Modelling of Chitosan-Treating Palm Oil Effluent (POME) by Artificial Neural Network (ANN)

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Abstract: ***A chitosan-treating Palm Oil Mill Effluent (POME), anaerobic wastewater from anaerobic pond was modelled by artificial neural network (ANN). The ANN model was developed to simulate the coagulation and flocculation of POME with varying parameters including coagulant and flocculant's dosage, pH, speed, and time of rapid mixing. The model's predictive ability for the COD, TSS, and TDS from POME were investigated. Nineteen experiments were carried out, involving the collection of experimental data and tabulation of all the variables and responses. The prediction using ANN showed that for chitosan coagulation, the maximum percentage removal of COD (48.5%), TSS (88.5%), and TDS (34.9%) was obtained with coagulant dosage of 10mg/L, flocculant dosage of 8mg/L, pH 6, rapid mixing speed 293rpm, and rapid mixing time 30s.***

Keywords: chitosan, coagulation, flocculation, artificial neural network (ANN), palm oil mill effluent (POME).

1. Introduction

Palm oil industry has become a significant agriculture based-industry in Malaysia due to its rapid development. The high production of crude palm oil results in large amount of palm oil mill effluent (POME). It is estimated that 5-7.5 tonnes of water are required in the production of 1 tonne of crude palm oil and half of the water will end up as POME [1].Thus large amounts of POME from palm oil mills industry can have adverse environmental impacts if it is not treated properly prior to discharge to the environments.

POME is a colloidal suspension formed from the mixture of a sterilizer condensate, separator sludge and hydrocyclone wastewater which consists of 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids [2]. Fresh POME is brownish in colour. POME which is high in temperature (80-90°C) has a very high biological oxygen demand (BOD) as well [3]. The effluent contains organic acids in complex forms which can be used as carbon source and causes the effluent to be acidic with a pH around 4.5 [4].

POME contains a high content of degradable organic matter due to the presence of unrecovered palm oil. Depletion of oxygen and other effects can occur due to discharge of this highly polluting effluent into the waterways [1]. Oxygen depletion occurs when the dissolved oxygen in waterways are taken up by microorganisms for the oxidation of organic matters that present in POME. The standards for POME discharges into the watercourses was proposed and legalized by Malaysian Government in 1977 [5]. Since then, POME from palm oil mills need to be treated before being discharged into the waterways. The number of palm oil mills in Malaysia has increased from about 10 mills in 1960 to 423 mills in 2011[6].The production of such a large amount of crude palm oil results in even a large amount of palm oil mill effluent (POME) being produced when lots of water are being used during the extraction of crude palm oil from fresh fruit bunch [1], [3]. It has been reported that at least 44 million tonnes of POME being generated in Malaysia in 2008 alone and the figure is expected to increase every year with the increasing production of crude palm oil [3]. Realizing the dramatic increase of crude palm oil production followed by the generation of highly polluting POME, it is crucial therefore to treat POME prior to discharge into the receiving river in a proper manner besides a stringent standard limit imposed by The Malaysian Department of Environment for effluent discharged [1].

Due to more stringent regulations, many studies have been conducted in the field of POME treatment and various treatment systems have been developed in order to treat POME to an acceptable level before it is discharged into the receiving rivers. The most common and conventional treatment method applied by most of the palm oil mills for POME is ponding system. The organic contents in the effluent are progressively degraded in this system consists of a series of de-oiling tank, acidification, anaerobic and facultative ponds. However, this conventional method requires long retention time and large land area. Therefore, physiochemical treatment which includes sedimentation and centrifugation, coagulation and flocculation, flotation and adsorption has been developed to improve the POME treatment process.

In this study, coagulation and flocculation method had been applied in the treatment of palm oil mill effluent. A coagulant which is chitosan with the aid of flocculant had been used to investigate their effectiveness in treating POME. Based on the percentage removal of chemical oxygen demand (COD), total suspended solids (TSS) and total dissolved solids (TDS), the use of chitosan in the coagulation process gives a higher percentage removal. An artificial neural network (ANN) model was developed to simulate the coagulation and flocculation of POME with varying parameters such as dosage of coagulant and flocculant, pH, speed and time of rapid mixing. The predictive ability of ANN model for the COD, TSS and TDS from POME were investigated. Sample used during experiment were collected from a FELDA Palm Industries Sdn. Bhd mill, Serting Hilir Palm Oil Mill, which is located at Bandar Seri Jempol, Negeri Sembilan The efficiency of coagulation and flocculation was assessed based on the removal of chemical oxygen demand (COD), total suspended solids (TSS) and total dissolved solids (TDS).

2. Materials and Methods

2.1 Experimental Procedures Set-up (Jar Test)

Coagulation and flocculation of POME was carried out using the jar test apparatus (VelpScientifica JLT 6). A series of six beakers were filled with 500ml of POME respectively for each test run. The initial pH of each sample was measured using pH meter and adjusted to the desired initial pH (pH 2, pH 7 and pH 9) by adding 5M of H_2SO_4 or 5M of NaOH. Coagulation and flocculation tests were performed using dosage of coagulant (1mg/L, 5mg/L and 10mg/L) and dosage of flocculant (1mg/L, 20mg/L and 40mg/L). After the desired dosage of coagulant was added, the POME samples were agitated at desired rapid mixing speed (250rpm and 300rpm) and rapid mixing time (30s and 180s). The slow mix (50rpm and 20min) operation was then applied, flocculant was added according to the desired dosage. This is followed by final settling of 2 hours. At the end of sedimentation process, supernatants are pipetted out for COD, TS and TSS analysis.

2.2 Preparation of Chitosan

Analytical grade of chitosan ($C_{12}H_{24}N_2O_9$) was obtained from Sigma Aldrich. Chitosan is used as a coagulant in this study. To prepare the coagulant to be used in the experiments, 1.5g of chitosan was dissolved in 150ml of 0.1M HCl(R&M Chemicals). The solution was stirred using a magnetic stirrer until the chitosan was completely dissolved in HCl. An amount of 150ml of distilled was added into the solution. The solution was prepared fresh before each set of experiments to prevent microbial decomposition of organic compounds in chitosan during storage.

2.3 Sample Preservation

The POME was preserved at a temperature less than 4 ^{0}C, but above the freezing point in order to prevent the wastewater from undergoing biodegradation due to microbial action [7]

2.4 Characteristics of Palm Oil Mill Effluent (POME)

The raw POME was collected from the anaerobic pond of Serting Hilir Palm Oil Mill, Serting, Negeri Sembilan, Malaysia; its characteristic is presented in Table 1.

Table 1: Characteristics of POME

*Parameter**	*Mean*	*Range*
pH	4.2	3.4-5.2
Biochemical Oxygen Demand (BOD)	25,000	10,250-43,750
Chemical Oxygen Demand (COD)	51,000	15,000-100,000
Total Solids	40,000	11,500-79,000
Suspended Solids	18,000	5000-54,000
Volatile Solids	34,000	9000-72,000
Oil and Grease	6000	130-18,000
Ammoniacal Nitrogen	35	4-80
Total Nitrogen	750	180-1400

*Units in mg/l except pH

2.5 Analytical Methods

The COD, TSS and TDS of samples are measured based on APHA Standard Methods for the Examination of Water and Wastewater [8]. All experiments were duplicated.

2.6 Neural Network Optimisation

A software package of NeuralPower version 2.5 was applied in the ANN studies. The experiments were carried out with dosage of coagulants, dosage of flocculant, rapid mixing speed, rapid mixing time and pH of samples as variables. The experimental response or output variable were measured as the percentage removal of COD, TSS and TDS. The procedures of developing ANN architecture is shown in Figure 1.

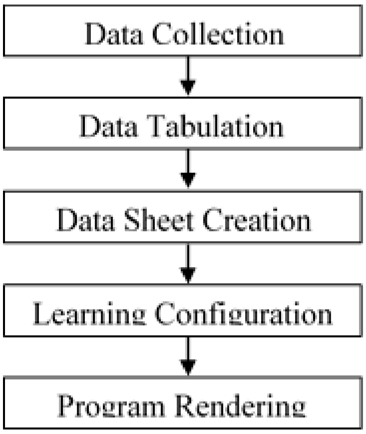

Figure 1: Flow chart of developing ANN architecture

In this study, 19 experiments were carried out. Data collection and tabulation involved the collection of experimental data and tabulation of all the variables and response. During the learning stage, trial and error method was used to obtain the suitable parameter such as number of node and transfer function which gives the highest regression correlation coefficient (R^2).

The number of iterations was set to 1000 as concluded in Table 2. Other parameters for network were chosen as the default values of the software (learning rate = 0.8 and momentum = 0.8). The optimum number of hidden nodes was determined by trial and error method using different number of nodes. The performances of the network were measured by correlation coefficient R^2 which was used as the error function. $R^2$was calculated according to the following equation:

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y}_i)^2} \quad (1)$$

Where y_i = experimental y values

$\hat{y}_i$ = predicted values

$\bar{y}_i$ = mean of y_i

i = number of inputs

The model with the highest R^2 was selected. A second set of data that contained six individual data records (3 individual

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data records for each coagulant) was taken out to evaluate the predictability of the network.

Table 2: Training Parameters of Model using NeuralPower v2.5

Coagulant	*Chitosan*
Learning algorithm	QuickProp
Connection type	Multilayer normal feed forward
Number of hidden layer	1
Number of nodes in hidden layer	6
Transfer function of hidden layer	Tanh
Transfer function of output layer	Tanh
Learning rate	0.8
Momentum	0.8
Iterations	1000
Root Mean Square Error (RMSE)	0.01

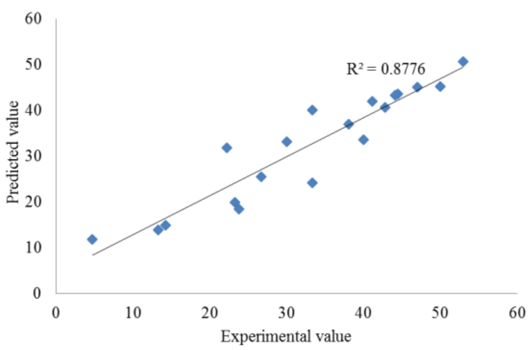
3. Results and Discussion

In this study, experiment works were carried out to investigate the effect of various parameters i.e. types of coagulant, dosage of coagulant and flocculant, speed and time of rapid mixing and the pH of raw POME on the coagulation and flocculation of POME. Nineteen experiments were carried out for coagulant and the efficiencies of coagulation and flocculation process were assessed based on the percentage removal of COD, TSS and TDS from POME.

The results showed that the ANN model was able to predict the experimental results well. The prediction using ANN showed that the maximum percentage removal of COD (48.5%), TSS (88.5%) and TDS (34.9%) was obtained with dosage of coagulant 1000mg/L, dosage of flocculant 8mg/L, pH 6, rapid mixing speed 293rpm and rapid mixing time 30s.

3.1 Evaluation of Experimental Results with ANN

Regression correlation coefficient R^2 was obtained after the plots of predicted values versus experimental to evaluate the predictability of ANN model. The R^2 obtained from the plots of the other two parameters (TSS and TDS) were tabulated in Table 3. From both figures and Table 3, it can be observed that R^2 obtained for all parameters were more than 0.8 which showed good fitness of response models. Besides that, the R^2 obtained from the plots of test data were more than 0.95 for all parameters of both coagulants indicated that ANN was able to predict the percentage removal of COD, TSS and TDS.



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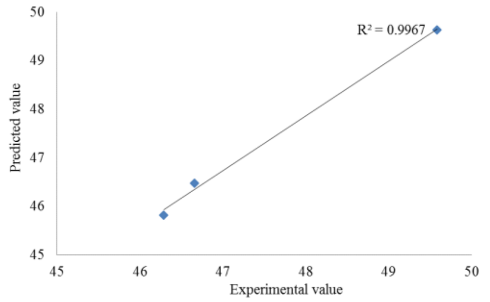

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Figure 2: Goodness-of-fits plots for ANN model developed for coagulation and flocculation process using chitosan. Experimental data (A) and test data (B) for percentage removal of COD.

Table 3: Regression correlation coefficient, R^2 obtained from the plots of actual versus predicted TSS and TDS removal and also test data for coagulants.

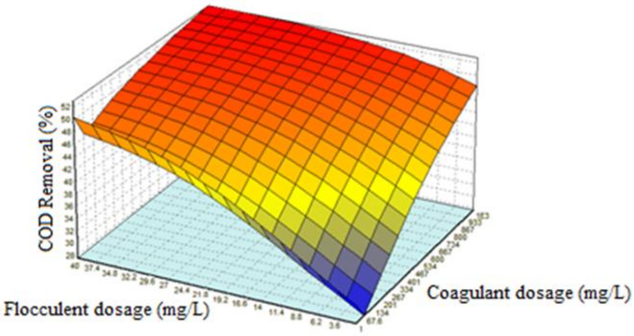
Types of coagulant	*Plots of actual versus predicted plot, R^2*		*Plots of test data, R^2*	
	TSS	TDS	TSS	TDS
Chitosan	0.8612	0.8856	0.9949	0.9835

3.2 Effect of Dosage of Coagulant

Figure 3 shows the influence of the dosage of chitosan on the percentage removal of COD, TSS and TDS from POME. From the figure, it can be seen that the percentage removal of COD, TSS and TDS increase with the increase in the dosage of chitosan. Figures 3 also show that the increase of dosage for chitosan lead to better coagulation performance, the use of chitosan at the same applied dosage as inorganic coagulant records a higher reduction of parameters. This can be explained based on charge density. Chitosan has a characteristic of high cationic charge density compare to other coagulants [8]. Chitosan poses strong charge neutralization ability due to the fast adsorption that comes from its large positive charge [9] which can lead to rapid destabilization of particle. Besides that, in acidic solution (chitosan was added to 0.1M HCl) the amine group of chitosan is protonated. An increase in the number of charged group can bind to larger number of negatively charged organic particles in POME. Those particles are destabilized to form larger and denser flocs for rapid settling.

3.3 Effect of Dosage of Flocculant

The addition of flocculant which act as a coagulant aid helps in the removal of fine colloidal particles. It can be observed from both figures that the increase in the dosage of flocculant was able to increase the percentage removal of COD, TSS and TDS from POME. This was due to an increase in flocculant dosage leads to an increase in the stability of flocs [10]. The strength of flocs depended on the attractive forces between component particles. Inter-particle bridging was formed by the addition of flocculant. Thus, a higher dosage of flocculant can create stronger bridges between flocs so that larger and denser flocs which settle rapidly can be formed. From Figures 3, it can be seen that the addition of flocculant into the coagulation process has a more effect on the removal of COD, TSS and TDS.



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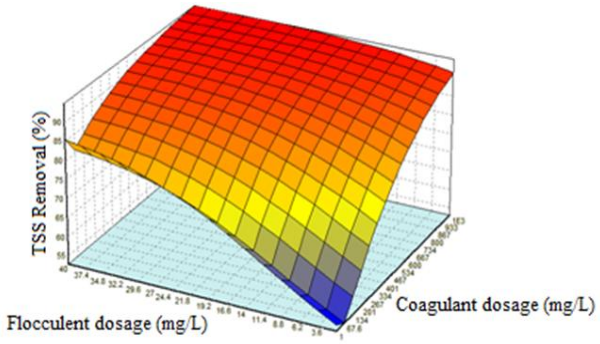

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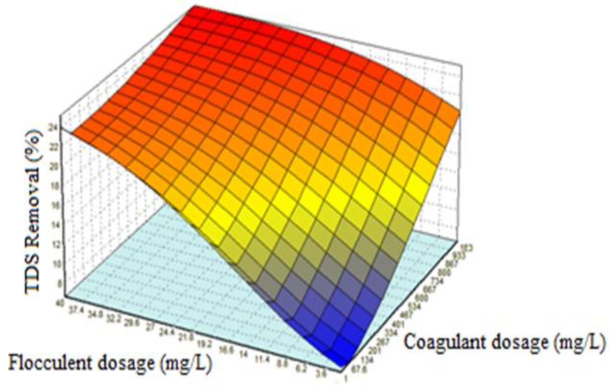


(C)

Figure 3: The effect of dosage of chitosan and dosage of flocculant on the percentage removal of COD (A), TSS (B), TDS (C) (pH=5.5, rapid mixing speed=275rpm and rapid mixing time=105s).

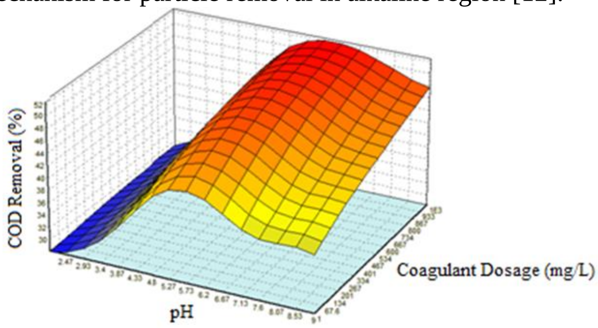
3.4 Effect of pH

The effect of pH on coagulation and flocculation process was studied by adjustment of the pH of raw POME samples to 2, 7 and 9 using dilute H_2SO_4 and NaOH solution. Figure 4 represents the effect of pH and interaction effects with dosage of coagulant (chitosan) with the value of dosage of flocculant, speed and time of rapid mixing were constant at 20.5mg/L, 275rpm and 105s respectively. It can be observed that chitosan demonstrated the best percentage removal of COD, TSS and TDS in slightly acidic condition (pH 6) while portrays poorer removal efficiencies in strongly acidic and alkaline condition. This phenomenon can be explained based on the behaviour of the functional amino group of chitosan that strongly influenced by pH. The equilibrium reaction for amino group was shown in Equation 2.

$$-NH_3^+ + H_2O \leftrightarrow -NH_2 + H_3O^+ \qquad (2)$$

In strongly acidic condition, the concentration of H^+ ion was high and cause the reaction to shift to the left to form protonated chitosan. The presence of protonated chitosan was favour for the removal of anionic organic particles but excess protonated chitosan in strong acidic condition is believed to create more possibility for particles re-stabilization due to surface charge reversal. Besides that, chitosan is very soluble and incapable of producing flocs at very low pH value [11]. Thus the percentage removal of COD, TSS and TDS were low in strongly acidic condition (low pH value). Charge neutralization will be the only mechanism for POME destabilisation at low pH.

From Figure 4, it can be seen that pH 6 provides the optimum removals compared to other pH. This is because at optimum pH (i.e. pH 6), the coagulation of POME by chitosan was brought by the combination of charge neutralization and polymer bridging mechanism. Polymer bridging mechanism became significant as pH increased. Thus, chitosan can itself acts as a coagulant aid for particle entrapment (flocculating effect) when the positive charges on its surface decreased in slightly acidic condition. On the contrary, the removal efficiencies of chitosan decreased in alkaline condition. The positive charge on chitosan surface reduced significantly as pH increased to alkaline region caused the charge neutralization of chitosan to destabilize the particles became insignificant. Bridging mechanism which is not strong enough to efficiently destabilize the particles will be the only mechanism for particle removal in alkaline region [12].



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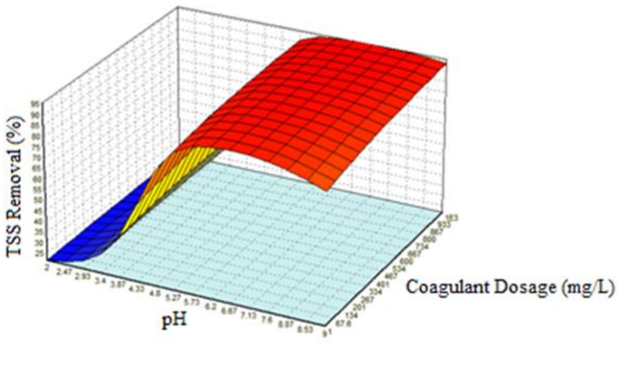

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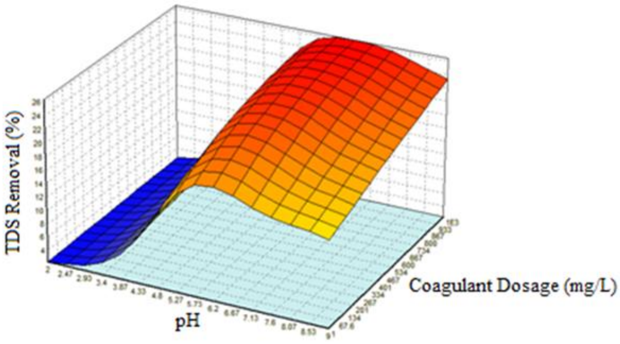

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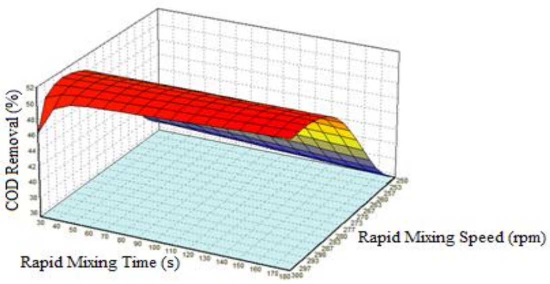
Figure 4: The effect of pH and dosage of chitosan on the percentage removal of COD (A), TSS (B), TDS (C) (dosage of flocculant=20.5mg/L, rapid mixing speed=275rpm and rapid mixing time=105s).

3.5 Effect of Rapid Mixing Speed

Rapid mixing speed is crucial in the coagulation of colloidal particle in POME as it controls the number of particle collision which can impact the degree of flocculation [10]. Figures 5 demonstrate the effect of rapid mixing speed on the percentage removal of COD, TSS and TDS in coagulation process using chitosan respectively. The value of dosage of coagulant, dosage of flocculant and pH were constant at 500.5mg/L, 20.5mg/L and 5.5 respectively. Figure show that at longer mixing time, the rapid mixing speed increased the percentage removal of COD, TSS and TDS until a critical point is reached. This phenomenon was due to an increase in rapid mixing speed increased the number of particle collision and attachment which then cause more particle to aggregate and form larger flocs. Besides that, denser flocs with higher settling velocity can be produced by increasing the rapid mixing speed. Density of flocs decrease as flocs grow, by increasing the rapid mixing speed was able to increase the shear stress applied on flocs and lead to formation of more compact and denser flocs [10]. However, when the rapid mixing speed was increased further beyond the critical point, the percentage removal of COD, TSS and TDS decreased. This is caused by restabilization of particles occurred at fast mixing speed [13]. High mixing speed tends to break up the flocs which cannot withstand the high shear stress and cause the aggregated flocs to be dispersed and reintroduced into the medium [14] Based on Figures 5, it can be observed that, decrease in the percentage removal of COD, TSS and TDS beyond the critical point is not significant. This may be due to the high strength flocs which were formed by chitosan coagulation can withstand the shear stress induced by fast mixing speed. Thus they are not easily break up under high mixing speed.



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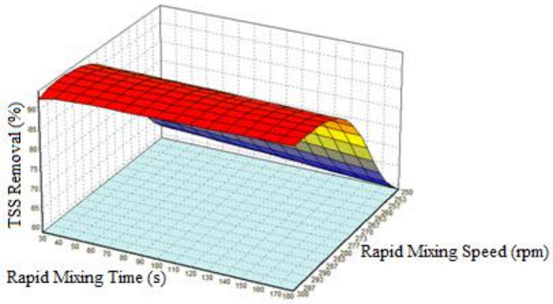

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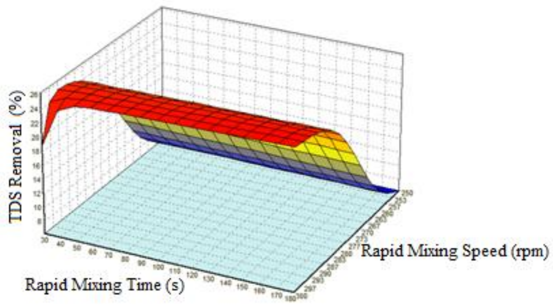

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Figure 5: The effect of rapid mixing time and rapid mixing speed on the percentage removal of COD (A), TSS (B), TDS (C) (dosage of chitosan=500.5mg/L, dosage of flocculant=20.5mg/L and pH=5.5).

3.6 Optimisation of Process Optimisation

The ANN model was optimized by deterministic methods with known parameters i.e. dosage of coagulant, dosage of flocculant, pH, rapid mixing speed and rapid mixing time to obtain an optimal operating condition. The optimal operating condition for chitosan coagulation was tabulated in Table 4.1. It can be observed that the maximum percentage removal of COD for chitosan coagulation, the maximum percentage removal of COD (48.5%), TSS (88.5%) and TDS (34.9%) was obtained with dosage of coagulant 1000mg/L, dosage of flocculant 8mg/L, pH 6, rapid mixing speed 293rpm and rapid mixing time 30s.

Table 4: Optimization Results of Operation Efficiency Related to COD, TSS, and TDS Removal

Type of Coagulant	*Chitosan*
Dosage of Coagulant (mg/L)	1000
Dosage of Flocculant (mg/L)	8
pH	6
Rapid Mixing Speed (rpm)	293
Rapid Mixing Time (s)	30
COD Removal (%)	48.5
TSS Removal (%)	88.5
TDS Removal (%)	34.9

4. Conclusion

The efficiencies of coagulation and flocculation process used in the treatment of palm oil mill effluent (POME) were investigated and were assessed based on the percentage removal of COD, TSS and TDS from POME. The use of chitosan revealed that chitosan performed better than inorganic coagulant for POME coagulation, in terms of effluent quality. Developed artificial neural network (ANN) models for coagulants was used to predict the effect of various parameters i.e. dosage of coagulant, dosage of flocculant, pH, speed and time of rapid mixing on the percentage removal of COD, TSS and TDS from POME. The developed models showed a high degree of predictive ability on experimental data. The prediction using ANN for chitosan as coagulant shows that maximum percentage removal of COD 48.5%), TSS (88.5%) and TDS (34.9%) could be achieved.

5. Recommendations

For future studies, it is recommended experiments on other types of natural coagulants be carried out to replace the chemical coagulants as natural coagulants are environmental friendly and create health risk free waste. Different natural coagulants will bring different effectiveness to the coagulation process. Thus it is advisable to perform a study to determine more effective natural coagulants. A wider range of parameters can be included in future research as various parameters might play an important role in determining the effectiveness of coagulation and flocculation of POME.

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