CHARACTERISTICS OF LEACHATE UPON HYDROTHERMAL TREATMENT PROCESSING: CASE STUDY OF AMPANG DISTRICT MUNICIPAL SOLID WASTE LEACHATE

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ABSTRACT: Municipal solid waste (MSW) leachate is a hazardous liquid produced from decomposition of solid waste with high amount of organic matter and ammonia-nitrogen with obnoxious smell. This study aimed to investigate the behavior of MSW leachate when subjected to hydrothermal treatment using an autoclave set up at below water critical points (temperatures of 100 °C, 150 °C, and 200 °C at 0.1 MPa, 0.4 MPa and 1.6 MPa, respectively) with 15 min and 60 min holding time. Physicochemical characterization of the setup at 200 °C and 1.6 MPa at 60 min holding time indicates a feasible parameter when materials that caused the dark color and obnoxious smell were almost completely removed. Over 99% of chemical oxygen demand and ammonia nitrogen was eliminated when treated with hydrothermal treatment and yielded a condensed liquid product that complied with permissible limits set by the National Water Quality Standard Malaysia and the World Health Organization for wastewater discharges for irrigation purposes. Chromatographic analysis indicated that most of the organic compounds present in the raw leachate was removed. This processing is believed to be an environmentally friendly method that can treat MSW leachate rapidly, and it has the potential to be used as an effective alternative to existing leachate treatment technologies.

ABSTRAK Larut lesap daripada sisa pepejal perbandaran merupakan cecair merbahaya yang berlaku semasa penguraian sisa pepejal dengan jumlah bahan organik dan ammonianitrogen yang tinggi dengan bau menjengkelkan. Kajian ini bertujuan bagi mengkaji sifat larut lesap ini apabila melalui rawatan hidroterma menggunakan autoklaf yang ditetapkan di bawah titik kritikal air (suhu 100 °C, 150 °C, dan 200 °C pada 0.1 MPa, 0.4 MPa dan 1.6 MPa masing-masing) dengan tempoh masa 15 minit dan 60 minit. Sifat fizikal kimia yang dirawat pada suhu 200 °C, 1.6 MPa selama 60 minit menunjukkan satu parameter yang boleh dilaksanakan apabila warna gelap dan bau yang menjengkelkan hampir dikurangkan sepenuhnya. Lebih 99% ammonia nitrogen disingkirkan apabila dirawat dengan rawatan hidrotherma dan menghasilkan air bersih yang mematuhi had yang dibenarkan oleh Piawaian Kualiti Air Kebangsaan Malaysia (NWQSM) dan Pertubuhan Kesihatan Sedunia (WHO) bagi pelupusan air sisa pepejal bagi tujuan pengairan. Analisis kromatografi menunjukkan bahawa sebahagian besar sebatian organik yang terdapat dalam larut resap telah disingkirkan. Pemprosesan ini diyakini merupakan kaedah mesra alam yang dapat merawat dengan cepat, dan berpotensi digunakan sebagai alternatif efektif untuk teknologi rawatan larut lesap sedia ada.

KEYWORDS: municipal solid waste; leachate; hydrothermal; organic compound

1. INTRODUCTION

The recent economic, demographic, and technological development of society have led to an increase in the production of municipal solid waste (MSW), which consequently causes a waste disposal problem. Landfills are the most widely used method to dispose MSW since it is simple, feasible and cost effective; it minimizes carbon dioxide (CO₂) and controls methane (CH₄) and leachate emissions [1] especially in sanitary landfills. However, the conventional landfilling method has a lot of negative impacts on the environment. Open MSW dumpsites nowadays have become looming hotspots for water, air, and land pollution [2]. As waste generation increased, more waste would be dumped into landfill that would simultaneously lead to an increase in landfill leachate generation. Unfortunately, waste is still being wantonly discarded in open dumps all over the world, while the substantial resources spent in remediation suggest that landfill leachate is a significant source of groundwater pollution [3]. In Malaysia, Act 672, gazetted in 2007, is the law that deals with solid waste and public cleansing management. The plans and strategies formulated in line with Act 672 were projected to bring about huge transformation in MSW management in the country. However, the authorities face a huge challenge in the implementation of the National Policy regarding MSW management [4]. The strategies to reduce waste to be sent to landfill do not seem to produce the expected results. Landfill is still the main MSW disposal approach [5] and solid waste sent to landfill is increasing every year [6].

Landfill leachate generally contains organic matter (biodegradable, but also refractory to be biodegraded), ammonia-nitrogen (NH₃-N), heavy metals, and chlorinated organic compounds and inorganic salts [7]. The main concern about those compounds in environmental matrices is that they are hazardous and of difficult decomposition by soil and aquatic microorganisms [8]. Inhabitants who live near the dumps are particularly at risk of consuming contaminated water. Domestic water use for drinking, bathing, or washing in nearby areas may lead to exposure to volatile organic compounds (VOCs) [9], mercury [10], polychlorinated biphenyl (PCBs) [11], or polyaromatic hydrocarbon (PAHs) [12]. A laboratory analysis by Griffith et al. [13] identified 593 sites in the US where contaminated groundwater was used for drinking purposes. In the state of New Jersey for example, leachate from the site of Lipari Landfill has migrated into nearby streams and lakes adjacent to a residential area and contaminated most of the water pathways causing an increase in the proportion of low-birth-weight babies (2.5 kg) and lowering the birth weight for the population living closest (within 1 km radius) to the landfill. Studies on leachate demonstrate that it contains compounds such as PAHs, alkenes, ketones, esters, alcohols [14], phthalates, phenols and nitrogen compounds [15], carboxylic acids, amines, amides, aldehydes and carbohydrates [16]. These pollutants have accumulative, threatening, and detrimental effects on the survival of aquatic life forms, ecology, and food chains leading to enormous problems in public health including carcinogenic effects, acute toxicity, and genotoxicity [12,17-19].

Solid waste landfills are often reported to have serious and recurring leachate contamination issues, and the pollution is caused by the design of the landfill and existing leachate treatment system that are not able to fully accommodate the increasing volume of solid waste received [20]. Biological processing is usually carried out to remove the contaminants, especially the organic contents and total Kjeldahl nitrogen (TKN) in the form

of ammonium – from leachate, to meet the compliance limits before being discharged into the environment [21]. Conventional biological treatment process usually consists of two stages: denitrification and nitrification. However, the conventional pathway involves higher operational cost due to the requirement of high amounts of oxygen during the nitrification when pure oxygen is used to supplement the air system and carbon during the denitrification process [22]. The most common approach to leachate treatment involves biological and physical or chemical leachate treatment in combinations. Leachate contains recalcitrant to biological process substance that cannot be treated using either one of the processes alone. All the contaminants make the treatment of leachate complex and expensive [23].

Advanced oxidation process (AOP) has gained importance over the past few years due to its potential to biologically destruct resistant organic molecules and micro pollutants, enhancing the quality of discharge waters from secondary treatment units [24]. Of all the AOPs, the hydrothermal oxidation process (sub- and super-critical) has received particular attention for its complete conversion without producing any harmful intermediates [25]. AOP is also referred to as hydrothermal treatment process. Hydrothermal treatment below the critical points of water has been widely employed for the solubilization, extraction, and liquefaction of target materials [26]. Subcritical water has hydrolytic and pyrolytic reaction characteristics, which result from a decrease in the dielectric constant and increase in the ion product of water at temperatures and pressures below and near 374 °C and 22.1 MPa [27-28]. Most researchers have focused on solubilization and extraction to recover valuable organic compounds such as glucose and organic acids [27,29-31]. Some researchers have dealt with hydrothermal treatment as pretreatment prior to fermentation, gasification, composting, and other processes [26,32-35]. Many have focused on treatment using supercritical water, which is the process that occurs in water above its critical points [36-41]. Only a few researchers focus on treating MSW leachate by employing hydrothermal treatment below the critical points water. Kirmizakis et al. [42] employs hydrothermal treatment below the critical points water to treat landfill leachate at temperatures in the range of 100 °C to 374 °C but requires chemicals as a catalyst for the treatment. In this work, hydrothermal treatment below critical points condition was performed to treat MSW leachate samples from the area of Ampang district, Selangor, Malaysia. Physicochemical characteristics of the leachate samples such as color, odor, pH, chemical oxygen demand (COD), ammonia-nitrogen (NH₃-N) and the organic compound composition of the leachate were mainly investigated. The experimental results were then compared with the standard discharge limit by the National Water Quality Standard Malaysia (NWQSM) and the World Health Organization (WHO) at the permissible limits for contaminants present in wastewater discharges for irrigation purposes.

2. MATERIALS AND METHOD

2.1 Material

Fresh MSW leachate was collected from several garbage trucks for municipalities in the area of Ampang district, Selangor owned by *KDEB* Waste Management Sdn Bhd (KDEBWM) for the sampling. Each garbage truck had a temporary leachate storage tank below it, which allowed excess liquids in the MSW to infiltrate and accumulate in the tank. MSW leachate sample went directly from the tank into container. Collected MSW leachate was filtered using a 1.5 mm mesh to remove solid particles and was stored at 4 °C.

2.2 Hydrothermal Treatment Processing Setup

Fig. 1 shows the laboratory-scale experimental apparatus for the hydrothermal treatment. The reactor was loaded up to ³/₄ volume of the reactor. Raw MSW leachate (50 mL) and 130 mL distilled water were put in a batch type autoclave reactor and sealed. Saturated steam and pressure were set at 100-200 °C and 0.1-1.6 MPa depending on working temperature. The reactor was held for 15 min or 60 min after reaching all the setup conditions. The reactor was quenched with cooling water at room temperature in the condenser to terminate further reactions from occurring after the intended holding time. The clean liquid was collected as the product of the hydrothermal treatment and the inorganic particles that had settled at the bottom of the reactor were discharged.



Fig. 1: Laboratory-scale experimental apparatus for the hydrothermal treatment.

2.3 Physicochemical Analysis

The parameters for characterization were chosen according to the leachate pollution index (LPI) that provides an overall pollution potential of a landfill site in identifying whether the MSW leachates are hazardous or not. Physicochemical parameters were analyzed for color, odor, pH, chemical oxygen demand (COD), and ammonia-nitrogen (NH₃-N) composition. Color and odor were observed according to the physical appearance of the sample and indicated using sensorial technique by smelling the samples respectively. pH was analyzed using a pH meter, COD was determined by the colorimetric method, and NH₃-N was measured by the salicylate method (385 HACH DR/3900 Spectrophotometer) using the APHA standard methods [43]. The removal percentage of COD and NH₃-N was computed based on following equation:

Percentage of removal (%) = ((Xi - Xf)/Xi) * 100%

where percentage removal represents percentage of COD and NH_3 -N removed from raw MSW leachate, *Xi* refers to average initial raw reading of COD and NH_3 -N before treatment, and *Xf* is the average final reading of COD and NH_3 -N after treatment.

2.3.1 pH Sampling

The pH values were measured immediately after the samples were taken from the garbage truck. Three representative samples from each garbage truck were put into glass closed containers. The fresh sample was stirred, and pH meter electrode was placed in the leachate sample and measurement recorded when the readings stabilized. The electrode was rinsed several times with distilled water and blotted dry before placing into the sample. The same steps were followed for pH measurements of treated leachate.

2.3.2 Chemical Oxygen Demand (COD)

A high range COD digestion reagent vial was used for the sample concentration up to 15000 mg/L range like MSW leachate. The leachate sample was made homogenous by gently swirling and inverting the container several times for 30 sec, before 0.2 mL leachate was pipetted into the COD digestion reagent vial. The vial was capped tightly, rinsed with deionized water, and wiped clean with paper towel. The vial was inverted gently several times to make sure the content was mixed and was placed into the 150 °C preheated DRB 200 reactor for two hours. A blank sample was prepared with 0.2 mL deionized water instead of the leachate. After 20 minutes, the DRB 200 reactor was turned off. Both sample and blank vials were gently inverted before allowing them to cool down to room temperature. Measurements were made with a spectrophotometer set at 620 nm wavelength.

2.3.3 Ammonia Nitrogen (NH₃-N)

The blank sample was prepared by filling the sample cell with 10 mL deionized water, followed by the leachate sample preparation by filling the cell with 10 mL leachate sample. Both were filled with ammonia salicylate reagent powder pillow (Hach Malaysia Sdn Bhd), and the cells were inverted to dissolve the reagent well. After three minutes of reaction time, both cells were filled with ammonia cyanurate powder pillow. The cap was closed, and cells were shaken to mix well. After 15 min, the green color formed in the presence of NH₃-N was measured at 655 nm.

2.4 Organic Compound Composition

The organic compound composition was determined based on the standard APHA method [43]. Samples were prepared according to Turki et al. [44] with slight modifications. Sample (0.01 g) was brought to 1 mL volume with ethanol and filtered (0.2 μ m nylon membrane) prior to gas chromatography – mass spectrometry (GC-MS) analysis using a HP-5MS fused silica capillary column (30 m × 250 μ m i.d. and 0.5 μ m film thickness; Agilent Technologies). The GC oven temperature was programmed as follows: 80 °C held for 2 min and raised at 10 °C/min to 250 °C (held for 10 min). Helium was the gas carrier, and the flow rate was set at 1.07 mL/min. The sample injection (1.0 μ L) was set on a splitless mode at 250 °C with solvent delay of 4 min. Detection was conducted by a mass selective detector with electron impact ionization at 70 eV, in selected ion monitoring mode. MS transfer line temperature was at 250 °C, and the MS was operated in full scan in electron ionization mode with an electron multiplier voltage of 1588 V. The mass scanning was set to be of a range of m/z 40 to 500. The semi-quantification and the removal of persistent compounds in each stage of the process were performed by comparing the corrected areas of specific peaks to the peak area.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characteristics

MSW raw leachate was a dark-cloudy colored liquid (brown and black), very acidic, offensive, and sometimes had a very pervasive smell. The pH of the samples collected from several garbage trucks owned by KDEBWM during the transportation of the MSW to the landfill were between 3.00–3.54 (average of 3.27). The COD ranges between 47000–55000 mg/L in raw leachate samples (average of 51000 mg/mL) and the NH₃-N varied between 2950–4042 mg/L in the raw leachate samples (average of 3496 mg/L). The pH of the samples when subjected to hydrothermal treatment as a function of temperature is shown in Fig. 2. The pH of hydrothermal treatment from 15 min to 60 min holding time was maintained within acceptable range limit.



Fig. 2: Effect of temperature on pH change after hydrothermal.

Table 1: The physicochemical characteristics of MSW leachate from Ampang district, Selangor

| No. | Parameter | Raw leachate | Hydrothermal treated | | | NWQSM | NWQM |
|-----|-----------------------------|-----------------------|-----------------------------|----------------------------|----------------------------|-----------|-----------|
| | | | 100 °C, 0.1 MPa, 15 min | 150 °C, 0.4 MPa, 30 min | 200 °C, 1.6 MPa, 60 min | standard* | standard* |
| 1 | Color | Dark brown, cloudy | Very light yellow, clear | Light yellow, clear | Almost transparent, | - | - |
| 2 | Odor | Obnovious | Less obnovious | Less obnovious | No odor | | |
| 2 | Odol | Obiloxious | Less oblioxious | Less oblications | NO OUOI | - | - |
| 3 | pН | 3.00-3.54 | 4.00-4.03 | 5.00-5.20 | 5.00-5.05 | 5.0-8.0 | 6.5-8.5 |
| 4 | COD (mg/L) | 47000-55000 | 7800-8800 | 230-248 | 48-52 | 100 | 250 |
| 5 | NH ₃ N (mg/L) | 2950-4042 | 2301-2809 | 12.8-15.9 | 0.20-0.21 | 2.7 | - |

*Discharge standard at Class IV for irrigation.

The result shows that with the increasing pH value, COD and NH₃-N showed decline, and organic compounds in the treated leachate became significantly simpler than raw MSW

leachate, as can be seen in Table 1. Raw leachate is a potentially hazardous material to lifeforms because biochemically it exhibited low pH, high COD, and high NH₃-N. Among the three set up parameters, temperature of 100-200 °C, pressure of 0.1-1.6 MPa and holding time of 15 min or 60 min, the conditions of 100 °C, 1.6 MPa and 15 min holding time yielded condensed treated leachate that is characterized by very light yellow and clear liquids with some obnoxious smell. Only 30% of NH3-N and 84% of COD was eliminated when treated with hydrothermal treatment that required further treatment to reach permissible limits. The conditions of 200 °C, 1.6 MPa with 60 min holding time provided the highest hydrothermal treatment performance on the raw MSW. Under these conditions, the final condensed liquid, which is clear and without any obnoxious smell (Table 1), complies with the National Water Quality Standard Malaysia (NWQSM) and the World Health Organization (WHO) standards at the permissible limits for contaminants presents in wastewater discharges for irrigation purposes. Percentage removal of COD and NH₃-N under minimum and maximum condition of hydrothermal treatment is shown in Table 2, calculated based on equation in section 2.3. Treatment at 100° C, 0.1 MPa with 15 min holding time causes 84% of COD and only 30% of NH₃-N to be degraded and removed. Treatment at higher temperature and longer holding time of 200 °C, 1.6 MPa with 60 min results in removal of over 99% of COD and NH₃-N. The results indicate that the hydrothermal treatment has significant impact on the reducing of organic substances in the leachate to meet the standard content in the wastewater discharging for irrigation purposes.

| No. | Parameter | Percentage removal | |
|-----|---------------------------|----------------------------|----------------------------|
| | | 100 °C, 0.1 MPa, 15 min | 200 °C, 1.6 MPa, 60 min |
| 1 | COD (mg/L) | 84% | 99% |
| 2 | NH ₃ -N (mg/L) | 30% | 99% |

Table 2: Percentage removal of COD and NH₃-N

3.2 Organic Compound Composition

A large number of organic compounds were identified in GC-MS based on a query mass spectrum with reference mass spectrum in the library of PAHs and PCBs. There were no detectable PCBs in MSW raw and treated leachate samples. Table 3 shows the list of PAHs found in the tested raw MSW samples. PAHs distribution data for the raw MSW leachate showed major contribution of low molecular weight PAHs (2-3 rings) molecular structures such as 2-fluorobiphenyl, 4-terphenyl-d4, naphthalene-d8, phenanthrene-d10, etc. Besides, there was also minor presence of higher molecular weight PAHs (4-6 rings) structures such as chrysene-d10, perylene-d12, chrysene, 3-methylchloanthrene, benzo(k)fluoranthene, and benzo(a)pyrene. Compounds that have more rings are much more stable and may hardly experience losses due to weathering processes such as solubilization, evaporation/ volatilization and natural biodegradation.

The presence of benzo(a) pyrene consisting of five fused benzene rings for example, even at the smallest composition, in the distribution data of the leachate is enough to be of concern and requires effective efforts to eliminate it. Immediate steps should be taken to limits its spread to the environment. This is because this compound is highly hazardous and is listed as a Group 1 carcinogen by the International Agency for Research on Cancer, IARC [45]. Benzo(*a*) pyrene is hazardous to human health because it will attack the nervous system, immune system, and reproductive system, react and bind to DNA, and result in mutations and eventually cancer in the body [46-48].

The compounds of concern in MSW leachate are those that are potentially hazardous, belonging to xenobiotic organic compounds including PAHs and halogenated organics like the PCBs. PAH organic pollutants are the most long-lived families of toxic chemicals. PAHs are strongly hydrophobic and lipophilic as well as have the propensity to accumulate in the tissue of any living thing [49] that can undergo long range transport and move into otherwise pristine environments. PCBs are toxic persistent organic pollutants that are harmful to humans and the environment due to their lipophilic characteristic and not easily degraded in the environment. Both PAHs and PCBs are therefore the focus of the MSW leachate analysis. The elimination of PAHs and PCBs in treated leachate is important to avoid undesirable adverse effects on human health.

| No | RT (min) | Compound | % PAHs | % PCBs |
|----|----------|-------------------------------------|----------|----------|
| | | • | detected | detected |
| 1 | 7.16 | 2-Fluorobiphenyl | 12.66867 | nd |
| 2 | 10.89 | 4-Terphenyl-d4 | 11.98621 | nd |
| 3 | 6.09 | Naphthalene-d8 | 8.62133 | nd |
| 4 | 9.31 | Phenanthrene-d10 | 7.87956 | nd |
| 5 | 8.66 | Chrysene-d10 | 7.49305 | nd |
| 6 | 4.5 | Phenol-d5 | 7.41990 | nd |
| 7 | 6.34 | Phenanthrene-d10 | 6.91754 | nd |
| 8 | 11.94 | Chrysene-d12 | 6.78624 | nd |
| 9 | 5.39 | Nitrobenzene-d4 | 6.53955 | nd |
| 10 | 3.6 | 2-Fluorophenol | 6.37875 | nd |
| 11 | 7.83 | Acenaphthene-d10 | 4.64253 | nd |
| 12 | 4.85 | 1,2-Dichlorobenzene-d4 | 3.66190 | nd |
| 13 | 13.28 | Perylene-d12 | 3.65857 | nd |
| 14 | 8.61 | 2,4,6-Tribromophenol | 2.47231 | nd |
| 15 | 4.85 | 1,4-Dichlorobenzene-d4 | 2.47227 | nd |
| 16 | 9.89 | Benzyl butyl phthalate | 0.33581 | nd |
| 17 | 5.24 | 3&4-Methylphenol | 0.03793 | nd |
| 18 | 8.84 | Di-n-butyl phthalate | 0.00669 | nd |
| 19 | 11.97 | Bis(2-ethylhexyl) phthalate | 0.00368 | nd |
| 20 | 11.97 | Di-n-octyl phthalate | 0.00368 | nd |
| 21 | 12.52 | 7,12-Dimethyl benz (a) anthracene | 0.00340 | nd |
| 22 | 7.86 | Diethyl phthalate | 0.00201 | nd |
| 23 | 11.97 | Chrysene | 0.00181 | nd |
| 24 | 7.69 | Acenaphthylene | 0.00175 | nd |
| 25 | 12.4 | 3-Methylchloanthrene | 0.00114 | nd |
| 26 | 6.08 | 4-Chlorophenol | 0.00073 | nd |
| 27 | 6.11 | Naphthalene | 0.00064 | nd |
| 28 | 11.92 | Benz(a)anthracene | 0.00059 | nd |
| 29 | 12.93 | Benzo(b)fluoranthene | 0.00057 | nd |
| 30 | 4.65 | 2-Chlorophenol | 0.00054 | nd |
| 31 | 12.96 | Benzo(k) fluoranthene | 0.00041 | nd |
| 32 | 13.22 | Benzo(<i>a</i>)pyrene | 0.00023 | nd |

Table 3: List of PAHs found in raw MSW leachate

RT (retention time); nd (not detected)

The chromatograms of raw MSW leachate and two hydrothermally treated leachates at 200 °C are shown in Fig. 2. The behavior of the chemical changes on the organic loads in the leachate during hydrothermal treatment can be seen clearly in the changes of chromatogram peaks. Most compounds, especially PAHs, existed in raw leachate, went missing when held at 200 °C, 1.6 MPa with 15 min of holding time. But some new compounds that are hazardous to environment like benzene, nitroso-, 2-pyrrolidinone, secbutyl nitrite, and cetene appeared. This means exposing raw leachate with hydrothermal treatment at 15 min of holding time has removed PAHs and the reaction may cause the derivatives of new compounds from PAHs of smaller molecular weight and change their molecular structure. For example, benzene, nitroso- is a single-ring benzene structure that

derives from the existence of benzene. Improper setup parameters in hydrothermal process may result in some hazardous compounds appearing. However, in this case, the compounds that appeared were selectively less reactive and not stable due to their lower molecular weight.



Fig. 2: The chromatograms of raw MSW leachate (bottom) and hydrothermally-treated leachate at 200 °C held for 15 min (middle) and 60 min (top), respectively.

As the treatment holding time increased, the intensity and/or peak abundance became smaller. As indicated earlier, the conditions of 200 °C, 1.6 MPa with 60 min holding time showed the highest performance for the hydrothermal treatment of raw MSW leachate. Under these conditions, there was no detectable presence of PAHs but there were new compounds with significant peak intensity corresponding to alpha-amyrin, lupeol, and eicosane. All these compounds come from the lipid family and do not have any record of being hazardous compounds by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) report. Lipids formed from the process are believed to be the natural oils that come out from the hydrothermal processing of MSW leachate in a hot and pressurized environment. Hydrothermal liquefaction of organic content in the leachate may happen along the treatment in the thermochemical conversion of the organics into liquid fuels. Temperature and pressure that is set in a closed reactor causes a thermal depolymerization process converting the wet organics, and other macromolecules, into a crude-like oil result.

The hydrothermal conversion of leachate into clean water involves the process of vaporization, condensation, and collection of condensate product (clean water). Leachate is a mixture of liquids containing organic and inorganic components. The hot and pressurized conditions vaporize the leachate and cause compounds in the mixture to break-up into smaller fragments, some of which are dissolved in water. The organic matter that makes

leachate hazardous are converted into simpler dissolved compounds during the process and the gaseous species was collected as clean water following condensation. Inorganic components were collected as residues of the process.

4. CONCLUSION

Characteristics and behavior of raw municipal solid waste leachate sampled from the Ampang district, Selangor, Malaysia were experimentally investigated under hydrothermal treatment at various temperatures. The fresh raw leachate was dark brown and black color cloudy liquid that was potentially hazardous with average pH, COD and NH₃-N of 3.27, 51000 mg/L, and 3496 mg/L. The decrease in the area of intensity in the GC-MS chromatograms reflects the removal of compounds from the raw leachate and their greatly reduced quantity after the hydrothermal treatment. Treatment at 15 min holding time is insufficient to cause the compounds in the leachate to be degraded and removed which is inferred from peak areas comparison in the chromatograms for treated and raw leachate. Treatment at longer holding time of 60 min and higher temperature appear to cause more compounds to be removed. Most compounds were removed from the leachate sample that was hydrothermally treated at 200 °C, 1.6 MPa and 60 min, thus giving favorable parameters: 99% of COD and NH₃-N were removed over raw leachate and complied with the National Water Quality Standard Malaysia and the World Health Organization standards for permissible limits for contaminants present in wastewater discharges for irrigation use. The results indicated that proper parameter setup on hydrothermal treatment cause an effective conversion of poisonous aromatic and complex organic compounds in the leachate into clean water so that burden to the environment can be reduced. It would provide a potential solution to leachate problems and reduce water pollution if the proposed process was implemented to process leachate on an industrial scale.

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REFERENCES

- [1] Ramírez-Sosa DR, Castillo-Borges ER, Méndez-Novelo RI, Sauri-Riancho MR, Barceló-Quintal M, Marrufo-Gómez JM. (2013) Determination of organic compounds in landfill leachates treated by Fenton–Adsorption. Waste Management, 33(2): 390-395. https://doi.org/10.1016/j.wasman.2012.07.019
- [2] Peter AE, Nagendra SS, Nambi IM. (2019) Environmental burden by an open dumpsite in urban India. Waste management, 85, 151-163. https://doi.org/10.1016/j.wasman.2018.12.022
- [3] Christensen TH, Kjeldsen P, Bjerg PL, Jensen DL, Christensen JB, Baun A. (2001) Albrechtsen H.-J. r.; Heron G. Biogeochemistry of landfill leachate plumes. Appl. Geochem, 16, 659-718. https://doi.org/10.1016/S0883-2927(00)00082-2
- [4] Manaf LA, Samah MAA, Zukki NIM. (2009) Municipal solid waste management in Malaysia: Practices and challenges. Waste Manag 29: 2902-2906. https://doi.org/10.1016/j.wasman.2008.07.015
- [5] Abas MA, Wee ST. (2014) The Issues of Policy Implementation on Solid Waste Management in Malaysia. Int J Conceptions Manag Soc Sci 2(3): 12-17.
- [6] Mahidin DSDMU. (2020) Department of Statistics Malaysia Press Release: Compendium of Environment Statistics, Malaysia 2020. Dep Stat Malaysia 2015(2)
- [7] Li W, Zhou Q, Hua T. (2010) Removal of organic matter from landfill leachate by advanced oxidation processes: A review. International Journal of Chemical Engineering.

https://doi.org/10.1155/2010/270532

- [8] Nascimento Filho ID, von Mühlen C, Caramão EB. (2001) China DDP Despachante de Frete Marítimo taxas transporte da para Saba/em todo o mundo. Química Nova, 24(4): 554-556. https://doi.org/10.1590/S0100-40422001000400017
- [9] Hamar GB, Mcgeehin MA, Phifer BL, Ashley DL. (1996) Volatile organic compound testing of a population living near a hazardous waste site. Journal of Expo Anal Environ Epidemiol 6(2): 247-255.
- [10] Reif JS, Tsongas TA, Anger WK, Mitchell J, Metzger L, Keefe TJ, Tessari JD, Amler R. (1993) Two-stage evaluation of exposure to mercury and biomarkers of neurotoxicity at a hazardous waste site. Journal of Toxicol Environmental Health, 40(2-3): 413-422. https://doi.org/10.1080/15287399309531808
- [11] Stehr-Green PA, Burse VW, Welty E. (1988) Human exposure to polychlorinated biphenyls at toxic waste sites: Investigations in the United States. Arch Environ Health 43(6): 420-424. https://doi.org/10.1080/00039896.1988.9935861
- [12] Moraes PB, Bertazzoli R. (2005) Electrodegradation of landfill leachate in a flow electrochemical reactor. Chemosphere, 58(1): 41-46. https://doi.org/10.1016/j.chemosphere.2004.09.026
- [13] Griffith J, Duncan RC, Pellom AC. (1989) Cancer mortality in U.S. Counties with hazardous waste sites and ground water pollution. Arch Environmental Health, 44(2): 69-74. https://doi.org/10.1080/00039896.1989.9934378
- [14] Sang YM, Gu QB, Sun TC, Li FS. (2008) Color and organic compounds removal from secondary effluent of landfill leachate with a novel inorganic polymer coagulant. Water Science and Technology, 58(7): 1423-1432. https://doi.org/10.2166/wst.2008.446
- [15] Marttinen SK, Kettunen RH, Rintala JA. (2003) Occurrence and removal of organic pollutants in sewages and landfill leachates. Science of the total environment, 301(1-3): 1-12. https://doi.org/10.1016/S0048-9697(02)00302-9
- [16] Monje-Ramirez I, De Velasquez MO. (2004) Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation–ozonation coupling processes. Water Research, 38(9): 2359-2367. https://doi.org/10.1016/j.watres.2004.02.011
- [17] Park JY, Batchelor B. (2002) A multi-component numerical leach model coupled with a general chemical speciation code. Water research, 36(1): 156-166. https://doi.org/10.1016/S0043-1354(01)00207-X
- [18] Gajski G, Oreščanin V, Garaj-Vrhovac V. (2012) Chemical composition and genotoxicity assessment of sanitary landfill leachate from Rovinj, Croatia. Ecotoxicology and Environmental Safety, 78: 253-259. https://doi.org/10.1016/j.ecoenv.2011.11.032
- [19] Mukherjee S, Mukhopadhyay S, Hashim MA, Sen Gupta B (2015) Contemporary environmental issues of landfill leachate: assessment and remedies. Critical Reviews in Environmental Science and Technology, 45(5): 472-590. https://doi.org/10.1080/10643389.2013.876524
- [20] Hemananthani S. (2017) Minister: Leachate contamination must be addressed. The Star. https://www.thestar.com.my/news/nation/2017/07/10/a-very-dirty-dirty-headache-ministerleachate-contamination-must-be-addressed/
- [21] Hoang VY, Jupsin H, Le VC, Vasel JL. (2012) Modeling of partial nitrification and denitrification in an SBR for leachate treatment without carbon addition. Journal of Material Cycles and Waste Management, 14(1): 3-13. https://doi.org/10.1007/s10163-011-0033-x
- [22] Show PL, Pal P, Leong HY, Juan JC, Ling TC. (2019) A review on the advanced leachate treatment technologies and their performance comparison: an opportunity to keep the environment safe. Environmental monitoring and assessment, 191(4): 1-28. https://doi.org/10.1007/s10661-019-7380-9
- [23] Wang K, Li L, Tan F, Wu D. (2018) Treatment of landfill leachate using activated sludge technology: A review. Archaea, 2018: 1-10. Article ID 1039453. https://doi.org/10.1155/2018/1039453
- [24] Du X, Zhang R, Gan Z, Bi J. (2013) Treatment of high strength coking wastewater by supercritical water oxidation. Fuel, 104: 77-82. https://doi.org/10.1016/j.fuel.2010.09.018
- [25] Reddy SN, Nanda S, Hegde UG, Hicks MC, Kozinski JA. (2015) Ignition of hydrothermal

flames. RSC Advances, 5(46): 36404-36422. https://doi.org/10.1039/c5ra02705e

- [26] Hwang I-H, Aoyama H, Matsuto T, Nakagishi T, Matsuo T. (2012) Recovery of solid fuel from municipal solid waste by hydrothermal treatment using subcritical water. Waste Management, 32(3): 410-416. https://doi.org/10.1016/j.wasman.2011.10.006
- [27] Kang K, Quitain AT, Daimon H, Noda R, Goto N, Hu HY, Fujie K. (2001) Optimization of amino acids production from waste fish entrails by hydrolysis in sub and supercritical water. The Canadian Journal of Chemical Engineering, 79(1): 65-70. https://doi.org/10.1002/cjce.5450790110
- [28] Brunner G. (2009) Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. The Journal of Supercritical Fluids, 47(3): 373-381.
- [29] Ren LH, Nie YF, Liu JG, Jin YY, Sun L. (2006) Kinetics study on photochemical oxidation of polyacrylamide by ozone combined with hydrogen peroxide and ultraviolet radiation. Journal of Environmental Sciences, 18(4): 660-664.
- [30] Watchararuji K, Goto M, Sasaki M, Shotipruk A. (2008) Value-added subcritical water hydrolysate from rice bran and soybean meal. Bioresource technology, 99(14): 6207-6213. https://doi.org/10.1016/j.biortech.2007.12.021
- [31] Lamoolphak W, De-Eknamkul W, Shotipruk A. (2008) H production and characterization of protein and amino acids from silk waste. Bioresource Technology, 99(16): 7678-7685. https://doi.org/10.1016/j.biortech.2008.01.072
- [32] Eley MH, Guinn GR, Bagchi J. (1995) Cellulosic materials recovered from steam classified municipal solid wastes as feedstocks for conversion to fuels and chemicals. Applied Biochemistry and Biotechnology, 51(1): 387-397. https://doi.org/10.1007/BF02933442
- [33] Sawayama S, Inoue S, Minowa T, Tsukahara K, Ogi T. (1997) Thermochemical liquidization and anaerobic treatment of kitchen garbage. Journal of fermentation and bioengineering, 83(5): 451-455. https://doi.org/10.1016/S0922-338X(97)82999-6
- [34] Kato A, Matsumura Y. (2003) Hydrothermal Pulping of Wet Biomass as Pretreatment for Supercritical Water Gasification Studies Using Cabbage as a Model Compound. Journal of the Japan Institute of Energy, 82: 97-102. https://doi.org/10.3775/jie.82.97
- [35] Papadimitriou EK, Barton JR, Stentiford EI. (2008) Sources and levels of potentially toxic elements in the biodegradable fraction of autoclaved non-segregated household waste and its compost/digestate. Waste Management & Research, 26(5): 419-430. https://doi.org/10.1177/0734242X08088697
- [36] Onwudili JA, Williams PT. (2007) Hydrothermal catalytic gasification of municipal solid waste. Energy and Fuels, 21: 3676-3683. https://doi.org/10.1021/ef700348n
- [37] Marrone PA, Hong GT. (2007) Supercritical water oxidation. Environmentally Conscious Materials and Chemicals Processing, 385-453. https://doi.org/10.1002/9780470168219.ch13
- [38] Gidner A, Stenmark L. (2001) Supercritical water oxidation of sewage sludge–State of the art. In Proceedings of the IBC's Conference on Sewage Sludge and Disposal Options: 26-27 March 2001; Birmingham, England; 1-16. Elsevier Karlskoga.
- [39] Cocero MJ, Martín A, Bermejo MD, Santos M, Rincón D, Alonso E, Fdez-Polanco F. (2003) Supercritical water oxidation of industrial waste from pilot to demonstration scale. In Proceedings of the 6th International Symposium on Supercritical Fluids: 28-30 April 2003; Versailles, France.
- [40] Behnia I. (2013) Treatment of aqueous biomass and waste via supercritical water gasification for the production of CH₄ and H₂. Master thesis. The University of Western Ontario, Chemical and Biochemical Engineering Department.
- [41] Veriansyah B, Kim JD. (2007) Supercritical water oxidation for the destruction of toxic organic wastewaters: A review. Journal of Environmental Sciences, 19(5): 513-522. https://doi.org/10.1016/S1001-0742(07)60086-2
- [42] Kirmizakis P, Tsamoutsoglou C, Kayan B, Kalderis D. (2014) Subcritical water treatment of landfill leachate: Application of response surface methodology. Journal of Environmental Management, 146: 9-15. https://doi.org/10.1016/j.jenvman.2014.04.037
- [43] APHA (2005) Standard Methods for the Examination of Water and Wastewater. Stand Methods. https://doi.org/ISBN 9780875532356
- [44] Turki N. (2013) Determination of organic compounds in landfill leachates treated by

coagulation-flocculation and Fenton-adsorption. Journal of Environmental Science Toxicology Food Technology, 7(3): 18-25. https://doi.org/10.9790/2402-0731825

- [45] Baan R, Gross Y, Straif K. (2009) A review of human carcinogens-Part F: chemical agents and related occumations. The Lancet Oncology, 10(12): 1143-1144.
- [46] McCallister MM, Maguire M, Ramesh A, Aimin Q, Liu S, Khoshbouei H, Aschner M, Ebner FF, Hood DB. (2008) Prenatal exposure to benzo(*a*)pyrene impairs later-life cortical neuronal function. Neurotoxicology, 29(5): 846-854.
- [47] Clark RS, Pellom ST, Booler B, Ramesh A, Zhang T, Shanker A, Maguire M, Juarez PD, Patricia MJ, Langston MA, Lichtveld MY, Hood DB. (2006) Validation of research trajectory 1 of an Exposome framework: Exposure to benzo(*a*)pyrene confers enhanced susceptibility to bacterial infection. Environmental Research, 146: 173-184.
- [48] Ramesh A, Inyang F, Lunstra DD, Niaz MS, Kopsombut P, Jones KM, Hood DB, Hills ER, Archibong AE. (2008) Alteration of fertility endpoints in adult male F-344 rats by subchronic exposure to inhaled benzo(*a*)pyrene. Experimental and Toxicologic Pathology, 60(4-5): 269-280.
- [49] Vane CH, Kim AW, Beriro DJ, Cave MR, Knights K, Moss-Hayes V, Nathanail PC. (2014) Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. Applied Geochemistry, 51: 303-314. https://doi.org/10.1016/j.apgeochem.2014.09.013