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Multivariate models for the effect of two coagulants on palm oil mill effluents

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ABSTRACT

Two coagulants ($Al_2(SO_4)_3$ and $FeSO_4$) were investigated for their performance in treating raw and anaerobic effluents from a palm oil mill. The treatment efficiencies for both palm oil mill effluents (POMEs) were assessed based on chemical oxygen demand (COD) removal. Different dosages of $Al_2(SO_4)_3$ and $FeSO_4$ were investigated in terms of COD removal in raw and anaerobic effluents under different pH levels. The results show that $FeSO_4$ performed better than $Al_2(SO_4)_3$ in removing COD from both effluents. The maximum COD removal efficiency (94%) was achieved when both effluents were treated with 0.4 g of $FeSO_4$ at pH 3, while the maximum COD removal achieved by $Al_2(SO_4)_3$ was 70% using 0.4 g at pH 7. Using these optimal operational conditions, the removal of 11 parameters, namely COD, color, total suspended solids (TSS), electrical conductivity, biochemical oxygen demand (BOD), pH, NH_3–N, Cu^{+2}, Fe^{+2}, Zn^{+2}, and Pb were measured and assessed. The results were analyzed statistically using factor analysis (FA) and cluster analysis (CA) to identify the main factors responsible for the differences in the parameters and to display the similarity and dissimilarity between the selected parameters among the different POME sources. The FA method produced four factors responsible for more than 99% of the differences in data. The first factor covered COD, color, TSS, and BOD and was responsible for explaining 36% of the differences, whereas the second factor was responsible for explaining 34% of the differences, including NH_3–N, Cu^{+2}, Fe^{+2}, and Zn^{+2}. The percentage variance explained by the third and fourth factors was 16% and 14%, respectively. The CA method produced three different groups (clusters). It was found that raw and anaerobic POMEs treated with Al^{+3} and raw POMEs treated with Fe^{+2} were close to each other, representing the second cluster, while the raw treatment represented the first cluster. The last cluster represents the anaerobic effluent before and after coagulation using Fe_2SO_4. The results reveal that Fe_2SO_4 is an efficient method for removing organic and heavy metal content from POME. The study provides essential data and knowledge that can be used to evaluate and manage POME treatment.

Keywords: Coagulation; Palm oil mill; Effluents; Factor analysis; Cluster analysis

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1. Introduction

There is an increasing global trend in vegetable oil production due to the growth of the global economy and higher demand for this type of oil in the current market [1,2]. Palm oil mills are considered one of the primary vegetable oil industries in different countries such as South Asia, West Africa, and Latin America [3]. Malaysia is considered the second largest producer and exporter of palm oil and oil derivatives globally, with an estimated palm oil plantation area amounting to 5.64 million ha [4]. Palm oil mill effluent (POME) contains a substantial amount of nutrients, which many indigenous microorganisms consume [5].

Water bodies and aquatic environments are highly affected by untreated POME because of its high organic content [6,7]; thus, POME must be adequately treated before it is discharged into the environment. Raw POME is usually treated in conventional biological ponding systems; however, organic and color concentrations are still higher than discharge standards for primary-treated effluent [6]. Therefore, an additional, efficient post-treatment process is needed before its final discharge.

Recently, several pre- and post-treatment methods for POME have been reported, including membrane bioreactor processes [8], adsorption [9,10], oxidation photo-oxidation [11], photo-oxidation [12], advanced oxidation [13,14], and coagulation [15]. In one study, Azmi and Yunos [7] used the adsorption process followed by ultrafiltration membrane separation to treat raw POME. They obtained a 71% removal efficiency of suspended solids. In another study, Bashir et al. [6] performed an electro persulfate oxidation for biologically-treated POME and obtained 77.7% chemical oxygen demand (COD) removal.

In a previous study, Ahmad et al. [16] compared the performance of aluminum sulfate with polyaluminum chloride and chitosan adsorption to treat raw POME. The authors reported that chitosan removed suspended solids more efficiently than polyaluminum chloride. Bashir et al. [17] reported achieving 71.3% COD removal by applying the electro-coagulation-peroxidation (ECP) technique for the post-treatment of biologically-treated POME. Recently, Moksin et al. [13] treated POME using photocatalytic fuel cells and achieved 74% COD removal. Nevertheless, the efficiency of the biologically-ponded system for POME was not evaluated. Moreover, the performance of the coagulation processes of raw and biologically-treated effluents has not been well documented. Previous studies on POME treatment have focused only on the removal of COD, color, and suspended solids [15]. The performance of physiochemical treatments such as coagulation in removing ammonia and heavy metals from POME is not well reported in the literature.

The current study evaluates the performance of a biologically anaerobic ponding system to treat raw POME. The effect of two coagulants ($Al_2(SO_4)_3$) and Fe_2SO_4) in treating both raw and anaerobic POMEs is investigated, compared, and discussed. Numerous multivariate statistical approaches are used to analyze the performance of various environmental concerns and to examine the effectiveness of different approaches, with numerous variables obtained from each method [18–21]. Factor analysis and cluster analysis have evolved into essential and appropriate statistical methods for studying the concepts of interactions between environmental parameters in life sciences and overall integration [22]. Cluster analysis is a multivariate approach for grouping system data into groups called clusters by using similarities and differences between two observations as criteria in the same group [23].

Many researchers in the field have addressed the use of multivariate analysis for assessing natural water and air quality [23]. Alkarkhi et al. [24] used factor analysis to assess surface water quality. Mohamed et al. [25] assessed river water quality using multivariate analysis. Multivariate analysis was also used by Hamzah et al. [26] to examine the physical and chemical characteristics of marine water quality. The same authors also used multivariate analysis to assess the physical and chemical parameters of marine water quality. Yusup et al. [27] assessed particulate matter (PM) and its metal concentration using factor analysis. Yusup et al. [28] used multivariate analysis to examine the influence of microclimate factors on carbon dioxide flow in the tropical coastal ocean in the South China Sea.

Alkarkhi et al. [24] used multivariate analysis to assess heavy metals in sediments from Malaysian estuaries. However, no study has yet used multivariate analysis to examine the parameters of wastewater treatment or compared them across different treatment procedures. Therefore, the goals of this work are as follows:

- To evaluate the performance of two coagulants ($Al_2(SO_4)_3$ and Fe_2SO_4) in treating both raw and anaerobic POMEs.
- To identify the source (factor) of differences (fluctuations) in the concentration of the POME parameters before and after the applied treatment processes, which can be accomplished using factor analysis.
- To investigate the similarities and differences between the different treatment processes applied and the raw POME.

2. Materials and methods

2.1. Sampling and characterization

The POME samples were collected from Sime Darby Research Company in Port Dickson, Negeri Sembilan, Malaysia. The samples were collected from fresh (raw) and anaerobic POME effluents. The temperature of the collected raw POME samples was between 75°C and 90°C. The raw POME samples were allowed to cool to a temperature lower than 30°C before being transferred into plastic containers. The anaerobic POME samples were collected from an anaerobic pond. A total of 20 L (raw and anaerobic) POME was collected from each pond, transferred, and stored following the Standard Methods for the Examination of Water and Wastewater (APH, 2005) [29].

2.2. Experimental procedures

Aluminum sulfate ($Al_2(SO_4)_3$, 342.15 g/mol) and ferrous sulfate heptahydrate ($Fe_2SO_4·7H_2O$, 278.02 g/mol) were used for the coagulation of raw and anaerobic POMEs.

Preliminary experiments were run by adding different dosages of $Al_2(SO_4)_3$ and $FeSO_4$ ranging between 0.1–0.4 g separately to coagulate the samples obtained from the raw and anaerobic POMEs to understand the behavior of the coagulation process on selected parameters (eleven parameters, as presented in Table 1).

During this stage of the trials, the starting pH for the raw (pH 5.4) and anaerobic (pH 7.31) effluents was not adjusted, and coagulation effectiveness was assessed based on COD removal efficiency. The impact of pH change between pH 5 and pH 9 on COD removal was investigated using the dose of the two coagulants that provided the highest COD removal in the previous stage. For pH correction, a 3 M hydrochloric acid solution and a 3 M sodium hydroxide solution were used [30,31]. All studies were carried out in a jar using 500 mL of the sample volume at a mixing rate of 200 rpm for 15 min, followed by 30 min of slow mixing at 60 rpm [32].

The removal efficiency for COD was calculated using Eq. (1):

$$\text{Removal}(\%) = \left[\frac{\left(C_i - C_f\right)}{C_i}\right] \times 100 \quad (1)$$

where C_i and C_f are the initial COD concentration and final COD concentration, respectively.

2.3. Analytical study

Biochemical oxygen demand (BOD_5), COD, ammonia (NH_3–N), total suspended solids (TSS), electrical conductivity (EC), pH, and four heavy metals, namely copper (Cu), iron (Fe), lead (Pb), and zinc (Zn), were examined for both raw and anaerobic POMEs. The same characteristics were examined for the effluents following optimum treatment conditions with $Al_2(SO_4)_3$ and $FeSO_4$ coagulation. BOD_5 concentration was measured using method 5210B. A DO meter (model 1000, YSI Inc., USA) was used to measure the dissolved oxygen (DO) [6]. The COD concentration was measured using a closed reflux colorimetric technique (5220B – DR2500 HACH) [33]. A DR 2600 HACH spectrophotometer was used to assess color concentration [34].

A portable digital pH/mV meter (model inoLab pH 720, WTW, Germany) was used to monitor pH and EC [35]. TSS was determined using the 2540C technique [1]. The concentration of NH_3–N was determined using the Phenate Method (4500-NH3 F) using a DR2500 spectrophotometer at 640 nm [34]. Atomic Absorption Spectroscopy (Unicam 929 AA Spectrophotometer, UNICO, USA) was used to

Table 1
Descriptive statistics including min, max, mean and standard deviation (SD)

Treatment	Measure	pH	EC	COD (mg/L)	Color (Pt. Co.)	TSS (mg/L)	NH_3–N (mg/L)	BOD (mg/L)	Cu (mg/L)	Fe (mg/L)	Zn (mg/L)	Pb (mg/L)
Raw	min	5.43	9.36	51,600.00	51,000.00	120.00	640.00	7,200.00	1.20	13.60	6.71	0.09
	max	5.59	9.96	52,550.00	52,200.00	130.00	720.00	7,800.00	1.27	13.72	6.95	0.15
	mean	5.49	9.77	52,250.00	51,425.00	126.25	682.50	7,525.00	1.23	13.67	6.84	0.13
	SD	0.07	0.27	437.80	531.51	4.79	33.04	250.00	0.03	0.05	0.10	0.03
Anaerobic	min	7.33	11.04	11,900.00	25,100.00	20.00	1,900.00	598.00	1.41	13.40	6.8	0.29
	max	7.35	11.25	11,950.00	26,200.00	20.00	2,050.00	655.00	1.45	12.84	6.37	0.41
	mean	7.34	11.16	11,937.50	25,800.00	20.00	1,975.00	629.50	1.43	13.20	6.58	0.36
	SD	0.01	0.09	25.00	483.05	0.00	64.55	23.61	0.02	0.31	0.3	0.05
Raw-Fe	min	3.11	52.00	2,980.00	1,054.00	60.00	181.00	183.00	0.02	0.34	0.11	0.02
	max	3.14	54.10	3,140.00	1,064.00	60.00	186.00	188.00	0.02	0.35	0.12	0.02
	mean	3.13	53.03	3,042.50	1,059.50	60.00	184.00	186.25	0.02	0.35	0.12	0.02
	SD	0.02	0.87	71.36	4.12	0.00	2.16	2.36	0.00	0.01	0.01	0.00
Anaerobic Fe	min	11.27	11.20	600.00	2,662	10.00	315.00	134.00	0.02	0.34	0.13	0.08
	max	11.58	11.37	698.00	2,690	10.00	322.00	138.00	0.02	0.37	0.14	0.08
	mean	11.44	11.31	642.00	2,675	10.00	318.75	136.50	0.02	0.36	0.14	0.08
	SD	0.16	0.07	43.11	12.4	0.00	2.99	1.91	0.00	0.01	0.01	0.00
Raw-Al	min	4.51	12.24	15,670.00	4,780.00	20.00	131.0	214.00	0.00	0.04	0.06	0.41
	max	4.52	12.30	15,840.00	4,820.00	20.00	135.0	220.00	0.01	0.05	0.10	0.42
	mean	4.52	12.27	15,787.50	4,797.50	20.00	133.0	217.00	0.01	0.05	0.08	0.42
	SD	0.00	0.03	79.32	17.08	0.00	2.8.0	2.58	0.01	0.01	0.02	0.01
Anaerobic-Al	min	6.56	11.23	7,850.00	1,455.00	30.00	100.0	216.00	0.01	0.01	0.03	0.21
	max	6.86	11.28	7,876.00	1,473.00	40.00	120.0	222.00	0.02	0.01	0.03	0.22
	mean	6.73	11.25	7,865.00	1,463.75	33.75	110.0	219.00	0.02	0.01	0.03	0.22
	SD	0.14	0.02	11.14	7.89	4.79	14.0	2.58	0.01	0.00	0.00	0.01
Standards*		5–9	–	1,000	–	400	200	100	–	–	–	–

examine heavy metals [17]. Calibration curves were produced using standard samples containing (0.2, 0.4, 0.8, 1.0, and 2.0) mg/L of Cu and (1.0, 2.0, 4.0, 8.0, and 10.0) mg/L of Fe, and (1.0, 2.0, 4.0, 8.0, and 10.0) mg/L Pb. The coefficient of determination for Cu, Zn, Fe, and Pb was 0.985, 0.956. 0.966 and 0.991, respectively.

2.4. Statistical analysis

2.4.1. Factor analysis

Factor analysis (FA) is a multivariate approach used to describe the relationship between highly correlated variables and a smaller set of new uncorrelated variables known as factors. The additional variables (factors) are linear combinations of the variables under consideration. Factor analysis (FA) is regarded as a data reduction strategy that recommends the number of variables required to explain the observed variations in data. The main component approach is commonly used to extract various variables. The first step in FA is to extract the components using the principal components approach (PCA) and the amount of variation explained by each component (the number of components is equal to the number of variables in the study); only components that correspond to an eigenvalue (represents the variation explained by the corresponding component) equal or greater than 1 are selected. The axis of the principal components approach (PCA) is generally rotated using rotation techniques such as Quartimax, Equamax, Direct Oblimin, Promax, and Varimax to minimize the contribution of less significant variables [18,27]. Varimax produces orthogonal factors, while others allow the factors not to be orthogonal. The rotation approach is usually used to minimize the complexity of the factor loadings and to make the structure simpler to interpret.

In this work, FA was applied to identify the sources of variations in the measured data between the raw and differently-treated POMEs and, as a result, to identify the contribution of variables (parameters) in explaining the total variance, and to identify the responsibility of each factor in explaining the differences for each treated effluent. R-statistical software version 3.6.0 was used to prepare and extract the factors.

2.4.2. Cluster analysis

The cluster analysis (CA) approach is a statistical technique that attempts to find similar observations and forms groups called clusters. The observations (records) are similar to the same cluster and different than other clusters. The process is continued to form a cluster of similar observations. It then attempts to merge the clusters in one cluster with the similarity index of each cluster with other clusters. The procedure depends on measuring similarity (similarity is represented in terms of Euclidean distance) to group a set of data into different clusters. The formula for calculating the Euclidean distance (d) between two points A and B ($A = (X_1, X_2, \ldots, X_k)$, $B = (Y_1, Y_2, \ldots, Y_k)$) is shown in Eq. (2):

$$d = \sqrt{\left(X_1 - Y_1\right)^2 + \left(X_2 - Y_2\right)^2 + \ldots + \left(X_k - Y_k\right)^2} \quad (2)$$

There are two procedures for hierarchical clustering: agglomerative and divisive. The agglomerative procedure considers each observation as a cluster starts, and then close observations (based on the distance) are placed in a new cluster. The procedure continues grouping similar observations in one cluster that are different from the other clusters. There are three approaches to the hierarchical approach (single linkage, complete linkage, and average linkage). The single linkage approach was used to produce the dendrogram for the data, while CA was extensively used to determine the quality and attribute of the data [18,20]. In this work, CA was applied to find the similarity and dissimilarity among the raw effluent and variously-treated effluents and study the possibility of grouping some treatments under the same group based on the performance of each treatment based on selected parameters.

3. Results and discussion

3.1. Effect of $Al_2(SO_4)_3$ and $FeSO_4$ on COD removal

The performance of two coagulants ($Al_2(SO_4)_3$ and $FeSO_4$) was investigated in treating raw and anaerobic effluents from a palm oil mill. The treatment efficiencies for both POMEs were assessed based on COD removal. The effect of $Al_2(SO_4)_3$ and $FeSO_4$ dosages on COD removal was investigated at different dosages of $Al_2(SO_4)_3$ and $FeSO_4$ (i.e., 0.1, 0.2, 0.25, 0.3, 0.35, 0.4 g) for both raw and anaerobic effluents, as presented in Fig. 1a and b. The highest COD removal was observed at 0.35 g $FeSO_4$ dosage, where the COD removal was 88% and 89% for the raw palm oil effluent and anaerobic palm oil effluent, respectively. In comparison, the highest COD removal was obtained by employing $Al_2(SO_4)_3$ at 0.4 g, where the COD removal for both the raw effluent and the anaerobic effluent was 51% and 31%, respectively.

The initial pH value was maintained at pH 5.3 for the raw effluent and pH 7.3 for the anaerobic effluent. The performance of $FeSO_4$ in removing COD under natural pH (pH 5.3) conditions was efficient. This result agrees with that of other studies [36–38], which found that the performance of $FeSO_4$ in organic degradation was better under acidic conditions. The mechanism of iron ions (Fe^{2+}) is to react with organics, and it is involved in the release of hydroxyl radicals ($^{\bullet}OH$) [36], which have a high oxidation potential ($E^0 = 2.7$ V), per Eq. (3).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \quad (3)$$

The effect of various pH values pH (3, 5, 7, 9, 11) on organic degradation was investigated for raw and anaerobic palm oil mill effluents, as in Fig. 2a and b, while maintaining 0.4 g dosage for $FeSO_4$ and $Al_2(SO_4)_3$. The highest COD removal (94%) was achieved when $FeSO_4$ treated both effluents at pH 3. Previous studies have reported similar results and have used electro-coagulation-peroxidation (ECP) as a post-treatment for POME and obtained 73.3% removal of COD at pH 4.4 [17].

At lower pH values, the higher concentration of proton H competes on the same anionic sites of the polymer and reduces the divalent cation binding [37]. Meanwhile, at natural pH (pH 6–pH 8), the saturated superficial adsorbed

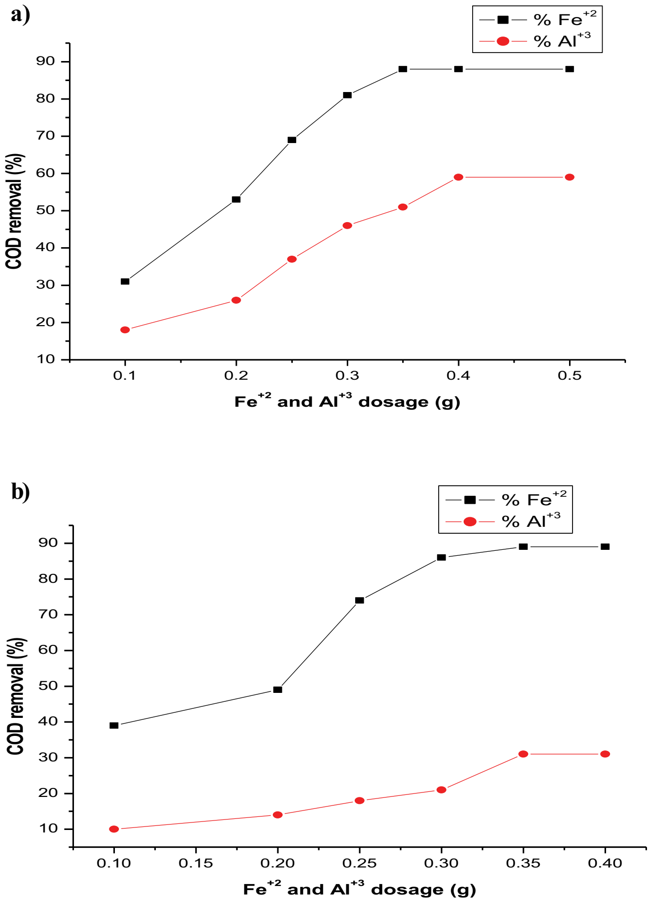

Fig. 1. Effect of $FeSO_4$ and $Al_2(SO_4)_3$ dosage on COD removal for (a) raw palm oil mill effluent and (b) anaerobic palm oil mill effluent (200 rpm for 15 min followed by 60 rpm for 30 min, initial pH (pH 5.3) for raw effluent and (pH 7.3) for anaerobic effluent).

by negative charges increases the efficiency of positive charges to bind to and adsorb metal ions [38]. However, hydroxide metals could be formed in an alkaline medium, and the adsorption sites on the surface did not bind the adsorbent [39]. Accordingly, the maximum removal of COD was achieved at pH 7 using $Al_2(SO_4)_3$. The removal efficiency declined to lower than pH 6 and higher than pH 8 (Fig. 2b), while the maximum removal efficiency was reported at a lower pH using $FeSO_4$.

The performance of $FeSO_4$ will be higher at a pH between pH 3 and pH 5, which leads to hydroxyl radicals that have higher oxidation potential than the organics 38–39. In contrast, at a pH of more than pH 8, the major part of Fe ions will be precipitated, and the reaction will be inhibited [40]. Lin et al. [14] employed electro persulfate oxidation to treat biologically-treated POME and obtained a 77.7% removal of COD at pH 4. Although the highest COD removal was obtained at 70% and 35% for the raw effluent and the anaerobic effluent, respectively, using $Al_2(SO_4)_3$ at pH 7, a study conducted by Ahmad et al. [16] obtained a 95% removal of suspended solids using 8 and 6 g/L of aluminum sulfate and polyaluminum chloride (PAC), respectively, for POME treatment during 30 min mixing time at pH 4.5.

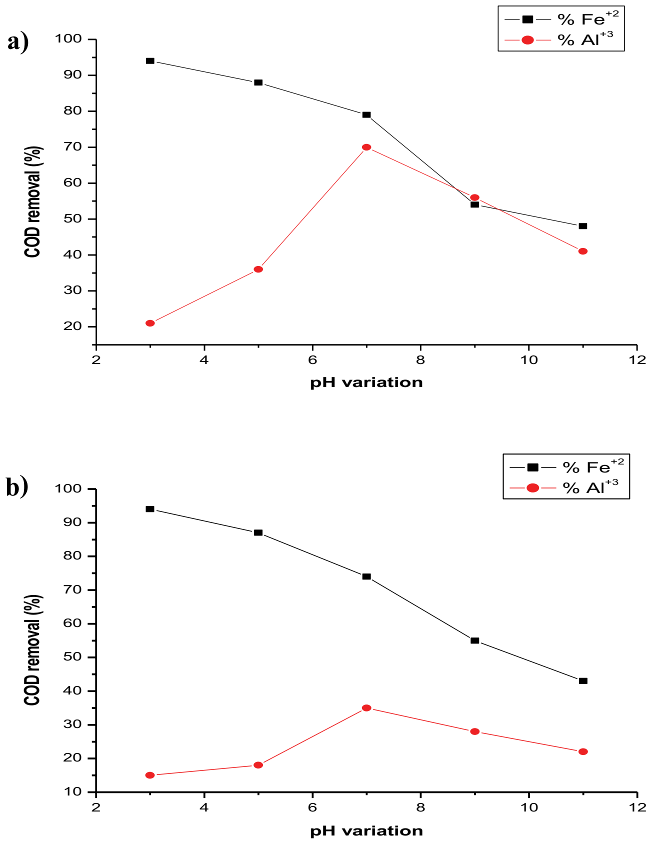

Fig. 2. Effect of pH variation on COD removal for raw effluent (a) and anaerobic effluent (b) (200 rpm for 15 min followed by 60 rpm for 30 min, 0.4 g $FeSO_4$ and $Al_2(SO_4)_3$ dosage).

3.2. Evaluation of treated effluents

Table 1 shows the descriptive statistics for parameters such as minimum, maximum, mean, and standard deviation (SD) for the raw and treated effluents. Based on the optimum operational conditions for both coagulants, eleven parameters were tested and compared with those of the raw and anaerobic treated POMEs. As shown in Table 1, although the level of COD (11,900 mg/L), BOD (625 mg/L), color (25,800 Pt. Co), and NH_3–N (1,975 mg/L) were reduced between 71% and 84% in the anaerobic ponding system, the residual levels of these parameters are still higher than those set by the effluent discharge standards for crude palm oil mills (COD = 1,000 mg/L, BOD = 100 mg/L, and NH_3–N = 200 mg/L) [41]. Heavy metals were not significantly affected by anaerobic treatment, while pH and ammonia were increased to pH 7.3 and 1,970 mg/L, respectively, during anaerobic processes. The normal pH for anaerobic treatment is between pH 6 and pH 7.5 [42,43], and ammonia is released during the anaerobic digestion of organic nitrogen, causing an increase in the pH value. The effect of both coagulants ($Al_2(SO_4)_3$ and $FeSO_4$) in the removal of COD, color, BOD, and NH_3–N in raw POME was stronger than that in anaerobic treatment. However, the performance of $FeSO_4$ in the treatment of raw and anaerobic POME was better than $Al_2(SO_4)_3$, which is in line with the study by Bashir et al. [6] which reported a significant removal of Zn, Cu, and Fe as well as organics and ammonia from POME using electro-persulfate oxidation.

3.3. Cluster analysis

A cluster analysis was used to determine the similarity between the various POME treatments. The cluster analysis is summarized in Fig. 3. As shown in Fig. 3, the behavior of the eleven parameters in eight different samples; raw POME, effluent after anaerobic digestion, raw and anaerobic POME treated by $Al_2(SO_4)_3$, and $FeSO_4$ is presented. The difference between the raw POME samples and others is revealed as a different group (cluster 1). In contrast, raw and anaerobic POMEs treated by Al (raw – Al, anaerobic – Al) were close to each other and formed cluster 2 with raw POME treated by Fe (raw-Fe). The last cluster includes anaerobic and anaerobic POME treated with Fe (cluster 3).

As a result, cluster analysis classified all five raw treatments into three groups. Cluster analysis revealed differences between the raw and even various treatments. This clustering demonstrates that the three treatment methods (anaerobic, $Al_2(SO_4)_3$, and $FeSO_4$ coagulation) effectively influence the raw POME (cluster 1). The results show that the treatment of raw effluent using $FeSO_4$ has a similar effect on the anaerobic effluent after being treated by $Al_2(SO_4)_3$ due to the higher potential of $FeSO_4$ in removing organics, as the initial concentration of organics in the raw effluent is higher than that in the anaerobic effluent. Moreover, Al has a higher efficiency in treating anaerobic effluent due to the higher organics in the raw effluents. This means that Al has a limited efficiency in treating effluent with higher organic content.

3.4. Factor analysis

To identify the cause of variation in data, a Varimax rotation with Kaiser Normalization (normalizing factor loadings before rotating them using the Varimax approach) was used on the gathered data for eleven variables acquired from the raw, anaerobic, raw-Fe, raw-Al, anaerobic-Fe, and anaerobic-Al effluents. The principal components approach was used to generate the factors using a correlation matrix of selected parameters. The factor analysis produced four factors with eight values greater than one that explained 99% of the overall variance and just 1% of the variation from other sources. Fig. 4 (Scree plot) shows the contribution of each extracted component based on the eigenvalues.

The four extracted factors are presented by Eqs. (4)–(7):

$$F_1 = -0.21\text{pH} - 0.26\text{EC} + 0.96\text{COD} + 0.74\text{color} + 0.91\text{TSS} - 0.01\text{NH}_3 + 0.98\text{BOD} + 0.45\text{Cu} + 0.10\text{Fe} + 0.21\text{Zn} - 0.20\text{pb} \tag{4}$$

$$F_2 = -0.08\text{pH} - 0.12\text{EC} + 0.17\text{COD} + 0.44\text{color} + 0.05\text{TSS} - 0.99\text{NH}_3^- + 0.17\text{BOD} + 0.87\text{Cu} + 0.98\text{Fe} + 0.96\text{Zn} - 0.26\text{pb} \tag{5}$$

$$F_3 = -0.97\text{pH} - 0.67\text{EC} + 0.17\text{COD} + 0.46\text{color} + 0.29\text{TSS} - 0.12\text{NH}_3 - 0.03\text{BOD} + 0.05\text{Cu} + 0.05\text{Fe} + 0.05\text{Zn} - 0.09\text{pb} \tag{6}$$

$$F_4 = -0.06\text{pH} - 0.68\text{EC} + 0.19\text{COD} + 0.10\text{color} + 0.28\text{TSS} - 0.7\text{NH}_3 - 0.06\text{BOD} + 0.11\text{Cu} + 0.16\text{Fe} + 0.15\text{Zn} - 0.93\text{pb} \tag{7}$$

The coefficient (loading) associated with each variable may be used to measure the contribution of each specified variable. For example, a value of 0.60 was chosen to represent a significant influence of the variable (a small coefficient (loading) associated with a variable means the variable

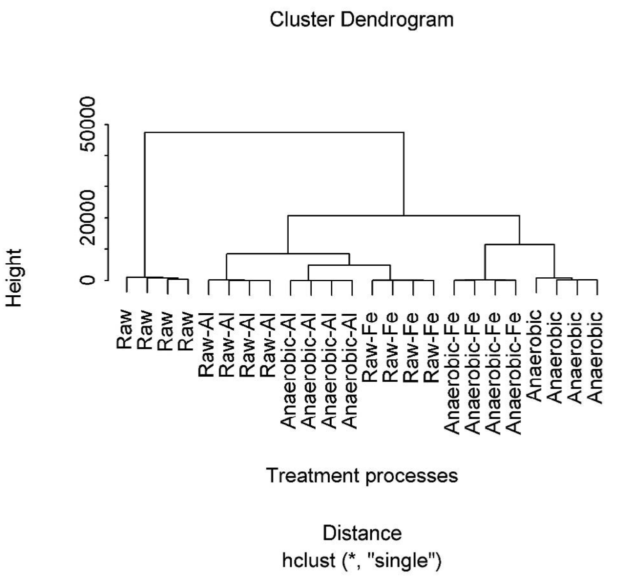

Fig. 3. Dendrogram for raw POME effluent, effluent after anaerobic digestion, raw and anaerobic POME treated by $Al_2(SO_4)_3$ and $FeSO_4$.

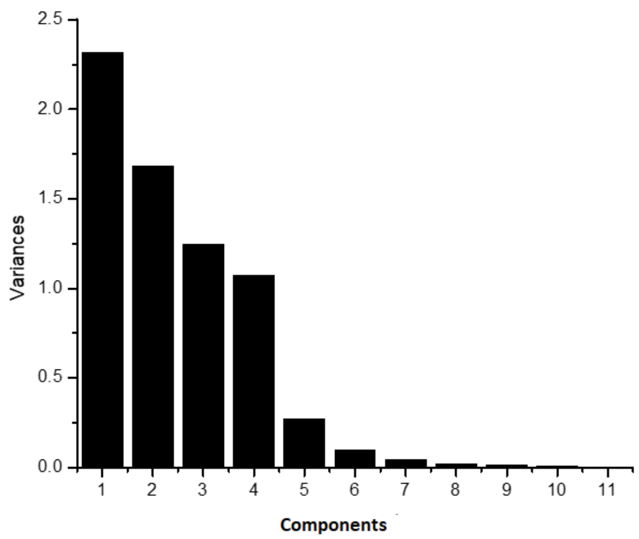

Fig. 4. Scree plot for the eigenvalues extracted from the chosen parameters in raw effluent, anaerobic effluent, raw-Fe effluent, raw-Al effluent, anaerobic-Fe effluent, and anaerobic-Al effluent.

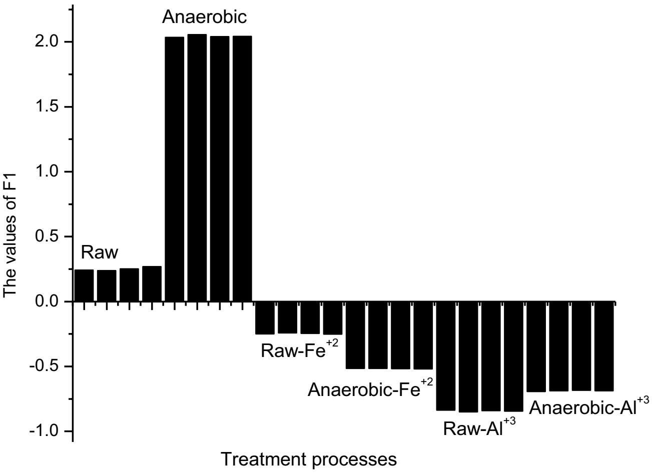

Fig. 5. The values of the first factor with different treatments.

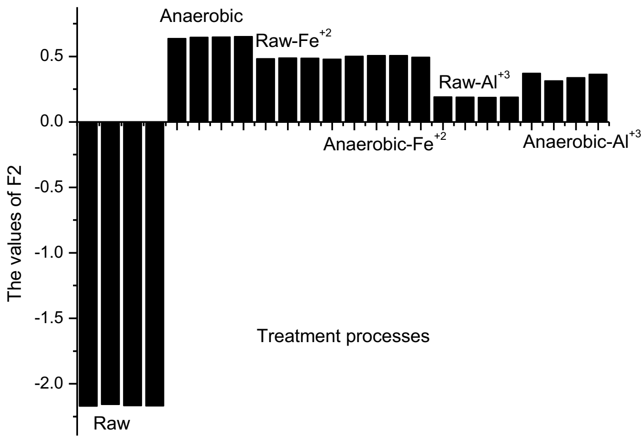

Fig. 6. The values of the second factor with different treatments.

does not contribute to this factor, and a large coefficient means the variable contributes to this factor). Five variables contributed significantly to the first factor (F1), including BOD, COD, TSS, N, and color, explaining roughly 36% of the total variation. In contrast, just four variables contributed significantly to F2 (NH_3–N, Fe, Zn, and Cu), explaining 34% of the total variance. Factors 3 and 4 accounted for 16% and 14% of the overall variation, respectively.

The link between various treatments, as well as the values of each component, was examined. The *y*-axis and *x*-axis reflect the values of the initial factor and alternative treatments, respectively (Fig. 5). The raw effluent is noticeably different from the other effluents after anaerobic and coagulation processes; the positive contribution was mostly due to the high impact of BOD_5, COD, TSS, and color, while the negative contribution was due to the low effect of BOD_5, COD, TSS, N, and color. This variance might be attributed to the significant impact of several treatment procedures (anaerobic, Fe, and Al coagulation) on the concentrations of organic matter, TSS, and nitrogen in the raw effluent. At the same time, their effects on heavy metals and other physiochemical parameters were not significant. Although the anaerobic digestion contributes a significant

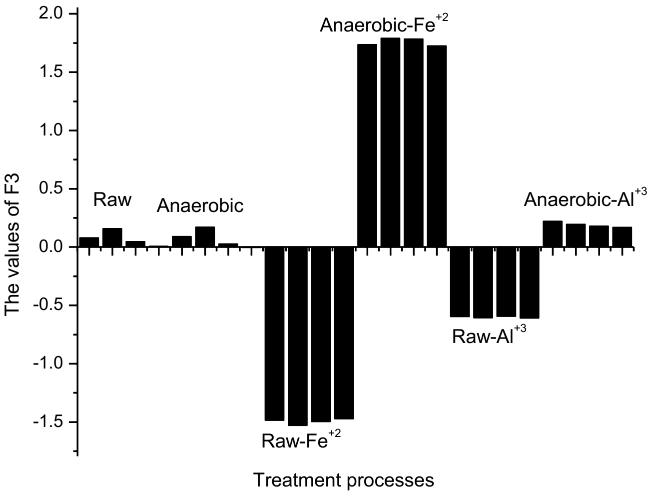

Fig. 7. The values of the third factor with different treatments.

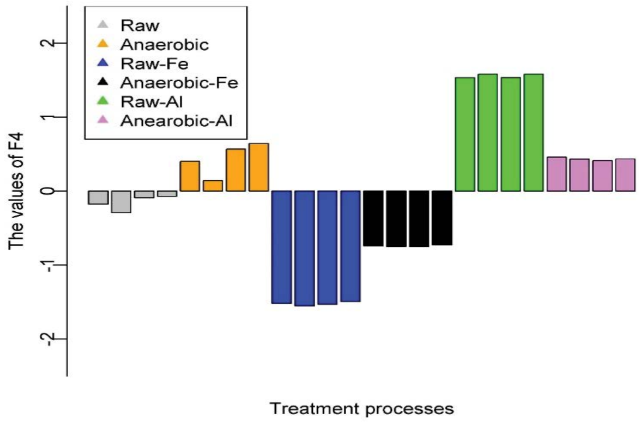

Fig. 8. The values of the fourth factor with different treatments.

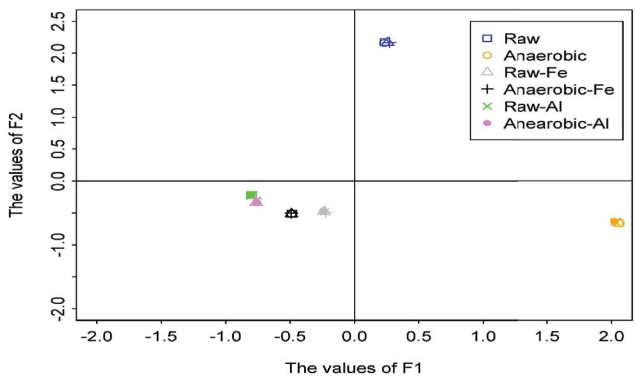

Fig. 9. The values of the first two factors.

reduction of these parameters from the raw POME, a significant reduction in the parameters was achieved using Fe and Al coagulations (Table 1).

The performance of anaerobic digestion and the coagulation processes for organic removal from POME was reported in several studies [6,15,16,42]. Fig. 6 depicts the values of the second component with various treatments. In the raw and anaerobic phases, NH_3–N, Fe, Zn, and Cu had a strong effect, but other treatments had a limited effect. Meanwhile, pH and EC had a strong influence on Factor 3 (Fig. 7), but pH, EC, and Pb dominated Factor 4 (Fig. 8). The anaerobic treatment stage raised the levels of ammonia and pH [38,43]. Fig. 9 depicts the values of the first two components, demonstrating that the first factor (*x*-axis) was responsible for distinguishing the raw treatment from others. In contrast, the second factor (*y*-axis) was responsible for the variance across differently-treated effluents. Although the effect of anaerobic treatment on raw effluent is present, the effect of both coagulants on raw and anaerobic effluents is also high.

4. Conclusion

Based on the above results, it can be concluded that multivariate techniques are important for analyzing environmental data involving several variables to extract hidden relationships and understand the actual behavior of the variables, including the relationships between them. The performance of the selected coagulants ($Al_2(SO_4)_3$ and $FeSO_4$) in the treatment of raw POME and anaerobically-treated POME was investigated and analyzed statistically based on the behavior of eleven parameters (COD, BOD_5, NH_3–N, TSS, pH, EC, Cu^{+2}, Fe^{+2}, Zn^{+2}, and Pb^{+}) before and after each coagulation process.

The selected effluents (raw effluent, anaerobic effluent, raw effluent after Al coagulation, raw effluent after Fe coagulation, anaerobic effluent after Al coagulation, and anaerobic effluent after Fe coagulation) exhibited different behaviors based on the selected parameters. Furthermore, FA identified four factors responsible for explaining the differences between the six effluents, which help control the source and take the right action for the treatments. Moreover, the main difference between the raw effluent and the other effluents was identified by Factor 1 (COD, color, TSS, and BOD). In contrast, the differences between different effluents were attributed to Factor 2 (NH, Cu, Fe, and Zn). Furthermore, cluster analysis showed a clear difference between different effluents, especially raw effluents. Overall, it can be concluded that multivariate methods could produce good results that guide the researcher to make intelligent decisions and quickly identify the source of the differences. The proposed method is considered a classical method that is cost-effective, as the treatment time would be shorter than the current conventional biological treatment.

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Declarations

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Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Availability of data and material

Not applicable

Code availability

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