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Evaluation of Different Treatment Processes for Landfill Leachate Using Low-Cost Agro-Industrial Materials

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Abstract: Leachate is a complex liquid that is often produced from landfills, and it contains hazardous substances that may endanger the surrounding environment if ineffectively treated. In this work, four leachate treatment applications were examined: combined leachate/palm oil mill effluent (POME) (LP), leachate/tannin (LT), pre-(leachate/tannin) followed by post-(leachate/POME) (LT/LP), and pre-(leachate/POME) followed by post-(leachate/tannin) (LP/LT). The aim of this work is to evaluate and compare the performance of these treatment applications in terms of optimizing the physicochemical parameters and removing heavy metals from the leachate. The highest efficiency for the optimization of the most targeted physicochemical parameters and the removal of heavy metals was with the LP/LT process. The results are indicative of three clusters. The first cluster involves raw leachate (cluster 1), the second contains LP and LP/LT (cluster 2), and the third also consists of two treatment applications, namely, LT and LT/LP (cluster 3). The results demonstrate that LP/LT is the most appropriate method for leachate treatment using low-cost agro-industrial materials.

Keywords: landfill; leachate treatment; tannin; coagulation; removal efficiency; heavy metals

1. Introduction

Landfills are generally regarded as one of the most economical of the currently available waste-disposal options. In the landfill process, leachate is often collected through collection reservoirs and drained into storage ponds outside the landfill site and then treated before discharge. Leachate is defined as a complex liquid consisting of hazardous substances that are recalcitrant to biodegradation with a low biological and chemical oxygen demand (BOD₅/COD), indicating the necessity for and complexity of its treatment. Moreover, leachate is not effectively treated biologically [1]. Leachate properties vary as a function of a number of factors such as the time that has elapsed, variations in climate, landfill size, site hydrology, landfill age [2,3], the moisture content, and the composition of the waste [2,4].

Generally, the composition of the leachate mostly reflects variations in the waste composition [2]. However, the composition plays a key role in developing remedial actions and in choosing the leachate treatment process [3,5]. Additionally, as the landfill site ages, more complex dissolved organic matter

is formed from the waste in the landfill's leachate, dramatically reducing the efficiency of biological treatments for COD removal; thus, physicochemical methods become necessary for the adequate removal of recalcitrant dissolved organic matter [6,7]. Leachate treatment can be categorized into biological and physicochemical methods. Biological treatment is not efficient for treating stabilized leachate; however, it can be improved by enhancing the biodegradability of the leachate. Commonly, a combination of different biological and chemical processes is used for leachate treatment [2]. Leachate has been treated with various applications such as coagulation and electrocoagulation, the electro-Fenton reaction [8,9], ozonation-based advanced oxidation processes [10,11], and adsorption and ion exchange [12,13]. Coagulation-flocculation is a simple process that has been widely used to treat stabilized leachate and it can eliminate COD, turbidity, color, and heavy metals with high efficiency depending on the types of contaminants and coagulants present [14,15]. Despite the potential shown by certain treatment processes, several questions remain unanswered about the economic evaluation of treatments, sludge production, and chemical residues in treated effluent. A number of scientists have recently turned their attention to the use of economical and natural materials for leachate treatment.

Malaysia is the second largest producer and exporter of palm oil and palm oil derivatives in the world, with a total estimated area of 5.64 million hectares. Palm oil mill effluent (POME)—one of the agricultural wastes from palm oil production—consists of the water-soluble components of palm fruits as well as suspended cellulosic materials such as palm fiber, fat, grease, and oil residues [16–19]. Additionally, [20] also argued that among the wastes that are generated from processing palm oil fruits, POME is considered the most harmful to the environment if discharged without proper treatment. A large quantity of untreated POME is discharged in nearby rivers or land resulting in serious environmental risks. Agricultural waste has recently been considered as a co-substrate to enhance bacteria for the biodegradation of organics in industrial wastewater. However, there is limited knowledge on the application of combined POME and tannin for stabilized leachate treatment. Many studies have been conducted over the past two decades to assess the efficiency of the replacement of chemical coagulants with natural polymers in coagulation processes, and polymers have been chosen as they result in a lower volume of biodegradable sludge from the output of the treatment process and fewer environmental risks [21]. Tannin contains organic compounds with a long polymer chain that are positively charged, and it can be used as a natural coagulant for leachate treatment. Tannin is a contaminant and has been identified as being capable of precipitating protein pollutants. However, there is scant research on tannin use for the treatment of stabilized leachate.

In this study, new processes are introduced by employing POME and tannin to treat stabilized leachate and to enhance the elimination of pollutants. The effectiveness of tannin-based natural coagulants used for leachate treatment is discussed in the present work. Experimental conditions for the tannin dosage, POME dosage, and potential hydrogen (pH) levels were optimized, and the ability of the different treatments to remove heavy metals and optimize the physicochemical properties of the leachate were determined. In addition, the efficacy of tannin in eliminating heavy metals from leachate was also investigated.

2. Materials and Methods

2.1. Study Area and Sampling

The Ampar Tenang closed landfill (ATCL) site is located about 4 km southeast of Dengkil town in Selangor, Malaysia, at a latitude of 02°48'9250" N and a longitude of 101°4'9330" E, 40 km southeast of Kuala Lumpur [22]. The annual rainfall in Dengkil is around 2450 mm/year with an average temperature of 27 °C [23]. Geologically, The ATCL is located on the Langat basin alluvial aquifer. Layers of silt and sand form the shallow confined aquifer; however, the ground surface is composed of more clay that varies from 5 to 12 m in thickness [19,24]. The area of the ATCL is 10 acres. It has been operational since 1994. The ATCL collects about 100 tons of municipal solid waste per day when

operating. The landfill has disposed of a total of 500,000 tons of solid waste to date [25]. In 2010, the landfill site was completely closed. The ATCL was elevated to a sanitary class site (Level 1) from a disposal site (Level 0) before it was re-opened [25].

Leachate samples were manually collected from the ATCL and stored in 500-mL polyethylene bottles. The samples were immediately taken to the laboratory and pre-cooled to 4 °C to minimize the biological and chemical interactions.

2.2. Tannin Characterization

Tannin is defined as a natural coagulant. It is an organic compound with long polymer chains that are usually positively charged. The tannin used in this study was a commercial ammonium-modified variety produced from Acacia bark (*Acacia mearnsii*) [26,27]. The particles without any electrical forces in the long chain of the polymer form dense flakes and produce a sediment [28]. In the past two decades, many studies have been carried out on using natural polymers to replace the inorganic compounds in the coagulation/flocculation process. Coagulants based on natural polymers have benefits as they are non-toxic for humans, they produce totally biodegradable sludge, they conserve the alkalinity of the treatment process and thus do not require treatment corrections, and they generate less sludge [21,29].

2.3. Experimental Design

Experimental design was used during preliminary experiment to identify the level of each selected factor (pH, tannin dosages) for tannin experiment and POME dosages and aeration time for POME experiment. The results of optimum operating conditions for using tannin [25] and the optimum operating conditions for using POME (unpublished paper, under review) that result in maximum COD, color, total suspended solids (TSS), and ammoniacal nitrogen (NH₃-N) removal were used to carry out combined experiments for leachate/tannin (LT) and the combined leachate/POME (LP) treatments. The optimum operating conditions are 6 and 0.74 g for pH and tannin dosages, respectively, while the operating conditions for using POME are 188.38 mL and 21 days for POME dosages and time respectively.

2.3.1. Effect of Tannin Dosage and pH

For the first stage, the coagulation of the stabilized leachate was undertaken using modified tannin. The dosages of powdered tannin ranged from 0.25 g to 1.25 g and they were added to 1000 mL of leachate samples. The initial pH for the leachate sample (8.4) was left unadjusted throughout, and coagulation was evaluated based on the removal efficiency of COD, color, TSS, and NH₃-N throughout this stage of experiment. The optimum tannin dosage identified in the previous experimental stage was then evaluated in terms of the influence of pH (ranging from 3 to 12) regarding removal efficiency for the targeted parameters. The pH adjustment was carried out by using 3M of hydrochloric acid solution and 3M of sodium hydroxide solution before the addition of the coagulant. Leachate samples were vigorously shaken before coagulation to reduce the possibility of solids settling.

The jar test is an effective tool that uses different coagulant dosages (in this case, tannin) to simulate the fluctuation/coagulation process to identify the optimum removal efficiency for the targeted parameters. The jar test was first undertaken at 250 rpm for 15 min, which was then followed by 60 rpm for 30 min. Then, the liquor was allowed to settle for 30 min. After settling, the efficiency of different tannin dosages in terms of eliminating the targeted parameters was calculated. The removal efficiency (%) for a target parameter was obtained using the following equation:

$$\text{The removal efficiency (\%)} = [(C_i - C_f)/C_i] \times 100 \quad (1)$$

where C_i and C_f are the initial and final target parameter concentrations.

2.3.2. Effect of POME Dosages and Aeration Time

For this experiment, POME was utilized to enhance the biodegradation of the stabilized leachate. The different LP ratios (1:0, 0.9:0.1, 0.7:0.3, and 0.5:0.50) were added to 1000-mL leachate samples. The initial pH for the leachate sample (8.4) was left unadjusted. The liquor was aerated with an aeration pump operating at 20 L/min for 24 days. The treatment efficiency was evaluated based on COD, TSS, color, and NH₃-N removal efficiency. The removal efficiencies (%) for the target parameters (COD, TSS, color, and NH₃-N) were obtained using Equation (1).

2.3.3. Comparison between Treatment Applications

A comparison was made between the four treatment applications: LP, LT, LT/LP, and LP/LT. This comparison was made in order to choose the most effective experimental condition to optimize the removal efficiency for the target parameters. Both the LP treatment and the LT treatment were carried out as explained in Section 2.3.3. The other treatment applications involved a combination of the LP and LT treatments.

The LT/LP treatment application was carried out in two steps. The first step was a tannin-based leachate treatment (LT), and the second step used the liquor from the first step with the optimum dosage of tannin for the optimum aeration time. The removal efficiencies for the target parameters were then calculated. Unlike the previous application, the LP/LT application was carried out through an LP treatment application followed by the liquor from this step being used to carry out the LT treatment application.

2.4. Analytical Statistics

The determination of the physicochemical parameters and heavy metal concentrations collected from the treatment applications of this study were analyzed using descriptive statistics. The similarity between the treatment applications was determined using cluster analysis (CA), which can summarize the results in a pictorial form called a dendrogram, as was done by [30]. The analyses were performed using the statistical software R [31].

2.5. Analytical Work

In this regard, for each treatment process, specific analytical methods were employed to test the physicochemical parameters such as the pH, electrical conductivity (EC), salinity, total dissolved solids (TDS), TSS, color, COD, BOD₅, NH₃-N, and dissolved oxygen (DO), while the heavy metals such as Fe, Zn, Cu, Cr, Cd, Pb, As, Co, and Mn were determined using atomic absorption spectroscopy (Unicam 929 AA Spectrophotometer, UNICO, Franksville, WI, USA).

The pH was tested using a portable digital pH/mV meter (YSI EcoSense meter, pH100A meter), while the EC, salinity, and TDS were tested using a portable electric conductivity meter (YSI EcoSense EC300A Conductivity Meter). The DO concentration was determined by a bench top meter (YSI 5000). The COD concentration was tested using the closed reflux colorimetric method (5220B-DR2500 HACH, Loveland, CO, USA). The BOD₅ concentration was examined by the 5210B method according to the Environmental Protection Agency (EPA) standard. The NH₃-N concentration was measured by the phenate method (4500-NH₃ F) using a DR2500 spectrophotometer at 640 nm. The Method 8025 system was used to determine the color concentration by adjusting the HACH DR 2800 spectrophotometer to a 455-nm wavelength. All of the parameters were measured according to the standard methods for examination of water and wastewater [32].

3. Results and Discussion

3.1. Leachate Characterization

The general leachate characterization for untreated leachate was carried out through studying the concentration of the physicochemical parameters and heavy metals (Table 1). The values in Table 1 are compared with the United States EPA (USEPA) and the Department of the Environment (DOE) guidelines, and one can see that the color concentration, COD, BOD₅, and NH₃-N values exceed the maximum permissible limits, as the values are 1570 mg/L, 2527 Pt-Co, 907 mg/L, 62 mg/L, and 750 mg/L for TSS, color, COD, BOD₅, and NH₃-N, respectively. In a problematic process known as eutrophication, the high concentration of unprocessed NH₃-N depletes the DO [12].

Table 1. Characteristics of the raw leachate collected from the Ampar Tenang closed landfill (ATCL).

Parameter	Max.	Min.	Mean	Sd. Dev.	(USEPA 2012) *; (DOE 2012) **
pH	7.95	7.95	7.95	0.00	6–9 **
EC (µS/cm)	9100	9100	9100	0	-
Salinity (ppt)	5.9	5.9	5.9	0.0	-
TDS (mg/L)	6740	6740	6740	0	-
TSS (mg/L)	1580	1560	1570	10	88 *
Color (Pt-Co)	2530	2520	2527	6	100 **
COD (mg/L)	910	900	907	6	400 **
BOD ₅ (mg/L)	64	60	62	2	20 **
BOD ₅ /COD	0.07	0.07	0.0680	0.0020	-
NH ₃ -N (mg/L)	750	750	750	0	5 **
DO (mg/L)	6.85	6.56	6.71	0.15	10 *
Mg (mg/L)	2.93	2.79	2.85	0.08	-
Ca (mg/L)	8.72	8.52	8.59	0.12	-
Fe (mg/L)	1.30	1.21	1.25	0.04	5 **
Zn (µg/L)	33.78	29.43	31.43	2.20	2000 **
Cu (µg/L)	4.88	3.67	4.25	0.60	20 **
Cr (µg/L)	12.05	10.73	11.27	0.69	10 **
Cd (µg/L)	3.28	3.09	3.19	0.10	10 **
Pb (µg/L)	2.43	1.03	1.81	0.72	10 **
As (µg/L)	17.03	16.64	16.80	0.21	50 **
Co (µg/L)	2.06	2.02	2.04	0.02	50 **
Mn (µg/L)	30.93	25.82	27.67	2.83	20 **

The presence of DO (6.71 mg/L) was outside the USEPA and DOE limits. The pH value (7.95) was within the limits of the USEPA and DOE guidelines; however, this value was closer to being alkaline, which affects the efficiency of leachate treatment. According to [33] and [34], the pH of the leachate increases over time with decreasing concentrations of partially ionized free volatile fatty acids. This leachate was classified as strong and stabilized with low biodegradability (BOD₅/COD = 0.0680). The other physicochemical parameters (EC, salinity, TDS, and TSS) were recorded at high concentrations (9100 µS/cm, 5.9 ppt, 6740 mg/L, and 83 mg/L, respectively). The concentrations of magnesium (Mg) and calcium (Ca) were 2.85 and 6.59 mg/L, respectively.

The order of the heavy metal content in the leachate was Iron (Fe) > zinc (Zn) > manganese (Mn) > arsenic (As) > chromium (Cr) > copper (Cu) > cadmium (Cd) > cobalt (Co) > lead (Pb), from the highest to the lowest concentration. The presence of these heavy metals is associated with a variety of wastes in the landfill in which some of these heavy metals were detected and reported in considerable amounts by [35]. The Fe concentration was the highest (1.26 mg/L), while Pb had the lowest heavy metal concentration in the leachate (1.81 µg/L). The Fe and Mn content is from scrap steel that is disposed of in the landfill. The oxidation of ferrous iron to ferric iron and the formation of ferric hydroxide colloids generate the dark brown color of the leachate [36]. The leachate could have Cu content resulting from

the disposal of paints, blades, bottle caps, insecticides, pharmaceuticals, and cosmetics in the landfill site [36]. The Zn concentration is linked to the disposal of batteries and fluorescent lamps, and Ni comes from the disposal of batteries [37]. The estimated Pb concentration in the landfill site results from the disposal of Pb batteries and Pb-based paints, plastics, and pipes [37]. The high levels of heavy metals in the leachate decrease the efficiency of the treatment process in terms of COD removal [38].

3.2. Descriptive Analysis of the Four Treatment Applications

A general characterization of all treatment applications was performed by studying the concentrations of the physicochemical parameters and heavy metals (Table 2).

3.2.1. Combined Leachate/POME Treatment Application (LP)

The pH value (9.12) slightly exceeded the limits of the USEPA and DOE guidelines. This value is closer to being alkaline. The color concentration, TSS, COD, BOD₅, and NH₃-N values exceeded the maximum permissible limits of the USEPA and DOE guidelines as the values were 1417 Pt-Co, and 1633, 470, 29, and 32 mg/L for color, TSS, COD, BOD₅, and NH₃-N, respectively. DO (6.79 mg/L) was outside the USEPA and DOE limits. This LP application was therefore classified as strong and stabilized with low biodegradability (BOD₅/COD = 0.0625). The other physicochemical parameters (EC, salinity, and TDS) were high (3614 µS/cm, 2.3 ppt, and 2815 mg/L, respectively). The concentrations of Mg and Ca were 22.77 and 6.81 mg/L, respectively.

The order of the heavy metal content in the leachate was Fe > Mn > Zn > As > Cr > Cu > Pb > Cd > Co, from the highest to the lowest concentration. The heavy metal concentrations were 460, 26.81, 16.14, 11.59, 9.82, 3.30, 0.50, 0.22, and 0.22 µg/L for Fe, Mn, Zn, As, Cr, Cu, Pb, Cd, and Co, respectively. Only the Mn concentration was outside the USEPA and DOE limits, and the other targeted heavy metals were within the limits.

3.2.2. Leachate/Tannin Treatment Application (LT)

The physicochemical parameters and the heavy metals found in the leachate that was coagulated with tannin (LT) are presented in Table 2. The pH (9.09) slightly exceeded the USEPA and DOE limits and was closer to being alkaline. The color concentration, COD, BOD₅, and NH₃-N values exceeded the maximum permissible USEPA and DOE limits, with the values for color, COD, BOD₅, and NH₃-N being found to be 217 Pt-Co, and 457, 37, and 260 mg/L, respectively. The LT treatment application was found to be strong and stable with low biodegradability (BOD₅/COD = 0.0810). The concentrations of Mg and Ca were 2.78 and 6.72 mg/L, respectively.

The order of heavy metals in the treated leachate from the highest to the lowest concentration was found to be Fe > Zn > Mn > Cr > Cu > As > Co > Cd > Pb. The concentrations of Fe, Zn, Mn, Cu, Cr, As, Co, Cd, and Pb were 80, 15.1, 8.24, 4.54, 2.45, 2.35, 1.75, 0.51, and 0.26 µg/L, respectively.

3.2.3. Pre-(Leachate/Tannin)-Post-(Leachate/POME) Treatment Application (LT/LP)

In this subsection, the physicochemical parameters and heavy metals post-LT/LP treatment are also presented in Table 2. The pH (5.68) value was slightly outside the USEPA and DOE limits, and this media was therefore more acidic. The color concentration, COD, BOD₅, and NH₃-N values exceeded the maximum permissible USEPA and DOE limits, at 547 Pt-Co, and 490, 26, and 67 mg/L for color, COD, BOD₅, and NH₃-N, respectively. The LT/LP treatment was found to be strong and stabilized with low biodegradability (BOD₅/COD = 0.0524). The other physicochemical parameters (EC, salinity, TDS, and TSS) were high (5200 µS/cm, 3.5 ppt, 3647 mg/L, and 910 mg/L, respectively). The concentrations of Mg and Ca were 8.51 and 12.10 mg/L, respectively.

The heavy metal content in the treated leachate from the highest to the lowest concentration was as follows: Fe > Zn > Mn > As > Cr > Cu > Cd > Co > Pb. The heavy metal concentrations were 230, 23.90, 22.08, 4.27, 3.28, 3.03, 1.82, 1.11, and 0.37 µg/L for Fe, Zn, Mn, As, Cr, Cu, Cd, Co, and Pb, respectively. The concentrations of all the targeted parameters were within the USEPA and DOE limits.

Table 2. Comparison of the four treatment applications in terms of the physicochemical parameters and heavy metals: combined leachate/palm oil mill effluent (POME) (LP), leachate/tannin (LT), pre-(leachate/tannin)–post-(leachate/POME) (LT/LP), and pre-(leachate/tannin)–post-(leachate/POM) (LP/LT).

Parameter	Raw Leachate	LT		LP		LT/LP		LP/LT		(USEPA 2012) *; (DOE 2012) **
		Residual	Removal (%)	Residual	Removal (%)	Residual	Removal (%)	Residual	Removal (%)	
pH	7.95 ± 0	9.09 ± 0.01		9.12 ± 0		5.68 ± 0.03		9.13 ± 0.03		6–9 **
EC (µS/cm)	9100 ± 0	6367 ± 29	30.04	3614 ± 5	46.85	5200 ± 0	23.53	3040 ± 0	55.29	-
Salinity (ppt)	5.9 ± 0	4.1 ± 0	30.51	2.3 ± 0	48.89	3.47 ± 0.1	22.96	2.00 ± 0	55.56	-
TDS(mg/L)	6740 ± 0	4450 ± 10	33.98	2815 ± 1	42.55	3647 ± 6	25.58	2440 ± 0	50.20	-
TSS (mg/L)	1570 ± 10	493 ± 6	68.58	1633 ± 29	65.25	910 ± 10	80.64	1700 ± 50	63.83	88 *
Color (PtCo)	2527 ± 6	217 ± 6	91.42	1417 ± 29	54.30	546.67 ± 6	82.37	810.00 ± '10	73.87	100 **
COD(mg/L)	907 ± 6	457 ± 6	49.63	470 ± 10	85.97	536.67 ± 0	83.98	420.00 ± 10	87.46	400 **
BOD ₅ (mg/L)	79.00 ± 2	37 ± 1	53.16	29.33 ± 2	86.23	19.00 ± 1	91.08	40.33 ± 1	81.06	20 **
BOD ₅ /COD	0.0871 ± 0.002	0.0810 ± 0.0024	7.00	0.0625 ± 0.0046	1.99	0.04 ± 0.0012	44.46	0.10 ± 0.0036	50.65	-
NH ₃ -N (mg/L)	750 ± 0	260.00 ± 5	65.33	32.33 ± 2	95.35	66.67 ± 6	90.41	2.00 ± 0	99.71	5 **
DO(mg/L)	6.71 ± 0.15	7.59 ± 0.13		6.79 ± 0.03		7.43 ± 0.02		7.51 ± 0.02		10 *
Mg ²⁺ (mg/L)	2.85 ± 0.08	2.78 ± 0.05	2.29	22.77 ± 0.25	52.44	8.51 ± 0.03	82.23	7.36 ± 0.08	84.62	-
Ca ²⁺ (mg/L)	8.59 ± 0.12	6.72 ± 0.89	21.72	6.81 ± 0.95	57.76	12.10 ± 2.05	24.92	5.65 ± 2.08	64.96	-
Fe ²⁺ (µg/L)	1250 ± 0.04	240 ± 0	80.66	460 ± 0.04	95.34	230 ± 0.07	97.70	280 ± 0.01	97.17	5 **
Zn ²⁺ (µg/L)	31.43 ± 2.2	2.72 ± 1.27	91.35	16.14 ± 3.88	97.03	23.90 ± 0.23	95.60	25.65 ± 9.1	95.28	2000 **
Cu ²⁺ (µg/L)	4.25 ± 0.60	0.41 ± 0.78	90.35	3.30 ± 0.53	98.97	3.03 ± 0.48	99.05	6.42 ± 2.99	97.99	20 **
Cr ²⁺ (µg/L)	11.27 ± 0.69	0.86 ± 0.08	92.41	9.82 ± 1.34	94.17	3.28 ± 0.37	98.05	5.54 ± 0.3	96.71	10 **
Cd ²⁺ (µg/L)	3.19 ± 0.1	2.57 ± 0.07	19.47	0.22 ± 0.07	99.10	1.82 ± 1.63	92.34	0.50 ± 0.04	97.91	10 **
Pb ⁺ (µg/L)	1.81 ± 0.72	0.07 ± 0.1	96.26	0.50 ± 0.26	95.72	0.37 ± 0.10	96.87	0.69 ± 0.19	94.11	10 **
As ³⁺ (µg/L)	2.81 ± 0.21	1.54 ± 0.09	45.40	11.59 ± 0.67	8.39	1.37 ± 0.43	89.21	1.69 ± 0.07	86.67	50 **
Co ²⁺ (µg/L)	2.04 ± 0.02	0.32 ± 0.02	84.47	0.22 ± 0.03	97.78	1.11 ± 0.03	88.64	1.38 ± 0.03	85.90	50 **
Mn ²⁺ (µg/L)	27.67 ± 2.83	2.77 ± 2.55	90.00	26.81 ± 3.53	26.80	22.08 ± 16.1	39.73	7.17 ± 5.8	80.44	20 **

3.2.4. Pre-(Leachate/POME)–Post-(Leachate/Tannin) Treatment Application (LP/LT)

Table 2 also provides an overall characterization by presenting the physicochemical parameters and heavy metal concentrations for the LP/LT treatment. The pH value (9.13) slightly exceeded the USEPA and DOE limits, and this media was closer to being alkaline. The color, TSS, COD, BOD₅, NH₃-N, and DO concentrations exceeded the maximum permissible USEPA and DOE limits, with values of 810 Pt-Co, and 1700, 420, 40, and 2 mg/L for color, TSS, COD, BOD₅, and NH₃-N, respectively. The EC, salinity, and TDS values were 3040 μ S/cm, 2 ppt, and 2440 mg/L, respectively. This treatment application was thus characterized as strong and stabilized with low biodegradability (BOD₅/COD = 0.0961). The concentrations of Mg and Ca were 7.36 and 5.65, respectively. The order of the heavy metals in the treated leachate was Fe > Zn > Mn > Cu > Cr > As > Co > Pb > Cd, from the highest to the lowest concentration. The heavy metal concentrations were 280, 25.65, 7.17, 6.42, 5.54, 3.18, 1.38, 0.69, and 0.50 μ g/L for Fe, Zn, Mn, Cu, Cr, As, Co, Pb, and Cd, respectively. All the concentrations of the targeted heavy metals were within the USEPA and DOE limits.

3.3. Evaluation of the Physicochemical Parameters and Heavy Metal Removal

3.3.1. The Effect of Different Treatment Applications on the Removal of Physicochemical Parameters

The reduction efficiencies of the physicochemical parameters during the various treatment applications are shown in Figure 1. The reduction efficiencies for the EC, salinity, TDS, TSS, color, COD, BOD₅, BOD₅/COD, and NH₃-N were 30.04%, 30.51%, 33.98%, 71.55%, 91.42%, 49.63%, 53.16%, 7%, and 74% for the LT treatment, respectively. With this treatment, the range of reduction efficiencies was from 30.04% for EC to 91.42% for color. During the LP treatment, the reduction efficiencies for the EC, salinity, TDS, TSS, color, COD, BOD₅, BOD₅/COD, and NH₃-N were 46.85%, 48.89%, 42.55%, 65.25%, 54.30%, 85.97%, 86.23%, 2%, and 95.35% respectively. The range of reduction efficiencies was from 42.55% for TDS to 95.35% for NH₃-N. The reduction efficiencies in our review were 23.53%, 22.96%, 25.58%, 80.64%, 82.37%, 83.98%, 91.08%, 44.46%, and 90.41% for the EC, salinity, TDS, TSS, color, COD, BOD₅, BOD₅/COD, and NH₃-N, respectively. The reduction efficiencies after the LT/LP treatment ranged from 22.96% for salinity to 91.08% for BOD₅. Finally, the reduction efficiencies for the EC, salinity, TDS, TSS, color, COD, BOD₅, BOD₅/COD, and NH₃-N for the LP/LT treatment were 55.29%, 55.56%, 50.20%, 63.83%, 73.87%, 87.46%, 81.06%, 50.65%, and 99.71%, respectively. The range of reduction efficiencies was from 50.20% for TDS to 99.71% for NH₃-N.

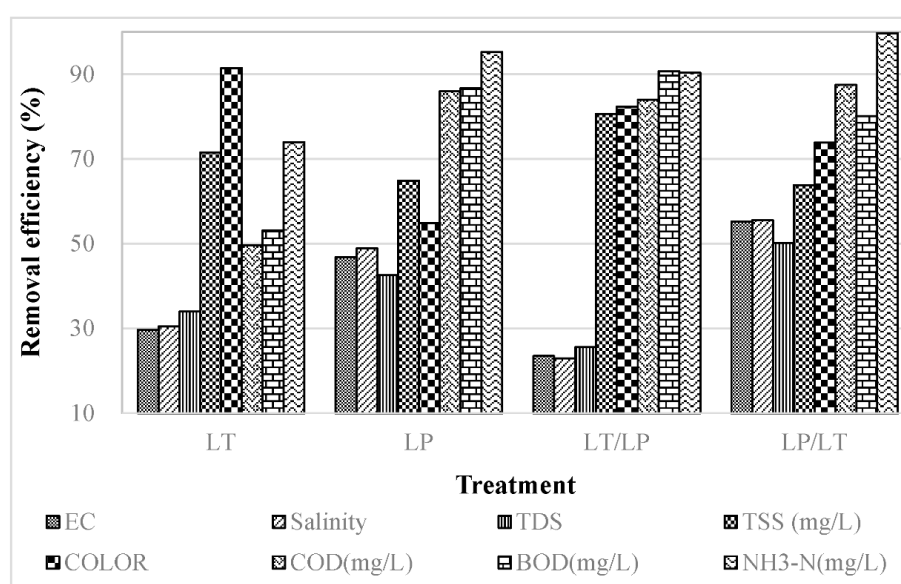


Figure 1. Reduction efficiencies for the physicochemical parameters in the four treatment applications.

3.3.2. Heavy Metal Removal with the Different Treatment Applications

Figure 2 shows the removal efficiency of the heavy metals for the LT, LT/LP, LP/LT, and LP treatment applications. The removal efficiency was ranged between 19.47% for Cd and 96.26% for Pb using LT treatment process. For LP, the highest removal was reported for Cd removal and the lowest was for As. Moreover, the removal efficiency ranged between 39.73% for Mn and 99.1% for Cu using LT/LP process, while it was ranged between 80.44% for Mn and 97.91% for Cd using LP/LT. The lowest removal efficiency for Cd²⁺ and Ca²⁺ in LT may be due to the pH value. Kumar et al. [39] reported the optimal pH for Cd removal during coagulation at 5 while the experiment for heavy metals removal was performed at pH 9. Moreover, the removal of Cd in the other three treatment applications was increased due to the acidic condition (pH 5.68) for LT/LP and LP/LT processes. The lowest removal of As in LP due to the low performance of combined leachate and POME process for As removal; the removal of As can be improved by using adsorption and/or coagulation processes [40].

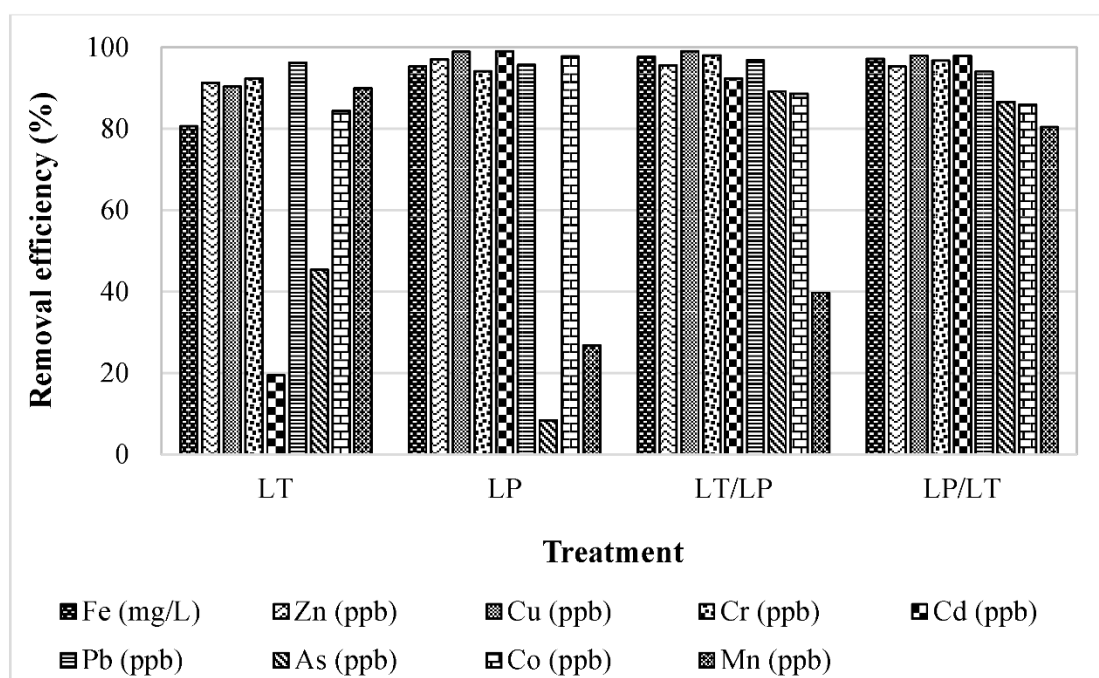


Figure 2. Removal efficiencies for the heavy metals in the four treatment applications.

3.4. Cluster Analysis of the Four Treatment Applications

Similarity and dissimilarity between the four treatment applications that were examined in this study were investigated using CA. A CA was performed for heavy metals and for the physicochemical parameters based on the residual concentrations. As shown in Figure 3, the four treatment applications are grouped into three dissimilar clusters. The first cluster includes raw leachate (cluster 1), and the second cluster consists of the LP and LP/LT treatment applications (cluster 2), whereas the third cluster also consists of two treatment applications, namely, LT and LT/LP (cluster 3). It was observed that the behavior of the parameters was completely different between raw leachate (cluster 1) and the other treatment applications (cluster 2 and cluster 3), whereas the dissimilarity between the raw leachate (cluster 1) was greater when compared to the treatment applications (cluster 2 and cluster 3). The variance between the raw leachate and the treatment applications is due to the effect of the treatment processes on the physicochemical parameters and heavy metals. The treatment applications resulted in two clusters being formed. The first cluster was the LP and LP/LT treatment applications (cluster 2), and the second cluster was the LT and LT/LP treatment applications (cluster 3). The treatment processes involving aeration and coagulation/fluctuation including tannin and POME clearly have an effect on the behavior of the parameters.

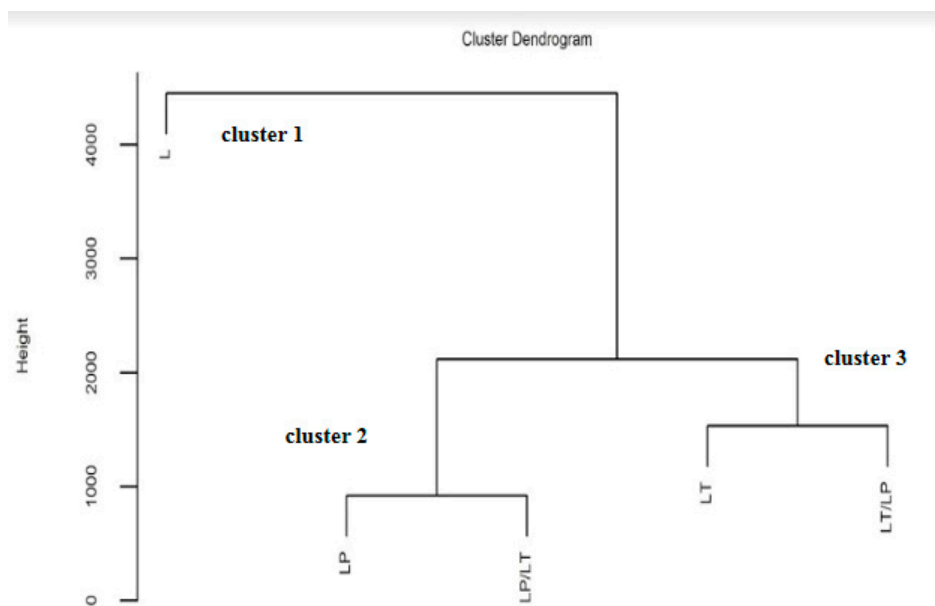


Figure 3. Cluster dendrogram of the four treatment applications based on the residual concentrations of heavy metals and the physicochemical parameters.

4. Conclusions

In this study, a general comparison was made between the four treatment applications; namely, LP, LP/LT, LT, and LT/LP. This comparison includes the optimum reduction and removal of 22 physicochemical parameters and heavy metals. The LP/LT process achieved the highest reduction and removal efficiency for the physicochemical parameters and heavy metals that were in focus during the study, including the EC, salinity, TDS, COD, BOD₅/COD, NH₃-N, Mg, Ca, and Mn. The treatment processes that include tannin dosages and POME and the experimental procedures that were carried out clearly have an effect on the behavior of the physicochemical parameters and heavy metals following such treatment applications.

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