegradable COD. The young leachate sample configured 32% of biodegradable COD higher than biodegradable COD in stabilized leachate in Figure 5 (b). Generally, biodegradable COD contains more two fractions including readily biodegradable COD (Sbsi) and slowly biodegradable COD (Sbpi). It was separated by physical properties which is soluble and particulate.

Biodegradable COD can be removed from leachate by aeration process. However, stabilized and young leachate were recognized as moderate stable and stable landfill from the characteristics analysis. The data from characteristics for both leachates prove that the leachate from PBSL contains more unbiodegradable COD and not classified as biodegradable landfill based on ratio of BOD_5/COD.



(a) (b)

Figure 5. (a) The percentage of biodegradable and unbiodegradable in stabilized leachate and (b) The percentage of biodegradable and unbiodegradable in young leachate.

4. Conclusions

In this study, COD fractions in leachate were investigated by using different methods based on physical and chemical separation process. Leachate with different ages was categorized as stabilized and young leachate from PBSL. Characterization of leachate shows that the COD value in stabilized leachate in range 2610-2830 mg/L while young leachate value was 3100-3310mg/L. The BOD_5/COD ratio for stabilized leachate is 0.086-0.09 and young leachate was 0.102-0.105. Young leachate has high COD and BOD_5/COD ratio compared to stabilized leachate because of the age of landfill. Although the COD and BOD_5 value of PBSL was lower than typical landfill, the analysis on characteristics of this landfill is continuous analysed in treat the leachate.

5. References

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