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Fractionation of Organic Content in Mature Leachate from Semi-Aerobic Landfill by Means Physico-Chemical Method

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Abstract: Chemical oxygen demand(COD) was the main characteristic in analyzed the quality of wastewater and leachate. Soluble COD(SCOD) and particulate COD(PCOD) previously determined by physico-chemical methods such as i) coagulation-flocculation ii) filtration. These meth-ods widely used in wastewater treatment. However, research on COD fraction for leachate is limited. This study aims to analyzed and de-termine the efficient method for PCOD and SCOD in mature leachate from semi-aerobic landfill. Three methods were applied in this re-search to compare the significant features of the three methods. Method 1(M1) and Method 3(M3) were applied from previous studies on COD fraction in wastewater. Modified method with optimum dosage of zinc sulphate known as Method 2(M2) was investigated in evaluate the correlation between COD particulate and coagulant. The result showed that PCOD in M2 is dominant (38.54%) due to the optimum dosage of coagulant while PCOD for M1 and M3 showed the results (M1=27.00%; M2=27.58%), respectively. In conclusion, the results of this study validate that M1, M2 and M3 in determine PCOD in wastewater and leachate. Effect of optimum dosage in M2 was consid-ered as new finding. Further research on COD fractions of leachate should be investigated to identify the appropriate treatment for mature leachate.

Index Terms: Leachate; COD Fraction; Soluble COD; Particulate COD,

I. INTRODUCTION

The Landfill process generates a great amount of leachate. Leachate also defined as any liquid which seeps through the landfill or comes in contact with waste. It formed from the percolation of water or other liquid through landfill waste and considered to be a contaminated liquid, since it contains many dissolved, suspended materials, inorganic substances and high concentration of organic substances [1]. Semi-aerobic landfill has many advantages compared with other landfill types. The quality of leachate improves significantly and more rapidly than in anaerobic condition. This system removes the leachate and gas continuously from the waste mass using leachate collection and gas venting system and improves the waste stabilization process [2]. Leachate may also carry insoluble liquids (such as oils) and small particles in the form of suspended solids [3]. The decomposition of organic matter such as humic acid(HA) and fulvic acid(FA) may cause the water to be yellow, brown or black. Humic matter contains probably at least 40 organic compounds with a complex chemical structure like a condensation product containing aromatic nuclei linked together with many functional groups [4]. COD usually represent as a main parameter in evaluate the quality of wastewater or leachate. The higher value of COD means the less oxygen available in the leachate that contributes to water pollution. Researchers focused on removal of COD in water treatment to make it suitable for reuse or discharging into natural water [5]. The BOD_5/COD ratio also provide useful criteria for choosing a suitable treatment process [6]. Landfill leachate from a fresh landfill usually has a higher BOD_5/COD ratio (< 0.1) and leachate from mature or stable one has a lower BOD_5/COD ratio. Low biodegradability of wastewater indicates that organic compounds such as humic compounds are hard-to-biodegrade [7]. Mature landfill contains large amount of non-biodegradable organic compound with high molecular weight which is not easily degradable [8]. The aromaticity group showed the higher value in mature landfill and contained the significant portions of aliphatic functional groups [9]. Commonly, the separation between PCOD and SCOD were identified by using 0.45 µm filter paper. Leachate samples were filtered through a 0.45 µm membrane to eliminate humins which are insoluble at any pH [10]. Coagulation using $ZnSO_4$ was employed for the determination of PCOD, in relation to physical–chemical separation techniques including destabilization with a non-hydrolyzing trivalent cation [11]. Natural coagulant was implemented in coagulation-flocculation method as treatment in landfill [12]. However, this study was suggested $ZnSO_4$ as coagulant for COD fraction compared to other coagulants because of the less adsorptive characteristic. The chemical reaction between $ZnSO_4$ and H_2O will form $Zn(OH)_2$ flocs. SCOD estimated using $ZnSO_4$ coagulation was 3.2% higher than that measured using $LaCl_3$ coagulation [12]. The characteristics that are analyzed for PBSL include, COD, BOD_5, ratio of BOD_5/COD, suspended solid, color and turbidity.

II. MATERIALS AND METHODS

2.1 Sample preparation

Leachate samples were collected from the Pulau Burung Sanitary Landfill (PBSL) using polyethylene bottles washed and rinsed with deionized water (DI) before used.

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The bottles were sealed and labelled once the sample was collected.

Then, the samples were transported to the laboratory within 48 hours and stored in cool room at 4˚C for a period of approximately two weeks [11].

III. METHODS

Method 1 (M1): 1.0ml of 0.6 M $ZnSO_4$ solution was added to 100 ml of samples. The beaker was shaken to homogeneous the samples and coagulant, and the pH value for each beaker was checked. Then, the pH solution was adjusted to approximately 10.5±0.3 with 6 M NaOH. After that, the sample was stirred with a magnetic stirrer for 1 min at high speed (approximately 200 rpm), and 5 min at low speed (30 rpm). PCOD was found out by equation (1).

$$PCOD = COD\ total - SCOD \qquad (1)$$

Method 2 (M2): 2.0 ml until 8.0 ml of 0.6 M $ZnSO_4$ solution was added to 100 ml of samples. pH solution was adjusted to approximately 10.5±0.3 with 6 M NaOH. Then, sample was agitated with a magnetic stirrer for 1 min at high speed (approximately 200 rpm), and 5 min at low speed (30 rpm). The samples were allowed for quiescent settling for 1 hour and withdrawn as approximately 30 ml supernatant aliquots with a 5.0 ml plastic pipette. The supernatant aliquots were passed through a pre-rinsed 0.45 µm mixed cellulose ester membrane filter(Milipore, MA) and measure for COD, turbidity and SVI value in triplicate samples. Value for PCOD in M2 was calculated by equation 1. The calculation on SVI value is shown in equation 2. All the procedures were repeated for different volumes of $ZnSO_4$ until the graph of $ZnSO_4$ volume verses COD value became constant. The maximum removal of COD, turbidity and SVI is also related with optimum dosage of coagulant. The optimum dosage of $ZnSO_4$ was used to determine the PCOD and SCOD for mature leachate.

$$SVI = (1000 \times SV)/SS \qquad (2)$$

Method 3(M3): 100 ml of sample was filtered (0.45 µm) using pressure pump. The filtrate was analyzed for SCOD and PCOD.

IV. RESULTS AND DISCUSSION

3.1 Leachate characteristic

Table 1 shows the characteristics of mature leachate from semi-aerobic landfill. COD value was in range 2690-2770mg/l and the BOD_5 values (239-254mg/l). The age of landfill is the main reason for these results which shows the lower values compare to standard fresh leachate [6]. In addition, semi-aerobic landfill type was improved the quality of leachate by semi-aerobic system. It is significantly reduced the COD and BOD_5 values compare to others landfill.2 As landfill age is increased, the COD value is decreased [9].

Table 1. Characteristic of mature leachate

Parameter	Range	Mean
COD (mg/l)	2690-2770	2738.30
BOD_5 (mg/l)	239-254	244.58
BOD_5/COD (mg/l)	0.086-0.091	0.089
Suspended Solid (ppm)	87.40-95.90	93.21
Colour (PtCo)	2450-2740	2526.70
Turbidity	55.60-59.20	57.57

The lower BOD_5/COD ratio (0.089) was found in this study and categorized the leachate in mature or stable type. It is approximately same to the exact age of landfill (>10 years). Low biodegradability of leachate indicates that organic compounds such as humic compounds are hard-to-biodegrad [7]. Result shows that leachate contains high level of colour which is 2556.67 (Pt-Co). Physically, colour of mature leachate from PBSL is dark brown to grey because of organic wastes as their major composition [1].

Suspended solid and turbidity in mature leachate show lower value compared to young leachate but higher in wastewater [7]. It is estimated that mature leachate has less suspended solid in the surface of leachate. It is also affected by the maturity and age of landfill. The high molecular weight is difficult to breakdown and became a reason for mature leachate to contain less suspended solid, in this research [8].

The relationship between turbidity and SS are depends on water bodies. Besides, the colour, SS and turbidity show similar trends, which concludes that these factors are attributed to organic matters. The colour for leachate is increased by age of landfill based on the effect of humicsubstances.4 However, the turbidity and SS for leachate are decreased with time [9]. Decomposition process in landfill is also affects the characteristics of leachate [8].

3.2 Particulate COD (PCOD) and Soluble COD(SCOD)

Fig. 1 depicts the PCOD (mg/l) in M1, M2 and M3. Comparative results show that M2 has the highest value of PCOD compared to M1 and M3. The results indicate that the value of SCOD in M2 must be affected by chemical reaction. The increase of coagulant (cation, Zn^{2+} from $ZnSO_4$) to achieve the optimum dosage of leachate has increased the potential of cation to bind with organic substances chemically and became flocs (particulate) [13].

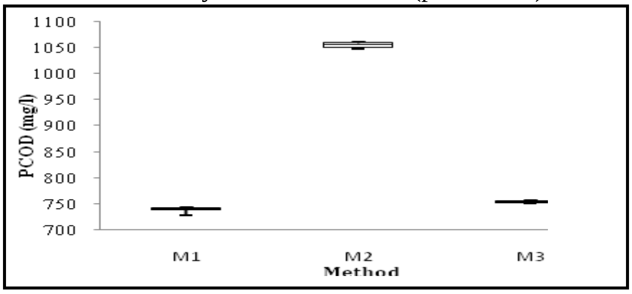

Figure 1. Box plot of PCOD in different methods

Hence, it would reduce the value of SCOD because the flocs contain soluble particles (organic material sized smaller than 0.45µm). In addition, the chemical process would modify the chemical composition of organic matter, and even it increased the removal of COD [14]. As shown in Fig. 2, the effect of $ZnSO_4$ dosage on turbidity and SVI were determined. The turbidity was decreased and the SVI was increased when the dosage of coagulant achieved to optimum level. Based on previous study, the mature leachate contained high molecular weight [8]. Thus, the effect of dosage(optimum dosage) may contribute to the highest removal of PCOD.

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Therefore, the coagulation and flocculation processes in this method could remove the organic materials such as humics like substances that exist more in mature leachate. Optimum dosage of coagulant indicates the optimum removal of COD [14].

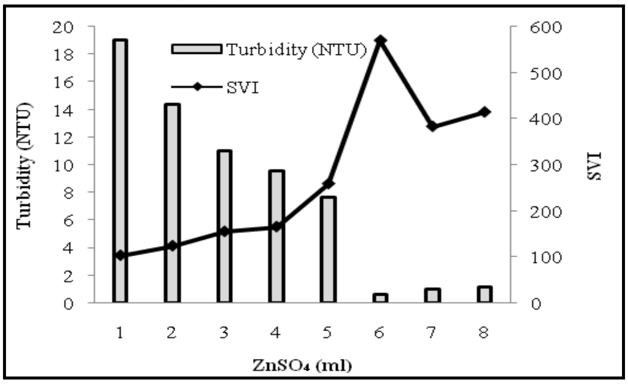

Figure 2. Effect of $ZnSO_4$ dosage on turbidity and SVI

Normally, the coagulation and flocculation processes cause to decrease the value of turbidity and eliminate the particulate from leachate samples [10]. The impurities were flocculated and removed by filtration process using 0.45 µm membrane filter paper. The sludge volume index (SVI) was calculated by using simple formulation. Fig. 2 expressed that the highest SVI value corresponds to 6.0 ml of $ZnSO_4$ in mature leachate. The optimum dosage of coagulant is determined by analyzing the turbidity and SVI data. The turbidity was decreased and the SVI was increased when the coagulant achieved to optimum level. This research found that the high amount of optimum dosage is due to the characteristics of the leachate [12]. The results might be affected by colour content. Colour is usually related to COD and turbidity of the sample. Mature leachate contains high value of colour (2526.67 Pt-Co). Therefore, mature leachate needs more coagulant to coagulate and flocculate all the organic materials (humic like substance), which causes the contamination of colour [2].

3.3 Statistical analysis

Statistical analysis on variance (ANOVA) in Table 2 was identified that the methods applied in determination of PCOD and SCOD were no significantly different. Four comparison were done in evaluate the data. The P-value in analyzed between methods (M1M2M3) shows the smallest value (P=2.665E-18) compare to others. This data was revealed that M1, M2 or M3 are accepted in define the PCOD for wastewater and semi-aerobic leachate.

Table 2. Analysis on variance (ANOVA) between methods

Between Methods			*P-value* [*]
M1	M2	-	1.027E-12
M1	M3	-	1.322E-03
M2	M3	-	1.551E-13
M1	M2	M3	2.665E-18

*(P-value<0.05)

The P-value in compared two methods (M1M2, M1M3 and M1M3) also shows the similar trend which are P-value smaller than 0.05. Methods derived from literature studies (M1 and M3) obtained P=1.322E-03. Thus, the filtration and coagulation followed by filtration process were significantly removed the particulate particles in leachate and wastewater.

V. CONCLUSION

Optimum dosage of coagulant in coagulation-flocculation process is significant as alternative method for PCOD and SCOD. Literature studies recommended single physical process (filtration) and physico-chemical method (coagulation-flocculation followed by filtration) for wastewater. However, this study was validated and clarified that these methods also sufficient methods for semi-aerobic leachate. Filtration was identified as efficient method in determine PCOD and SCOD in semi-aerobic leachate based on handling process, time consume, and energy save.

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