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Tawfiq J. H. Banch, Marlia M. Hanafiah, Salem S. Abu Amr, Abbas F. M. Alkarkhi, Mohammed Hasan

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Treatment of Landfill Leachate Using Palm Oil Mill Effluent

Tawfiq J. H. Banch [1], Marlia M. Hanafiah [1,2,*], Salem S. Abu Amr [3], Abbas F. M. Alkarkhi [3] and Mohammed Hasan [1]

1 Department of Earth Sciences and Environment, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia; banch4@gmail.com (T.J.H.B.); aldulaimi89_fst@yahoo.com (M.H.)
2 Centre for Tropical Climate Change System, Institute of Climate Change, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia
3 Universiti Kuala Lumpur Business School (Unikl bis), Kuala Lumpur 50250, Malaysia; sabuamr@hotmail.com (S.S.A.A.); alkarkhii@gmail.com (A.F.M.A.)
* Correspondence: mhmarlia@ukm.edu.my

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Abstract: Sanitary landfilling is the most common method of removing urban solid waste in developing countries. Landfills contain high levels of organic materials, ammonia, and heavy metals, thereby producing leachate which causes a possible future pollution of ground and surface water. Recently, agricultural waste was considered a co-substratum to promote the biodegradation of organics in industrial wastewater. The use of low-cost and natural materials for wastewater treatment is now being considered by many researchers. In this study, palm oil mill effluent (POME) was used for treating stabilized leachate from old landfill. A set of preliminary experiments using different POME/leachate ratios and aeration times was performed to identify the setting of experimental design and optimize the effect of employing POME on four responses: chemical oxygen demand (COD), total suspended solids (TSS), color, and ammoniacal nitrogen (NH_3-N). The treatment efficiency was evaluated based on the removal of four selected (responses) parameters. The optimum removal efficiency for COD, TSS, color, and NH_3-N was 87.15%, 65.54%, 52.78%, and 91.75%, respectively, using a POME/leachate mixing ratio of 188.32 mL/811.68 mL and 21 days of aeration time. The results demonstrate that POME-based agricultural waste can be effectively employed for organic removal from leachate.

Keywords: landfill; leachate treatment; POME; removal efficiency; mixing ratio

1. Introduction

The landfilling of solid waste is still a significant problem in the solid waste management systems of all countries worldwide [1,2]. However, landfill leachate is a complex liquid generated from rainwater penetration through landfills that often includes high-strength contaminant resistance, such as humic acids, ammonia nitrogen, heavy metals, xenobiotics, and inorganic salts, which are important to avoid due to their adverse effects on the environment [3,4]. The factors that affect the composition of landfill leachate include the composition of waste, the level of compaction, the absorptive capacity of solid waste and age of solid waste, weather variations, precipitation, landfilling temperature, size of landfilling, hydrogeological conditions, factors of the landfill operation, pH, and chemical and biological activities in the process of landfilling [5,6]. In general, young leachate produced from new landfills (<5 years old) has a large biodegradation of comparatively low-molecular-weight materials, such as volatile organic acids, chemical oxygen demand (COD), total organic carbon (TOC), biological oxygen demand (BOD_5), and biodegradability (BOD_5/COD) [7]. On the other hand, old leachate (>10 years old) has high organic content of relatively high-molecular-weight materials, for instance,

humic and fulvic substances that are refractory and not rapidly degradable. Generally, old leachate has a lower concentration of COD, TOC, BOD_5, and BOD_5/COD [6,7]. Leachate is stabilized and has low biodegradability since most landfills are old [8–11]. As a landfill gets older, a change from a relatively shorter initial aerobic to a longer anaerobic decomposition period takes place. Due to the biological breakdown of organic compounds and precipitation of soluble components, such as heavy metals, the strength of leachate generally lowers over time. Because of its biodegradable nature, organic compounds decrease faster than inorganic compounds with the increasing age of leachate production.

Several treatment techniques, such as physico-chemical processes, are used to treat leachate (coagulation precipitation, activated carbon adsorption [12,13], membrane filtration, activated carbon adsorption [14,15], and/or other separation techniques) [16], in addition to biological treatment methods, such as aerobic and anaerobic processes. In the past two decades, many studies reported that biological processes in the treatment of young leachate are effective but are comparatively insufficient in the treatment of old leachate because of the existence of bio-refractory substances [6,7]. Currently used procedures often involve mixed methods intended as modular or multi-stage units that are capable of treating pollutants that change in concentration over time. The appropriate treatment of leachate is applied to enhance and develop an appropriate technique of treatment that meets the relevant quality standards and regulations [5].

In particular, the palm oil sector in Malaysia adopts four types of treatment technologies: waste stabilization ponds, activated sludge systems, closed anaerobic digesters, and land application systems [17]. However, many questions remain unanswered about the cost of treatment, the production of sludge, and chemical residues in treated wastewater. Usage of low-cost and natural materials of wastewater treatment are currently gaining increased attention from a series of studies. Palm oil mill effluent (POME) is classified as a pollutant which is known for its ability to enhance the biodegradability of pollutants due to the relatively high content of organic matter [18,19]. An aeration process supplies the oxygen to the wastewater and acts as an oxidation of organics. Moreover, oxygen can also enhance the biodegradation of organics by bacteria which use oxygen to break down the organic matter into the form of CO_2 and H_2O [20]. Stripping of ammonia is a simple desorption method utilized to reduce the ammonia concentration of leachate. Ammonia reacts with water to form ammonium hydroxide [21], as shown in Equation (1).

$$NH_4{}^{+} + OH^{-*} \leftrightarrow H_2O + NH_3{}^{*}. \quad (1)$$

The alkaline wastewater flows downward when the air enters through the bottle. As the air continues to flow, the wastewater moves in the opposite direction and ascends to the top of the aeration bottle. NH_3 is stripped from dropping water droplets into the air flow, and then released into the atmosphere [22]. In this research, the effectiveness of aeration processes used in the treatment of a leachate/POME mixture was evaluated. The optimum experimental conditions for POME dosages were designed, and the ability to remove the different medicines was studied. In addition, the efficacy of POME in the leachate removal of heavy metals was also investigated. The removal of heavy metals by POME during aeration may be attributed to the high level of suspended solids in POME, which may act as a natural coagulant [23].

2. Methodology

2.1. Collection of the Samples and Landfill Characteristics

Samples of leachate were sampled from the Ampar Tenang Closed Landfill Site (ATCL). ATCL is situated nearly 40 km southwest of Kuala Lumpur, Malaysia at a latitude of 02°48.9250 north (N) and a longitude of 101°4.9330 east (E) [23]. ATCL is mostly surrounded by oil palm plantations. Labu River flows along the landfill 300 m away. The ATCL area is characterized as tropical. The average temperature is 27.2 °C, and the average rainfall is 2287 mm/year [24]. The landfill site is located on the eastern sector of the confined alluvial aquifer of the Langat Basin, composed primarily of silt (50%–70%), clay (<25%), and sand (<25%) [25–27]. This site is more clayey close to the surface of

the ground, but changes to sandy in lower layers [25,26]. ATCL operated as of 1994 for a total of 15 years. About 100 tons of waste are dumped into this site every day during the operation of the landfill. This results in the on-site disposal of a total of half a million tons of solid waste. The site was completely closed in 2010. Before it was closed, it was converted to sanitary classification (Level 1) from a disposal site (Level 0) [8,27,28]. In 2018, the samples were manually collected and placed in 1000-mL containers manufactured from polyethylene. The samples were collected at 4 °C and immediately transformed to prevent significant biological degradation and chemical reactions. The samples were transported in a preservation refrigerator from the site to the laboratory before being stored in the laboratory refrigerator until the next day where the experiment was prepared; no acids were used for preservation.

2.2. Leachate and POME Characterizations

The physico-chemical characterization of the leachate is presented in Table 1.

Table 1. Physico-chemical characteristics and heavy metals of leachate.

Parameter	Mean and Standard Deviation	(USEPA *; DOE **)
pH	7.88 ± 0.50	6–9 **
EC (µS/cm)	6565 ± 324	1400 *
TDS (mg/L)	4671 ± 174	1000 *
TSS (mg/L)	40.45 ± 8	50 **
COD (mg/L)	893.41 ± 202	400 **
BOD_5 (mg/L)	59.20 ± 10	20 **
NH_3-N (mg/L)	530.7 ± 22	5 **
DO (mg/L)	5.43 ± 2	5 *
Mg^{2+} (mg/L)	19.72 ± 4	0.2 *
Ca^{2+} (mg/L)	39.72 ± 34	0.1 *
Na^{+} (mg/L)	638.80 ± 303	0.02 **
Fe^{2+} (mg/L)	0.78 ± 0.6	5 **
Zn^{2+} (µg/L)	280 ± 16	2 **
Cu^{2+} (µg/L)	41.87 ± 24	0.2 **
Cr^{2+} (µg/L)	45.11 ± 17	0.01 **
Cd^{2+} (µg/L)	0.62 ± 0.7	0.01 **
Pb^{+} (µg/L)	4.18 ± 2.7	0.01 **
As^{3+} (µg/L)	17.3 ± 7	0.05 **
Co^{2+} (µg/L)	11.05 ± 8	0.05 *
Mn^{2+} (µg/L)	61.40 ± 49	0.02 **

* [29], ** [30]. Abbreviation. EC: electrical conductivity; TDS: total dissolved solids; TSS: total suspended solids; COD: chemical oxygen demand; BOD_5: biochemical oxygen demand; NH_3-N: ammoniacal nitrogen; DO: dissolved oxygen; USEPA: U.S. Environmental Protection Agency; DOE: Department of Environment.

The physico-chemical characterization of the POME is presented in Table 2.

Table 2. Physico-chemical characteristics and heavy metals of palm oil mill effluent (POME).

Parameter	Mean and Standard Deviation	(Standard of DOE *)
pH	4.40 ± 0.01	5.0–9.0
EC (µS/cm)	8553 ± 114	100
Salinity (ppt)	4.9 ± 0	NA
TDS (mg/L)	5713 ± 15	NA
TSS (mg/L)	3483 ± 76	200
Color (Pt/Co)	5517 ± 104	100
COD (mg/L)	17,400 ± 100	NA
BOD_5 (mg/L)	1243 ± 51	NA
BOD_5/COD	0.07 ± 0	NA

Table 2. *Cont.*

Parameter	Mean and Standard Deviation	(Standard of DOE *)
NH_3-N (mg/L)	308 ± 58	NA
DO (mg/L)	6.74 ± 0.05	NA
Mg^{2+} (mg/L)	285 ± 5	NA
Ca^{2+} (mg/L)	47.34 ± 0.03	NA
Fe^{2+} (mg/L)	45.31 ± 0.9	50
Zn^{2+} (μg/L)	2603 ± 5.77	10
Cu^{2+} (μg/L)	2130.00 ± 26.46	10
Cr^{2+} (μg/L)	910.00 ± 10	NA
Cd^{2+} (μg/L)	90.10 ± 0.03	NA
Pb^{+} (μg/L)	54.38 ± 0.31	NA
As^{3+} (μg/L)	100.22 ± 0.44	NA
Co^{2+} (μg/L)	41.08 ± 0.17	NA
Mn^{2+} (μg/L)	80.15 ± 0.26	10

* DOE: Department of Environment, Malaysia; NA—not available [30].

2.3. Experimental Procedure

A bubble column bioreactor was used for the aeration process. It is characterized by its simple construction, higher efficiency in removal, and efficient control of the liquid residence time [31]. The aeration process was conducted at room temperature (25 °C). In the aeration process, the air pump is connected to four bottles of one liter each by a tube of 1 mm in diameter; these bottles contain different ratios of leachate/POME, and the process continues for 21 days.

The experiment was conducted in two steps; the first step was a preliminary experiment performed utilizing one factor at a time to determine the area of concern for each influential variable of the leachate/POME ratio and the aeration time to determine the optimal levels. The selected levels for the leachate/POME ratio and the aeration time were utilized to conduct the second step utilizing response surface methodology (RSM). RSM consists of a group of experimental methods devoted to estimating the relationship between a group of experimental variables (factors) and the (targeted) measured responses. To build a more practical model, the process variables under investigation need to be understood. Central composite face-centered (CCF), a type of central composite design (CCD), was used for two independent variables to estimate the effect value of POME dosages and aeration time on four response variables: COD, TSS, color, and NH_3-N.

2.4. Effect of the Leachate/POME Ratio

For the first step, POME was used to improve the biodegradation of leachate. In 1000 mL of leachate samples, different leachate/POME ratios (1:0, 0.9:0.1, 0.7:0.3, and 0.5:0.50) were used. The initial pH for the leachate sample (8.4) was left unadjusted. The liquid was aerated using an aeration bump (HAILEA) model V-20 with output 20 L/min and pressure >0.02 MPa for 24 days. The treatment efficiency was evaluated based on COD, TSS, color, and NH_3-N removal efficiency.

The efficiency for COD removal was estimated using Equation (2).

$$\text{COD Removal (\%)} = [(C_r - C_k)/C_i] \times 100, \quad (2)$$

where C_r is the initial COD concentration, and C_k is the final COD concentration.

2.5. Optimization of Treatment Efficiencies of Targeted Parameters

Using Design-Expert software (version 6.0.7), a central composite design (CCD) for the leachate/POME ratio was developed to examine whether COD, TSS, color, and NH_3-N affected the leachate/POME ratio and aeration time. Depending on the preliminary experiments stated in Section 2.3, the amounts and rates of each factor were chosen. Thirteen experiments were conducted to include all possible combinations of the leachate/POME ratio and aeration time.

Data from different CCD experiments were utilized to appropriate a polynomial model and a second-order model (Equation (3)).

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} x^2{}_j + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} X_i X_j + e_i' \quad (3)$$

where Y is the response, X_i and X_j are the variables, β is the regression coefficient, k is the number of variables tested and optimized in this experiment, and e is the random error. A p-value less than 0.05 was reported as significant.

Analytical Work

The chemical oxygen demand (COD), pH, biochemical oxygen demand (BOD_5), electrical conductivity (EC), total suspended solids (TSS), ammoniacal nitrogen (NH_3-N), and heavy metals (magnesium (Mg^{2+}), calcium (Ca^{2+}), iron (Fe^{2+}), zinc (Zn^{2+}), copper (Cu^{2+}), chromium (Cr^{2+}), cadmium (Cd^{2+}), lead (Pb^{2+}), arsenic (As^{3+}), cobalt (Co^{2+}), and manganese (Mn^{2+})) were tested before and after each aeration run. The level of BOD_5 was estimated utilizing Method 5210B. The DO was tested utilizing a DO meter (model 1000, YSI Inc., Greene County, OH, USA). COD concentration was tested utilizing the closed reflux colorimetric method (5220B—DR2500 HACH, Loveland, CO, USA). Color was determined using the DR 2800 HACH spectrophotometer at 455 nm wavelength.

A portable digital pH/mV meter (model inoLab pH 720, WTW, Weilheim, Germany) was used to measure the pH and EC. TSS was determined utilizing method 2540D, dried at 103–105 °C, which included the following procedure: preparation of filter disc, selection of filter type and sample volume, analysis of samples, and calculation of Equation (4) (APHA 2012) [31].

$$\text{TSS mg/L} = [(\text{A} - \text{B}) \text{ mg/(V) mL}, \quad (4)$$

where A is the weight of filter-dried residue (mg), B is the weight of the filter, and V is the sample volume.

NH_3-N level was determined using the phenate method (4500-NH_3 F) utilizing a DR2500 spectrophotometer at 640 nm. Heavy metals were measured using atomic absorption spectroscopy (Unicam 929 AA Spectrophotometer, UNICO, Franksville, WI, USA). All physico-chemical parameters and heavy metals were measured according to standard methods for examining water and wastewater [32]. Different leachate/POME ratios (1:0, 0.9:0.1, 0.7:0.3, and 0.5:0.50) were prepared in 1000-mL bottles to investigate the removal efficiency of targeted parameters.

3. Results and Discussion

3.1. Effects of Aeration Time Variation on the Removal Efficiency during the Aeration Process of Leachate Treatment

The maximum removal efficiencies in only leachate aeration for COD, TSS, color, and NH_3-N reached 44.12%, 43.5%, 55%, and 97%. Figure 1 shows the removal efficiency influenced by the time of reaction for the targeted parameters. The removal efficiencies of both COD and TSS increased slightly in the same way. However, the increased color removal efficiency was characterized by fluctuation, as shown on Figure 1, while the removal efficiency of NH_3-N increased sharply in the first week of aeration, reaching 93% on the seventh day; it did not demonstrate a further marked increase in removal efficiency, reaching 97% by the 24th day. This is in line with many studies reporting that NH_3-N can be removed under the effect of the gas stripping process during aeration [21], while the removal is significantly improved with aeration time increasing up to a specific point [33] due to the reaction of NH_3 with water, as shown in Equation (5).

$$NH_3 + H_2O \leftrightarrow NH_4{}^{+} + OH^{-}. \quad (5)$$

From Equation (5), increasing the pH due to the formation of OH^- will increase the concentration of NH_3. The increase in pH enhances the ammonia stripping during aeration [21] and enhances the removal of ammonia, after which, owing to the recarbonation of lime in leachate, the pH begins to decline by absorbing CO_2 from the ambient air [34].

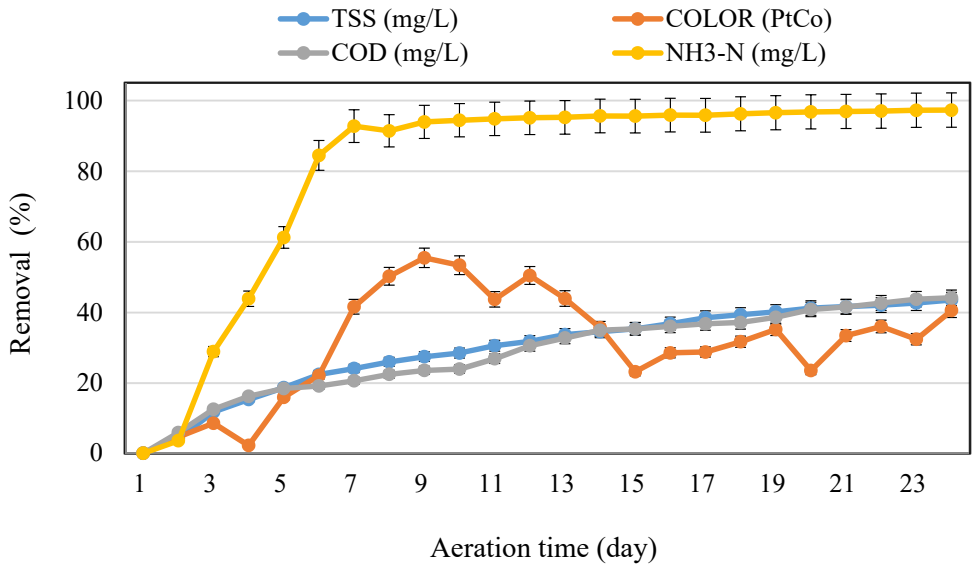

Figure 1. Effects of reaction time variation on COD, TSS, color, and NH_3-N removal efficiency (with natural pH, leachate only, aeration 20 L/min).

3.2. Effects of Reaction Time Variation on the Removal Efficiency during the Aeration Time of Leachate/POME Treatment (Ratio 900 mL Leachate/100 mL POME)

In this stage, the effect of the reaction time on leachate with a ratio of 900 mL leachate/100 mL POME was investigated during the aeration time. The optimum reaction time was reached on the 24th day of aeration, and the maximum removal efficiencies for COD, TSS, color, and NH_3-N reached 91%, 54%, 50%, and 98%, respectively. All targeted parameters increased as the aeration time increased (Figure 2).

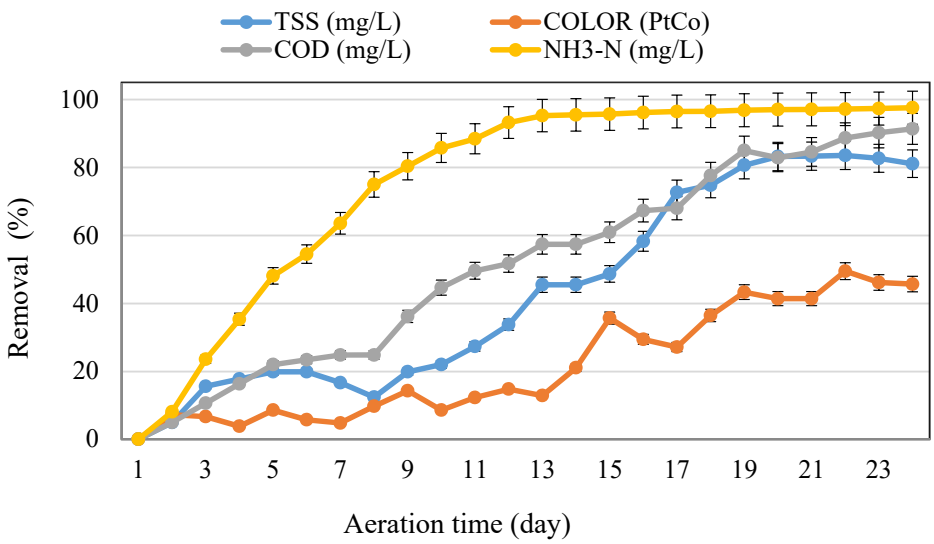

Figure 2. Effects of reaction time variation on COD, TSS, color, and NH_3-N removal efficiency (with natural pH, leachate/POME (900 mL leachate/100 mL POME), aeration power 20 L/min).

3.3. Effects of Reaction Time Variation on the Removal Efficiency during the Aeration Time of Leachate/POME Treatment (Ratio 700 mL Leachate/300 mL POME)

In this stage, the effects of reaction time variation on the removal efficiency during the aeration time of leachate/POME treatment with a constant ratio (700 mL leachate/300 mL POME) were investigated for the targeted parameters under the same condition of natural pH and an aeration power of 20 mL/min. The results showed an increase in the removal efficiency of all targeted parameters. The maximum removal of NH_3-N, COD, TSS, and color was 96%, 89%, 53%, and 41%, respectively. As shown in Figure 3, there was a higher removal efficiency for NH_3-N than COD, but color showed the lowest removal efficiency.

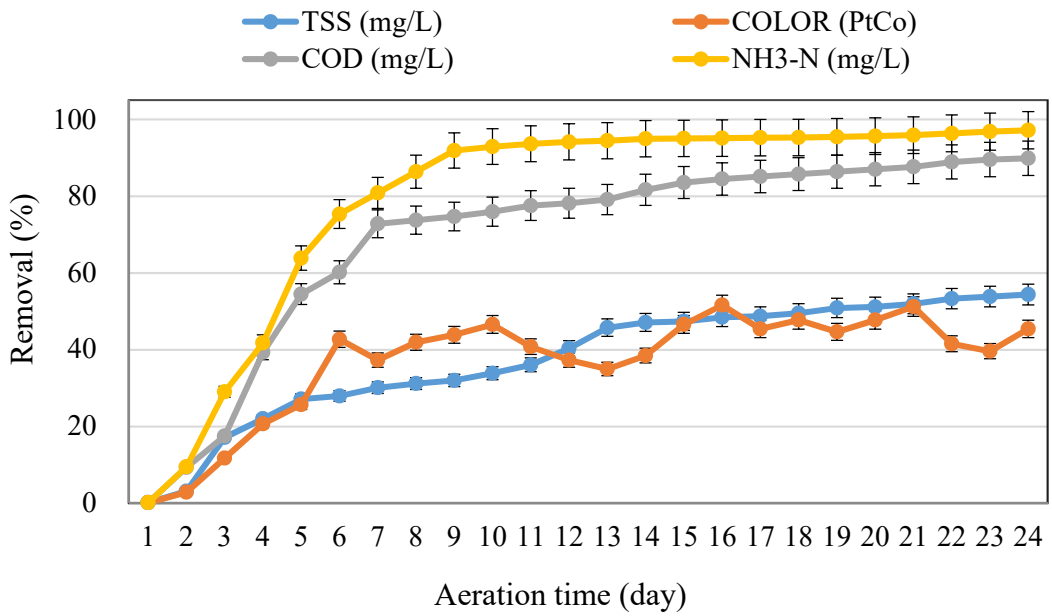

Figure 3. Effects of reaction time variation on COD, TSS, color, and NH_3-N removal efficiency (with natural pH, leachate/POME (700 mL leachate/300 mL POME), aeration power 20L/min).

3.4. Effects of Reaction Time Variation on the Removal Efficiency during the Aeration Time of Leachate/POME Treatment (Ratio 500 mL Leachate/500 mL POME)

As shown in Figure 4, the ratio between leachate and POME was 500 mL/500 mL. The effect of reaction time variation on the removal efficiency during the aeration time for targeted parameters was investigated with the same conditions for the other ratios (natural pH, aeration power 20 L/min). The maximum removal efficiencies for COD, TSS, color, and NH_3-N were 89%, 21%, 42%, and 94%. The removal efficiency of NH_3-N increased sharply in the first 10 days of aeration, reaching 90%, and it did not demonstrate a further marked increase in removal efficiency, reaching 94% by the 24th day.

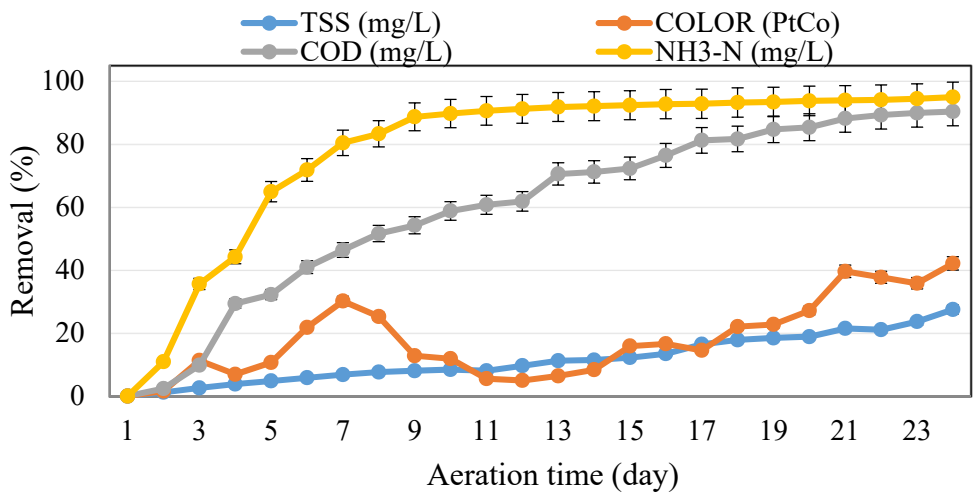

Figure 4. Effects of reaction time variation on COD, TSS, color, and NH_3-N removal efficiency (with natural pH, leachate/POME (500 mL leachate/500 mL POME), aeration power 20 L/min).

3.5. Effects of the Leachate/POME Mixing Ratio on the Leachate Aeration Process

The treatment of leachate was implemented using POME in four ratios (leachate only, 900 mL leachate/100 mL POME, 700 mL leachate/300 mL POME, and 500 mL leachate/500 mL POME) with a natural pH and an aeration power of 20 L/min. Accordingly, a limited removal efficiency of COD (43%) was found when treating leachate without any POME dosages. As shown in Figure 5, adding 100 mL, 300 mL, and 500 mL of POME improved the removal efficiency of COD (COD removal of 85%, 88%, and 88%, respectively).

The results of the removal efficiencies for the targeted parameters using several dosages (leachate only, 900 mL leachate/100 mL POME, 700 mL leachate/300 mL POME, and 500 mL leachate/500 mL POME) are illustrated in Figure 5. The maximum removal efficiency was NH_3-N, reaching 97% during the aeration process for leachate only and 900 mL leachate/100 mL POME, while the maximum removal for COD reached 88% (700 mL leachate/300 mL POME and 500 mL leachate/500 mL POME ratios). The lowest removal was 51% for TSS, followed by 52% for color for the 700 mL leachate/300 mL POME ratio.

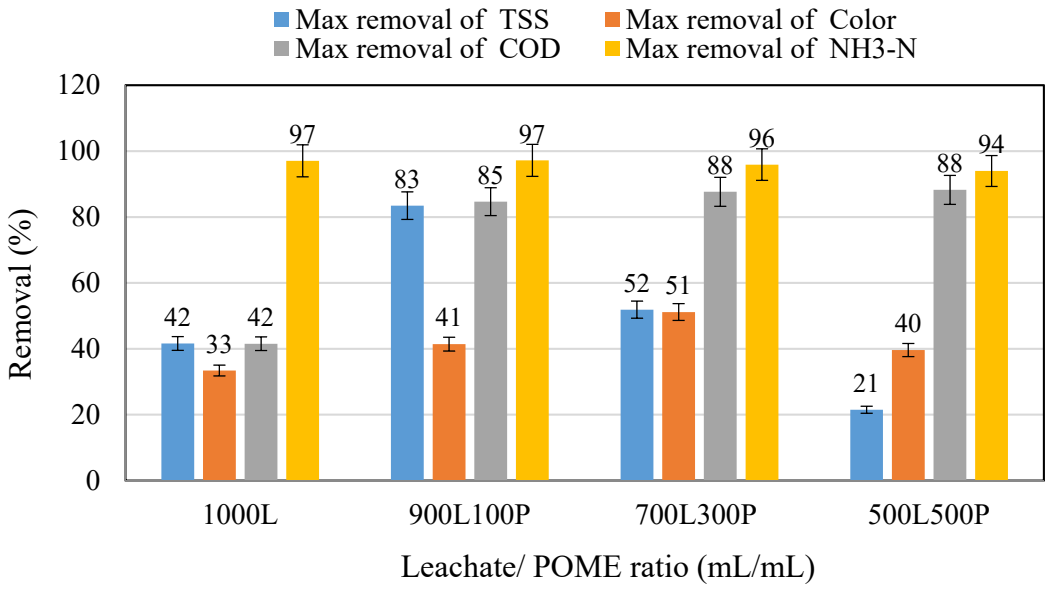

Figure 5. Effect of the leachate/POME ratios on COD, TSS, color, and NH_3-N removal efficiency after 24 days of mixing aeration (with natural pH, aeration power 20 L/min).

3.6. Analysis of Variance

One of the key objectives of the RSM is to calculate the best value for the control variables that can maximize or minimize a response over a particular area of concern. A good-fitting model is defined to provide a proper representation of the mean response to achieve the optimum value [34]. A total of 13 experiments with different dosages (leachate/POME) and reaction times at room temperature (28 °C) were performed using central composite design (CCD); the outcomes were analyzed using analysis of variance (ANOVA), as shown in Table 3. The POME dosage used to treat stabilized leachate was evaluated in terms of its effectiveness in the removal of COD, TSS, color, and NH_3-N.

The coefficient of determination (R^2) for COD, TSS, color, and NH_3-N was 0.9927, 0.8218, 0.9854, and 0.991, respectively. This mean that the models are good in Equations (6)–(9) due to the coefficient of determination being high and close to 1 (Table 4). Prior to the data analysis, the assumption of normality should be tested. The assumption of normality showed that the data roughly fit a bell-shaped curve for all responses, as presented in Figure 6.

$$\text{COD removal} = +80.18 + 25.81 \times A + 8.60 \times B - 19.97 \times A^2 - 4.00 \times B^2 - 0.98 \times A \times B; \quad (6)$$

$$\text{TSS removal} = +49.93 + 4.32 \times A + 15.76 \times B - 6.39 \times A^2 - 0.089 \times B^2 + 1.02 \times A \times B; \quad (7)$$

$$\text{Color removal} = +45.74 + 1.35 \times A + 16.14 \times B - 17.50 \times A^2 - 7.62 \times B^2 + 1.20 \times A \times B; \quad (8)$$

$$NH_3\text{-N removal} = +97.24 - 3.05 \times A + 6.72 \times B - 1.06 \times A^2 - 5.17 \times B^2 + 1.92 \times A \times B. \quad (9)$$

Table 3. Response value for different experimental conditions (POME dosages and aeration time).

Run	Factor A: POME (mL)	Factor B: Aeration Time (day)	COD Removal %			Color Removal %			TSS Removal %			NH_3-N Removal %		
			Actual	Predicted	Residual	Actual	Predicted	Residual	Actual	Predicted	Residual	Actual	Predicted	Residual
1	150	21	84.5	84.79	−0.29	51.89	55.1	−3.21	79	65.53	13.47	94	94.26	−0.26
2	150	14	78.81	80.18	−1.37	47.58	46.1	1.48	53.2	53.57	−0.37	93	92.83	0.17
3	150	14	78.31	80.18	−1.87	44.73	46.1	−1.37	51.3	53.57	−2.27	93	92.83	0.17
4	150	7	65.8	67.58	−1.78	24.21	21.37	2.84	25.6	36.92	−11.32	81	80.6	0.4
5	150	14	78.18	80.18	−2	47.69	46.1	1.59	54	53.57	0.43	93	92.83	0.17
6	300	14	84.9	86.02	−1.12	32.9	30.98	1.92	44	47.46	−3.46	90	88.93	1.07
7	0	14	33.46	34.4	−0.94	23.44	25.73	-2.29	36	30.38	5.62	94	94.93	−0.93
8	0	7	21.66	20.82	0.84	2.92	3.29	-0.37	18.46	15.07	3.39	85	84.7	0.3
9	300	7	75.32	74.39	0.93	1.5	3.97	−2.47	37.4	29.47	7.93	74	74.7	−0.7
10	0	21	40.08	39.98	0.099	35.1	32.44	2.66	32	41	−9	95	94.37	0.63
11	300	21	89.83	89.64	0.19	42.81	42.26	0.55	56.3	60.76	−4.46	92	92.37	−0.37
12	150	14	84.46	80.18	4.28	44.71	46.1	−1.39	54.4	53.57	0.83	93	92.83	0.17
13	150	14	83.22	80.18	3.04	46.15	46.1	0.052	52.8	53.57	−0.77	92	92.83	−0.83

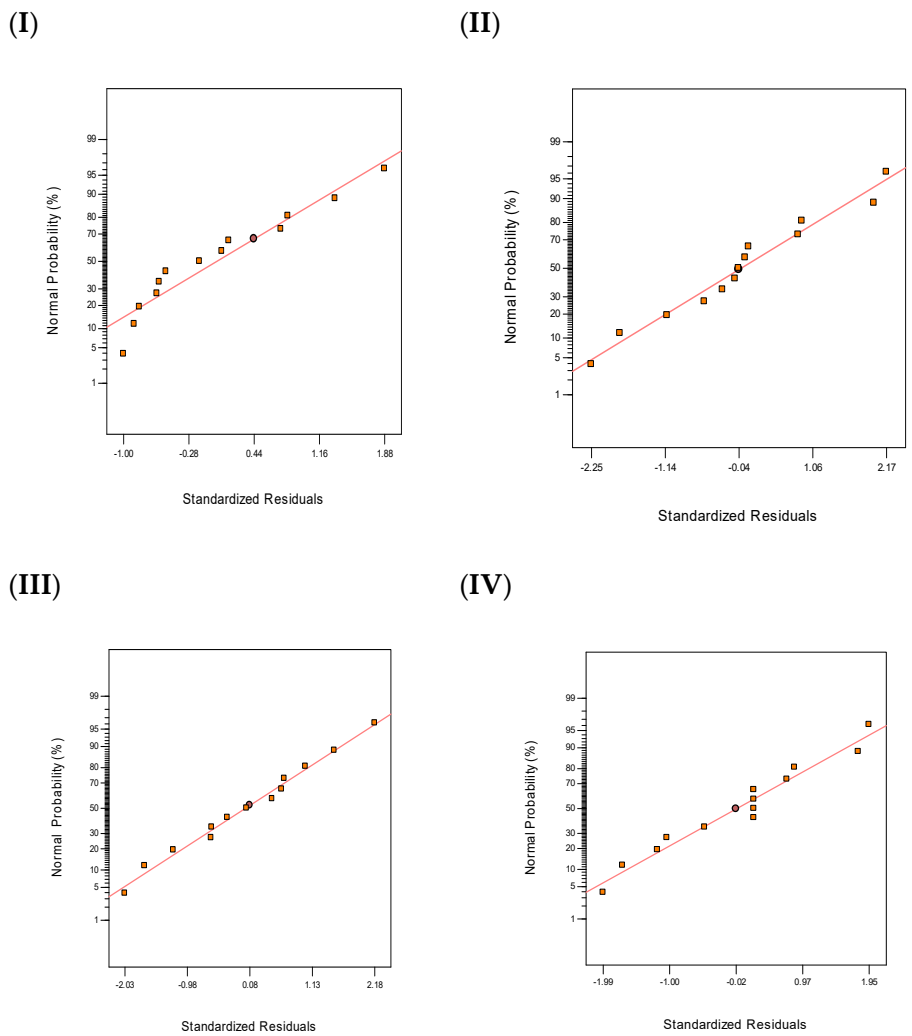

Figure 6. Normal probability plots for (**I**) COD, (**II**) TSS, (**III**) color, and (**IV**) NH_3-N removal.

The two variables, POME dosage and aeration time, displayed an important impact (p-value < 0.05) for the linear and quadratic models on the targeted factors of COD, color, and NH_3-N, as shown in Table 4 for the ANOVA results. On the other hand, a higher-order model like a third-order polynomial model or more complicated model can be used to improve the model for TSS removal.

Table 4. ANOVA for COD, TSS, color, and NH_3-N removal. A: POME dosage, B: aeration time.

	Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
COD Removal (%)	Model	5981.97	5	1196.39	190.7	<0.0001
	A	3996.42	1	3996.42	637	<0.0001
	B	444.28	1	444.28	70.81	<0.0001
	A^2	1101.81	1	1101.81	175.62	<0.0001
	B^2	44.26	1	44.26	7.06	0.0326
	AB	3.82	1	3.82	0.61	0.4607
	Residual	43.92	7	6.27		
	Lack of Fit	7.85	3	2.62	0.29	0.8314
	Pure Error	36.07	4	9.02		
	Cor Total	6025.89	12			
	SD: 2.50, R^2: 0.9927, mean: 69.12, CV:3.62, Pred R^2: 0.9814, Adeq Precision: 40.447.					

Table 4. *Cont.*

	Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
TSS Removal (%)	Model	2468.26	5	493.65	6.46	0.0148
	A	437.59	1	437.59	5.72	0.048
	B	1228.08	1	1228.08	16.06	0.0051
	A^2	592.46	1	592.46	7.75	0.0272
	B^2	15.2	1	15.2	0.2	0.6691
	AB	7.18	1	7.18	0.094	0.7681
	Residual	535.16	7	76.45		
	Lack of Fit	529.33	3	176.44	121.02	0.0002
	Pure Error	5.83	4	1.46		
	Cor Total	3003.43	12			
	SD: 8.74, R^2: 0.8218, mean: 45.73, CV:19.12, Pred R^2: −0.7897, Adeq Precision: 8.495.					
	Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Color Removal (%)	Model	3328.56	5	665.71	94.36	<0.0001
	A	41.34	1	41.34	5.86	0.046
	B	1705.89	1	1705.89	241.8	<0.0001
	A^2	869.58	1	869.58	123.26	<0.0001
	B^2	170.8	1	170.8	24.21	0.0017
	AB	20.84	1	20.84	2.95	0.1294
	Residual	49.39	7	7.06		
	Lack of Fit	40.88	3	13.63	6.41	0.0523
	Pure Error	8.5	4	2.13		
	Cor Total	3377.94	12			
	SD: 2.66, R^2: 0.9854, mean: 34.28, CV: 7.75, Pred R^2: 0.8733, Adeq Precision: 28.712.					
	Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
NH_3-N Removal (%)	Model	458.76	5	91.75	154.36	<0.0001
	A	54	1	54	90.85	<0.0001
	B	280.17	1	280.17	471.33	<0.0001
	A^2	2.22	1	2.22	3.73	0.0446
	B^2	80.43	1	80.43	135.32	<0.0001
	AB	16	1	16	26.92	0.0013
	Residual	4.16	7	0.59		
	Lack of Fit	3.36	3	1.12	5.6	0.0647
	Pure Error	0.8	4	0.2		
	Cor Total	462.92	12			
	SD: 0.77, R^2: 0.991, mean: 89.92, CV: 0.86, Pred R^2: 0.9238, Adeq Precision: 38.623.					

Abbreviation. DF: degrees of freedom; Cor: corrected; CV: coefficient of variation; Pred: predicted; Adeq: adequate.

In addition, the *p*-values for the interaction effect were 0.4607, 0.7681, and 0.1294 for the removal efficiency of COD, TSS, and color. In other words, the interaction effect between POME dosage and aeration time was insignificant (*p*-value > 0.05) for the removal efficiency of COD, TSS, and color. That implies that the two factors function independently. Conversely, the *p*-value (0.0013) for the interaction effect was significant for NH_3-N removal efficiency. Figure 7 shows the interaction between the two (variables) factors (POME dosage and aeration time) and their behaviors in terms of removal of the targeted parameters (COD, TSS, color, and NH_3-N). The *p*-values for lack of fit were 0.8314, 0.0523, and 0.0647, which indicates that the lack of fit was insignificant (*p*-value > 0.05), which means that the model is appropriate for the removal efficiency of COD, color, and NH_3-N, while the *p*-value for lack of fit was significant (*p*-value < 0.05) for TSS removal efficiency, indicating the model is not appropriate.

The impact of POME dosage and aeration time on the selected responses is illustrated in Figure 8. The descriptions for the behavior of each response for POME dosage and aeration time are shown as

the surface of a three-dimensional plot for the maximization of the four targeted responses (COD, TSS, color, and NH_3-N) (Figure 8). All response plots demonstrate clear peaks, suggesting that the maximum area of impact is well known with the selected boundaries of the POME dosage and aeration time.

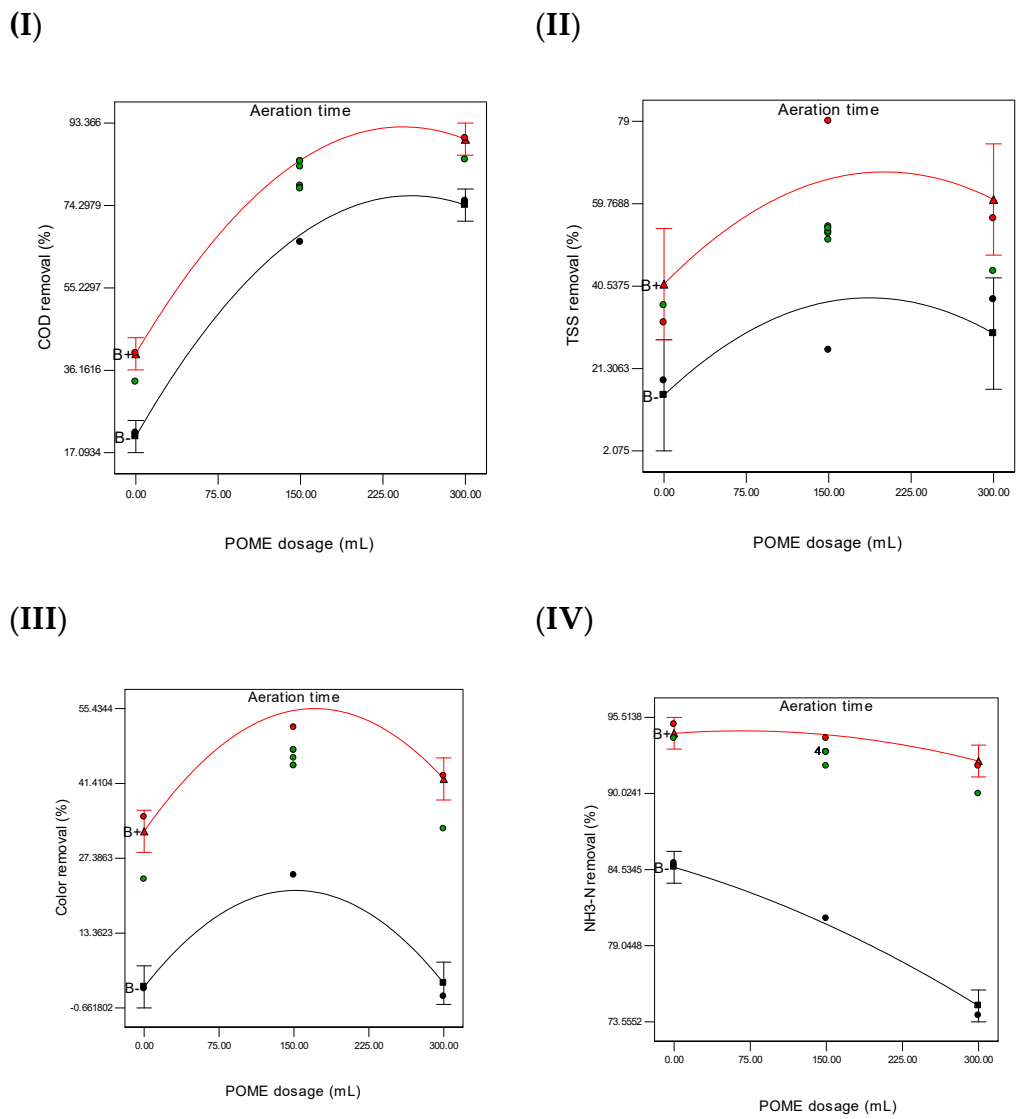

Figure 7. The impact of the POME dose combination and the aeration time for the removal of (**I**) COD, (**II**) TSS, (**III**) color, and (**IV**) NH_3-N.

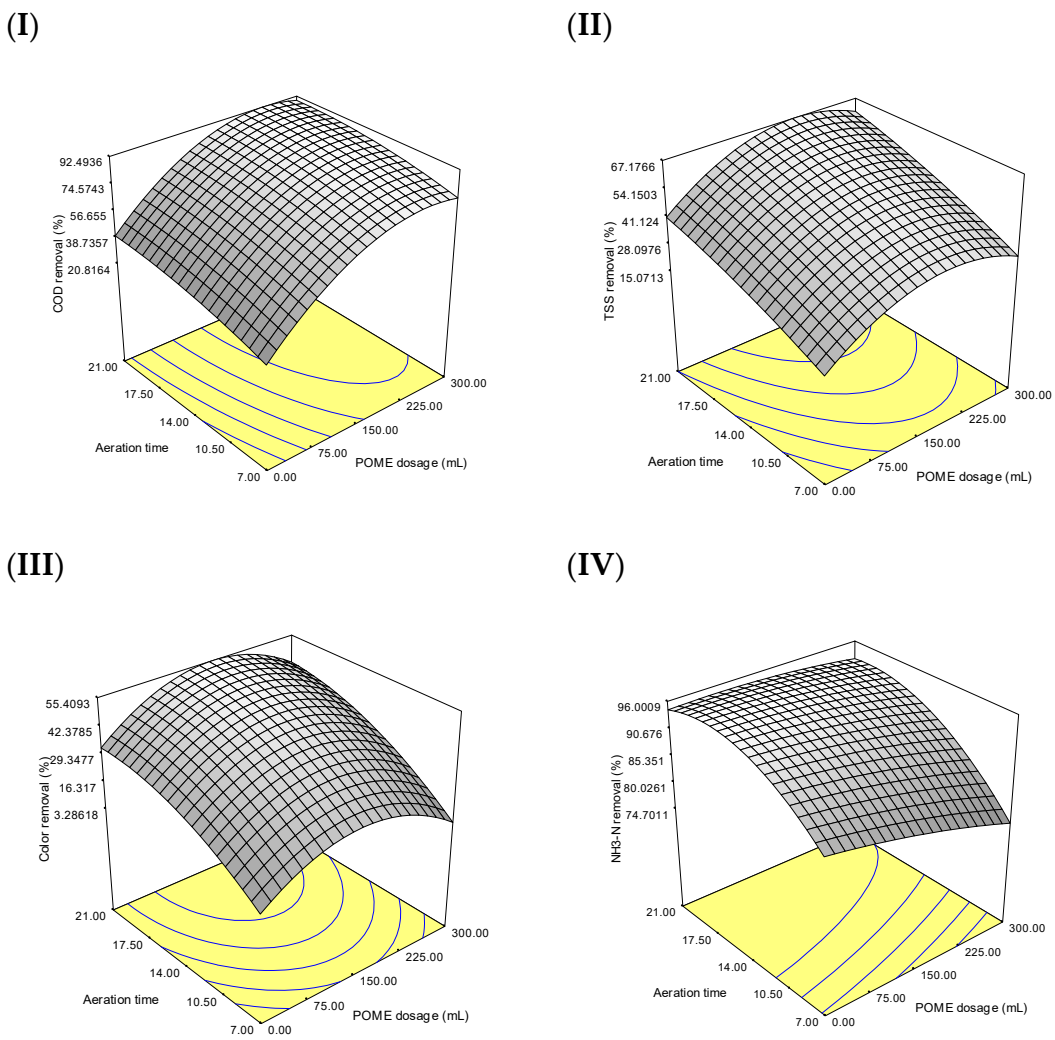

Figure 8. Response surface plot for (**I**) COD, (**II**) TSS, (**III**) color, and (**IV**) NH_3-N removal.

3.7. Optimization of Leachate Treatment Using POME

Design-Expert 6.0.7 software offers strong tools for setting up an optimal experiment of the treatment process to identify the optimum value of removal efficiency for COD, TSS, color, and NH_3-N. In accordance with the approach of software optimization, the required target was within the range for each experimental condition (POME dosage and aeration time). To obtain the highest output, the responses (COD, TSS, color, and NH_3-N) were described as a maximum value. The program incorporates individual desirability into a single number and then searches on the basis of the response target to optimize this feature. The optimum conditions and respective percentage removal efficiencies were established, and the COD (89.83%), TSS (66.7%), color (91.7%), and NH_3-N (94%) removal results are illustrated in Table 5 The desirability function for these optimum conditions was recorded as 0.935. Additional experiments under optimal conditions were performed to verify agreement with the outcome experiments from models and the experiments. The results from the laboratory experiment were 87.51%, 65.62%, 53.10%, and 91.8% for the removal of COD, TSS, color, and NH_3-N, respectively (Table 5). There was close agreement between the removal efficiencies for all response parameters gained from the experiments and those estimated by models. These results are more efficient than the result of Banch et al. [8], who conducted tests for the same parameters except for color. Tatsi et al. [35] achieved a color removal of about 100% for partially stabilized leachate. However, the reported residuals for COD, TSS, color, and NH_3-N were recorded as 430 mg/L, 1620 mg/L, 1780 Pt-Co, and 66 mg/L, respectively, which are still higher than the effluent discharge limits.

Table 5. Optimal response results from the model prediction and laboratory.

POME	Aeration Time	COD Removal (%)	TSS Removal (%)	Color Removal (%)	NH_3-N Removal (%)	Desirability
188.38	21.00	89.83	67.10	55.19	93.95	0.935
Lab experiment		87.15	65.54	52.78	91.75	

3.8. Heavy Metal Analysis

The removal efficiency of targeted heavy metals from stabilized leachate was evaluated under the achieved optimum experimental conditions, and the results are given in Table 6. The removal efficiency for the targeted heavy metals ranged between 99.00% (Cd^{2+}) and 6.85% (As^{3+}). The order of residuals of heavy metals in leachate was Fe^{2+} > Mn^{2+} > As^{3+} > Zn^{2+} > Cr^{2+} > Cu^{2+} > Co^{2+} > Pb^{+} > Cd^{2+} from highest to lowest concentration. The heavy metal residuals were 1856, 31.72, 16.15, 10.76, 2.80, 1.28, 0.53, 0.28, and 0.23 µg/L for Fe^{2+}, Mn^{2+}, As^{3+}, Zn^{2+}, Cr^{2+}, Cu^{2+}, Co^{2+}, Pb^{+}, and Cd^{2+}, respectively, while the removal efficiency was 90.73%, 34.75%, 6.85%, 96.16%, 93.78%, 96.95%, 95.24%, 93.30%, and 99.00% respectively. Only the concentration of Mn^{2+} existed out of the limits, while the other targeted heavy metals were within the limits. The removal of heavy metals is attributed to the high level of suspended solids and metal complexes in POME which may act as a natural coagulant. The suspended solids and metal complexes improve the charged exchange and accelerated the adsorption and deposition of dissolved heavy metals in wastewater [36–40]. This study showed more efficient removal than Banch et al. [8] for Fe^{2+}, As^{3+}, Zn^{2+}, Cr^{2+}, Cu^{2+}, Co^{2+}, and Cd^{2+}.

Table 6. Effect of the POME dosage and aeration time on heavy metal removal (POME dosage 188.32, aeration time 21 days).

Heavy Metals	Initial Concentration in Leachate	Residual after Treatment Process	Removal (%)
Fe^{2+} (µg/L)	20.04 ± 7.11	1856 ± 0.57	90.73
Zn^{2+} (µg/L)	280.00 ± 19.63	10.76 ± 2.10	96.16
Cu^{2+} (µg/L)	41.91 ± 20.19	1.28 ± 0.64	96.95
Cr^{2+} (µg/L)	45.11 ± 12.81	2.80 ± 1.01	93.78
Cd^{2+} (µg/L)	22.62 ± 3.51	0.23 ± 0.20	99.00
Pb^{+} (µg/L)	4.18 ± 2.91	0.28 ± 0.12	93.30
As^{3+} (µg/L)	17.34 ± 4.29	16.15 ± 2.37	6.85
Co^{2+} (µg/L)	11.05 ± 5.54	0.53 ± 0.39	95.24
Mn^{2+} (µg/L)	48.61 ± 14.99	31.72 ± 7.16	34.75

4. Conclusions

The current work evaluated the use of POME as an agro-industrial waste for landfill leachate treatment. Biological treatment using an aeration process for different mixing ratios between leachate and POME was performed. The optimization of the removal efficiencies for COD, TSS, color, and NH_3-N for the aeration treatment process of old leachate was investigated in this study. The optimum operational conditions were obtained at 188.32 mL of POME added to 1 L of leachate for 21 days of aeration time. The respective percentage removal efficiencies were 89.83%, 66.7%, 91.7%, and 94% for COD, TSS, color, and NH_3-N. Moreover, the treatment process reported an efficient removal of some heavy metals from landfill leachate. The results revealed that POME-based agricultural waste can be effectively used for organic removal from stabilized leachate.

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