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Research paper

Moringa Oleifera Dosage Clustering for Remediation Process of Batik Effluents Using Chemometric Technique

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Abstract

Batik has become one of the well-known industries because of the exclusive design and colours. The wastewater produced during the *Batik* production could contaminate the water bodies due to the contaminants present in the effluents. The need to remove the contaminants, in turn, calls for an efficient and effective *Batik* wastewater treatment prior to the disposal into the environment. The present study is purposely to determine the optimum *Moringa oleifera* dosage during the *Batik* effluents treatment process. The *Batik* effluent was treated using different *M. oleifera* seed powder dosages, swirled and allowed to settle down for 24 hours. The best dosage was determined by utilizing the cluster analysis (CA) and discriminant analysis (DA) on the observation data. The CA and DA verified that 2.5g and 5.0g are the optimum dosages to reduce the contaminants in the *Batik* wastewater. Additionally, both optimum dosages are the least dosage by which will also reduce the cost of *M. oleifera* used in the *Batik* wastewater treatment.

Keywords*: Moringa oleifera; Chemometric technique; Cluster analysis; Discriminant analysis.*

1. Introduction

Since past few decades, the water pollution cases keep on increasing corresponded to the increasing of human population, urbanization and industrialization activities [1]. Globally, the industrialists usually are a lack of awareness on environmental conservation as well as valuing their profit way better than the environment. The well-known organic pollutants produced from the textile industries such as azo compounds, derived from the whole processes occurring in producing one single design of textile which full of pattern and colors. In general, most of the industrialists in the textile sector avoid the effluent discharge treatment step in order to reduce the cost. The effluents are mostly discharged directly into the drain or river causing the water pollution occurrences. Water pollutants are renowned for being harmful to the aquatic organisms, which will lead to devastate the sustainability of the aquatic environment.

In textile industries, dyes are the most important component in producing a good quality of textile. They are the coloring agents which is organic substances will color the white clean fabric. The more complex structure of the textile dyes is more stable and highly non-biodegradable; therefore requires a more complex treatment to be applied. Besides that, there is a possibility in which the unreactive hydrolyzed dye is present in the dyebath, especially when the dye molecules have high tendency to react with the water molecules compared to the hydroxyl groups of the fiber cellulose. This implication occurs due to high water solubility or the brightness of dyes characteristics. Therefore the dyes need to be treated from the water bodies because of the changes they cause to the water column especially in the term of water coloration and chemical contents.

Generally, most of the textile industries discharged the polluted effluents into the river or water bodies surround. Water is known for its ability to flow and transfer the pollutants from a place to another in no time. Later it will spread out the polluted effluents to many places since the dyes are resistant to the temperature, detergents, chemicals, bleaching agent, light, water and soaps [2]. From one tone of produced dyes, approximately 2% of the dyes will be flushed into the wastewater, another 10% is lost because of some chemical reactions whereas the remaining is used to colour the fabric completely [3]. From the fact that water pollution caused by the dye effluents has raised concerns on the environmental sustainability, it is a necessity for the government to emphasize the textile industries to treat their wastewater before being flushed into the water bodies [4].

Recently, Malaysian *Batik* has gone global because of their exclusive pattern and colors. The high demand on Malaysian *Batik* led to the increasing of *Batik* production. This increment causes more dyes to be discharged into the water column surround. Terengganu and Kelantan state in Malaysia are *Batik* is produced through traditional methods in the rural areas; most of the produced wastewater is flushed into the nearest drains and eventually will be transferred into the rivers. This activity may cause major water pollution to the dyes and other pollutants present in the *Batik* effluents.

In Malaysia, the Malaysian Department (DOE) has constructed a permissible limit for the industrial effluents discharged under the Environmental Quality (Industrial Effluents) Regulations 2009. The Malaysian industrial effluents are allowed to reach below than the permissible limits prior discharging into the water bodies. There are two classes of standards namely Standard A and Standard B; as they differ based on the waste point source locations (DOE, 2010).

Several techniques that have been widely studied on their capability in reducing pollutants in the effluents which include the sedimentation, screening, aeration, filtration, flotation, degasification, chlorination, ozonation, neutralization, coagulation, adsorption, absorption and ion exchange. Most of the techniques used in removing the dyes will concentrate the dyes into a sludge or destruct the dye molecules completely [5]. However, even though the discovered techniques has the ability to reduce a high range of contaminants, the treatment is costly and time-consuming which makes most of the textile manufacturers neglect the necessity of having a water treatment plant in order to maintain their high profit. Besides that the techniques are not completely acceptable due to some of these techniques may produce secondary pollutants which are more harmful and toxic to the environment.

Coagulation process will occur when the external agents are added into the water bodies in order to destabilize the small particles present in the water and transform into bigger particles. The big and heavier particles will be settled down at the bottom of the tank. Basically, the particles present in the water system are negatively charged which will stabilize and produce an electrostatic repulsive force between those particles. Up until today, most of the countries have been practicing the similar method which is the conventional method by using aluminium sulphate and polymers as the coagulation and flocculation agents [6-7]. However, these chemical substances are not efficient enough in removing the dyes as it is costly and technically complicated mainly in the operational process. High level of aluminium could harm and toxic to the environment especially the plants [8].

M. oleifera; known as miracle tree, contains proteins (active agents) that allow the species to act as coagulant, flocculation, sedimentation or either antibiosis, in clarifying the turbidity of water [8-10]. It also resists to the heat, dryness and low quality of soil which may increase the efficiency of the biological adsorbent for the pollutants removal such as dyes, heavy metals and turbidity [11, 17]. *M. oleifera* is widely used as the water purification agent in Asia, Africa and Latin America. This new and Green Technology focuses on the application of natural sources in containing, accelerating and treating the polluted environment to eliminate the organic matter and nutrients present. Since most of the natural sources present in the ecosystem naturally, the application of the techniques is readily accepted by the public in most of the countries.

The condition optimization of the depigmentation process for the textile wastewater is required in order to obtain the best result of the dye removal percentages [3]. Many studies have been carried out to define the importance of the experimental design and its theoretical concept in the research field [13]. The best way to construct an experimental design is through the statistical methods. The chemometric approach or other statistical method has been used worldwide in many science-based studies and research; mainly in the analytical and environmental chemistry, as well as the engineering field [16]. This method uses an empirical statistical technique in order to perform a multiple regression analysis. The experimental design is normally carried out through the sequential experiments by using the quantitative data obtained to solve many equations of multivariate analysis, simultaneously.

The obtained experiment data set is commonly limited due to the laboratory and cost limitation. Therefore the main purpose of applying the experimental design is to reduce the limitations that are usually encountered during the conventional analytical techniques such as many variables need to be analyzed and manipulated in a shorter period of time. Besides that, the chemometric approach could decrease the experiment time development and lower the expenses needed in every experiment [3]. Furthermore, the application of statistical methods shows good results in many studies since the tools can explain more on the optimization process in conducting an experiment [13]. Nowadays, many researchers have widely utilized the statistical methods such as hierarchical agglomerative cluster analysis (HACA) and discriminant analysis (DA) due to their ability in optimizing the condition of a process [14]. In this study, the determination of the optimum *M. oleifera* dosage was performed using the cluster analysis (CA) and DA in response to obtain the maximum removal performance of the remediation process of *Batik* effluents.

2. Methodology

2.1. Sampling of Batik Industries Effluent

The *Batik* effluents were collected at a small scale *Batik* factory in Kampung Losong, Kuala Terengganu, Terengganu. The collected effluent samples were preserved and kept in an ice box in order to maintain its freshness before the remediation treatment is performed. The effluent samples were then transported back to the Environmental Forensic Laboratory at East Coast Environmental Research Institute (ESERI), Universiti Sultan Zainal Abidin (UniSZA) for further analysis.

2.2. M. Oleifera Fruits Collection

M. oleifera fruit samples were collected around Kuala Terengganu city since it can be found randomly all around the city. The dried and old *M. oleifera* fruits were chosen instead of the fresh *M. oleifera* because of the protein present, which will aid the coagulation and flocculation processes during the treatment process of *Batik* effluents. The collected *M. oleifera* pods were transported to Environmental Forensic Laboratory at ESERI, UniSZA.

2.3. Preparation of *M.* Oleifera Seed Powder

The collected *M. oleifera* dry pods were unshelled to obtain the seeds. Only qualified seeds were selected to be used as the coagulants in the waste water treatment process. The collected seeds were dried under 60ºC for 24 hours in the oven to ensure the seeds are completely dried.

The dried seeds were ground using the laboratory mill until it formed into a fine powder. The *M. oleifera* seed powder then was kept in an air-tight container and protected from direct light to avoid the oxidation and maintain the quality of the powder. The *M. oleifera* seeds powder were then be used as the coagulant and flocculants during the *Batik* effluents treatment.

2.4. Coagulation-Flocculation and Decolorization Process of Batik Effluents Using M. Oleifera

The treatment of the *Batik* effluents was carried out by adding a series of *M. oleifera* seed powder weight (2.5 g, 5.0 g, 7.5 g, 10.0 g, 12.5 g, 15.0 g, 17.5 g, 20.0 g, 25.0 g, 30.0 g, 35.0 g, 40.0 g, 45.0 g and 50.0 g) into 14 different container; filled with 1000 mL of *Batik* effluents each. The mixture *Batik* effluents and *M. oleifera* seed powder was vigorously mixed for 15 minutes and continued for 30 minutes with a slow mode-stirred at room temperature. After the swirling process, the containers were left to settle for 24 hours and the changes were observed. The observations were performed at each one hour, three hours, six hours, nine hours, 12 hours and 24 hours after the particles settlement.

2.5. Statistical Data Analysis

The statistical data analysis was carried out by using the percentage removal data obtained during the remediation process of *Batik* effluent, correspond to define the optimal conditions for the process to occur successfully. In this study, the statistical data analysis was performed using 2014 Addinsoft™ XLSTAT software Version 2014.5.03.

2.6. Hierarchical Agglomerative Cluster Analysis (HACA)

In the present study, HACA analysis was applied to determine the cluster for each of the parameters studied during the experiment. The obtained raw data set was normalized and tested against Ward's method in order to measure the homogeneity of the cluster based on the Euclidean distance. The results were illustrated through a dendogram obtained in the HACA. Based on the dendogram, the clusters were identified as the x-axis of the chart whiles the thread-lines as the y-axis. The distance between the clusters and thread-lines indicated the number of the clusters obtained from HACA. Parameters which have been classified in the same cluster have similarities in their removal performance on the *Batik* effluents. However, some of the raw data may provide a different number of clusters depending on the distance between the y-axis and x-axis compared to the number of clusters shown in the dendogram of the HACA, without losing any significant between each of the cluster. Therefore, HACA was able to point out the best dosage that can be obtained in performing the remediation of the *Batik* wastewater.

2.7. Discriminant Analysis (DA)

Discrimination in the different level of the removal performance of pollutant in *Batik* effluent using *M. oleifera* was carried out using DA [18-20]. The removal performance during the treatment process was classified as 'Excellent', 'Good', 'Moderate' and 'Poor' based on the clusters obtained in the HACA. DA was then applied to the original observations and the clusters to discriminate all groups. Based on the DA output, the canonical plot illustrates the discrimination between the variables perfectly. In the meantime, the Wilks' Lambda test discriminated the significant or insignificant groups at 95% confidence level (α = 0.05).

3. Results and Discussion

3.1. M. Oleifera Dosage on pH During the Remediation Process

Classification of the *M. oleifera* seed powder dosage was carried out using CA and the clusters obtained were justified using DA. As for the pH reduction, the dendogram and the canonical plot of the dosage are shown in Figure 1.

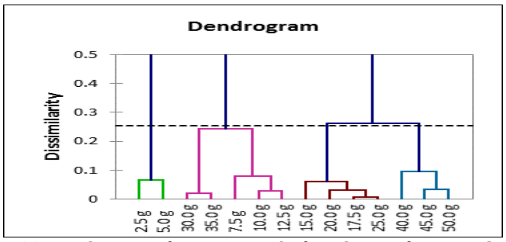

Fig. 1: (a) Dendogram of CA on *M. oleifera* dosage for pH reduction.

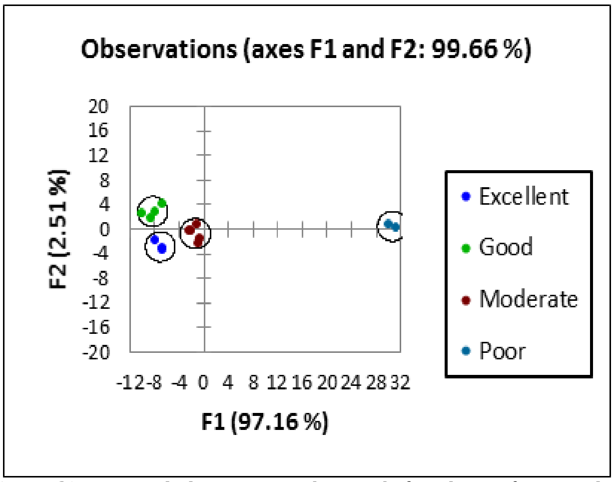

Fig. 1: (b) Canonical plot in DA on the *M. oleifera* dosage for pH reduction.

The dendogram in Figure 1(a) presents the classification performed on the *M. oleifera* dosage in the cluster analysis for the performance of pH reduction in the *Batik* effluents. The dosages of the *M. oleifera* were clustered into four groups significantly namely Cluster 1 (2.5g and 5.0g), Cluster 2 (7.5g, 10.0g, 12.5g, 30.0g and 35.0g), Cluster 3 (15.0g, 17.5g, 20.0g and 25.0g) and Cluster 4 (40.0g, 45.0g and 50.0g). The CA dendogram shows that the *M. oleifera* dosage of 2.5g and 5.0g has the least ability to reduce pH as well as the weakest removal performance. However, Cluster 2 and Cluster 3 have indicated the dosages in the clusters of the moderate and good removal performance respectively. In the meantime, the *M. oleifera* dosage of 40.0g, 45.0g and 50.0g in the Cluster 4 gave the excellent performance on the pH reduction in the *Batik* effluents.
The DA discrimination is presented in a canonical chart of DA as shown in Figure 1(b). The pH reduction performance in the *Batik* effluents showed that the excellent, good, moderate and poor groups were perfectly discriminated. The null hypothesis in the Wilk's Lambda test results shows that these four groups were significantly equal and the alternative hypothesis said it different. Hence, the result showed that the null hypothesis was rejected, meaning that the clustered groups were significantly different with p-value is less than 0.0001 (α = 0.05).

3.2. M. Oleifera Dosage on Chemical Oxygen Demand (COD) during the Remediation Process

As for the COD, the dendogram of the mass of *M. oleifera* classification obtained from the CA and the discriminant plot of the classes of DA can be shown in Figure 2.

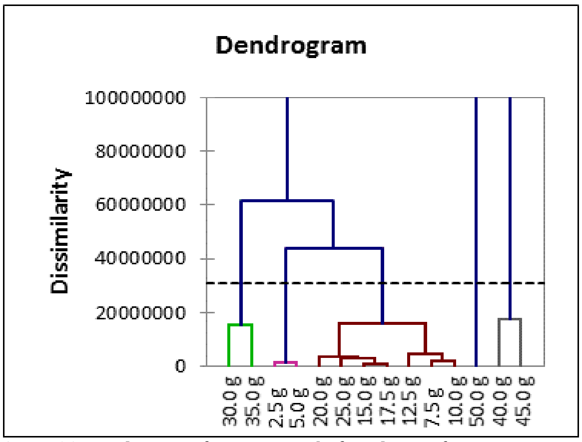

Fig. 2: (a) Dendogram of CA on *M. oleifera* dosage for COD removal

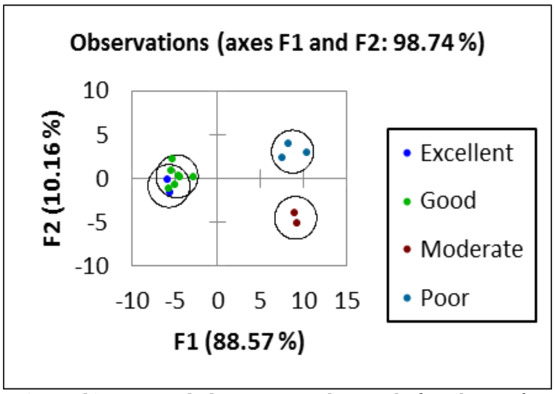

Fig. 2: (b) Canonical plot in DA on the *M. oleifera* dosage for COD removal

The cluster analysis dendogram for COD in Figure 2(a) shows that the 14 dosages of *M. oleifera* were clustered into four significant groups. They are Cluster 1 (2.5g and 5.0g), cluster 2 (7.5g, 10.0g, 12.5g, 15.0g, 17.5g, 20.0g and 25.0g), cluster 3 (30.0g and 35.0g) and cluster 4 (40.0g, 45.0g and 5.0g). Even though the dendogram shows that there were two different clusters of dosage 40.0g and 45.0g; and dosage 50.0g, it can be concluded that these three dosages of *M. oleifera* can be classified as one cluster due to a similar observation was found between those dosages. The four clusters obtained in the CA dendogram (Figure 2a) were classified as excellent, good, moderate and poor percentage removal of COD. The excellent cluster which consists of 2.5g and 5.0g was the best group to remove COD from *Batik* effluents which can be applied in next treatment.

The canonical plot of the DA (Figure 2b) shows 0.9874 possible relationships between F1 and F2. The plot also shows the best discrimination between the clusters as the excellent, good, moderate and poor groups. However, there was a slightly different between the excellent and good clusters which still can be discriminated. It was proven by the Wilk's Lambda test. The test proved that the null hypothesis has no significant different between all the four groups and the alternative hypothesis said otherwise. However, the result showed that the test has rejected the null hypothesis; hence concluded that the 4 clusters were significantly different between each other.

3.3. M. Oleifera Dosage on Total Suspended Solids (TSS) and Turbidity during the Remediation Process

The CA dendogram and DA canonical plot of the TSS and turbidity removal during the *Batik* wastewater treatment are shown in Figure 3.

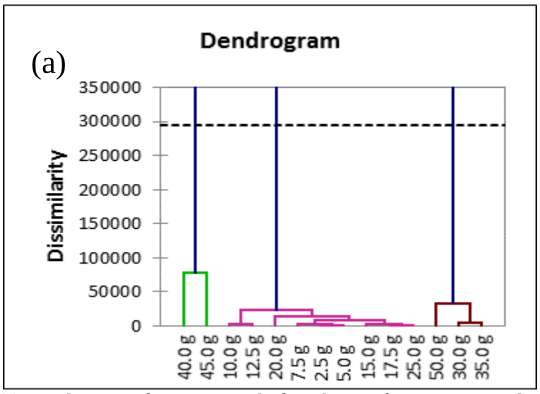

Fig. 3: (a) Dendogram of CA on *M. oleifera* dosage for TSS removal

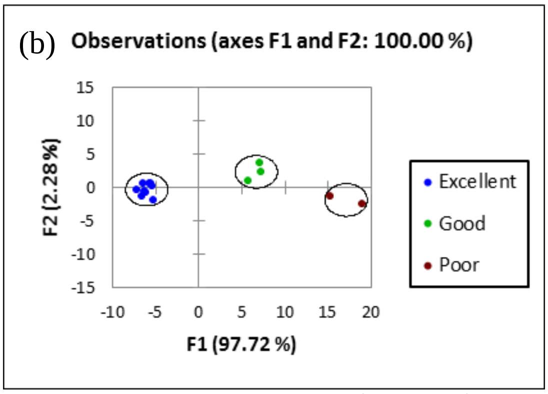

Fig. 3: (b) Canonical plot in DA on the *M. oleifera* dosage for TSS removal

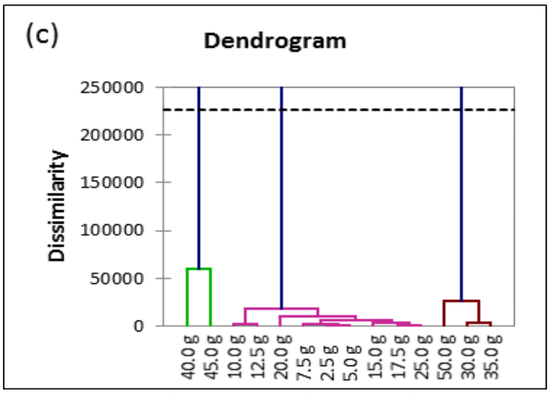

Fig. 3: (c) Dendogram of CA on *M. oleifera* dosage for turbidity reduction

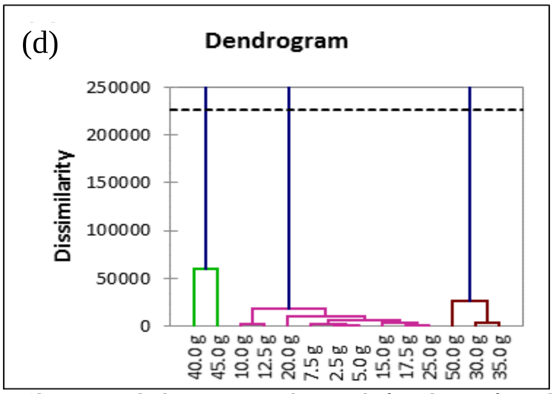

Fig. 3: (d) Canonical plot in DA on the *M. oleifera* dosage for turbidity reduction

Figure 3(a) and Figure 3(c) show that the dosages of the *M. oleifera* for the TSS and turbidity reduction were clustered in three significantly different groups. They are Cluster 1 (2.5g, 5.0g, 7.5g, 10.0g, 12.5g, 15.0g, 17.5g, 20.0g and 25.0g), cluster 2 (30.0g, 35.0g and 50.0g) and cluster 3 (40.0g and 45.0g) which indicate

the excellent, good and poor removal performance of TSS in *Batik* effluents, respectively. Both CA dendograms indicated the most efficient dosages for the TSS and turbidity removal are 2.5g and 5.0g. Therefore, these dosages can be used in the treatment procedure in the future.
The DA canonical plots (Figure 3b and Figure 3d) show three significant groups of TSS and turbidity removal performance. Additionally, the Wilks' Lambda proved that the three clusters formed for both parameters were significantly different as the null hypothesis was rejected, which described the mean vectors of the three groups are equal. The alternative hypothesis, however, mentions that the mean vectors of the group were significantly different with the α-value of 0.05 and the p-value is less than 0.0001.

4. Conclusion

The present study reclassified and discriminated 14 dosages of *M. oleifera* used in the *Batik* effluents treatment after being left for 24 hours. The CA shows that the dosage of the *M. oleifera* can be classified as Excellent, Good, Moderate or Poor. The Wilks' Lambda test has verified that each group is significantly different to the other groups as the p-value is less than 0.05. The present study concluded that the best dosages of *M. oleifera* for the *Batik* effluent treatment process are 2.5g and 5.0g. These dosages are the least amount which proved that the remediation process in treating *Batik* effluent needs a very small amount of *M. oleifera* seed powder.

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