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Application of response surface methodology to optimize coagulation–flocculation treatment of anaerobically digested palm oil mill effluent using alum

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ABSTRACT

The purpose of this research was to investigate further treatment of anaerobically treated palm oil mill effluent (POME) via optimized coagulation–flocculation process. Alum, as a metal salt coagulant was used in the process. Most favourable values of pH, alum dosage, and slow mixing time were obtained using the central composite design and response surface methodology (RSM). Results show the regression, linear, interaction, and quadratic terms are significant and the model is considered to be adequate in terms of reproducibility. The quadratic model was significance to give less than 0.05 of probability of error (p). Also, the values of the correlation coefficient (R^2), adequate precision (AP), and coefficient of variance (CV) was found to be 0.962, 15.726 and 7.31, respectively. After operating of coagulation process in optimum condition (pH = 6.4, alum dosage = 2124 mg/L, and slow mixing = 20 min.) the chemical oxygen demand (COD) reduced by 59%. This indicates that the application of optimized coagulation–flocculation process decreases the COD concentrations level less than the POME discharge limits enforced by Department of Environment.

Keywords: Palm oil mill effluent; Coagulation; COD; Alum; RSM

1. Introduction

Despite the abundant applications of biological treatment for removal of palm oil mill effluent (POME), such exertions are hampered by the constraints of its long hydraulic retention time (often in excess of 20 days), necessity of large digesters and plant size, sensitivity of microorganisms to the environmental alteration, and vast emission of corrosive biogas (methane, carbon dioxide, and trace amounts of hydrogen sulphide) [1,2]. In addition, many important pollutants may be found biodegradable under laboratory conditions. However, biodegradation under field conditions is a different matter. It is often observed that metabolic rates are much slower in the field for many reasons [3]. Environmental conditions such as temperature, pH, and oxygen may not be optimal. Microbial cultures isolated in the laboratory may not thrive or even survive in competition with the vast population of microbes that naturally occur in the field. Anaerobic digestion is one of the most common methods to treat highly concentrated POME. But, this process alone could hardly produce effluents to a

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level complying with discharge limits [4]. The reported results shown in Table 1 indicate that the anaerobically treated POME still contains high chemical oxygen demand (COD), biochemical oxygen demand (BOD), and solids concentrations.

Coagulation–flocculation is widely used for wastewater treatment, as it is cost effective, efficient, easy to operate, and energy-saving treatment alternative. Successful applications of coagulation–flocculation process have been reported for treatment of different discharges such as resin manufacturing wastewater [9] textile wastewater [10], municipal secondary effluents [11], olive mill effluents [12], combined wastewater [13] as well as slaughterhouse wastewater [14]. Among the available coagulants, aluminium sulphate (alum) is one of the most widely used coagulants due to its effectiveness, relatively low cost, and availability. Alum destabilizes oil droplets of POME and destroys emulsions. Different mechanisms are involved in a coagulation process, including ionic layer compression, adsorption and charge neutralization, inter-particle bridging, and sweep coagulation [15]. These mechanisms are important in forming of flocs of residue oil and suspended solid in POME which could be settled and finally removed. In addition, in coagulation–flocculation process, other factors can influence the efficiencies of process, such as the dosage of coagulant/flocculant, pH, mixing speed and time, temperature, and retention time. The optimization of these factors may increase the process efficiency [10]. Response surface methodology (RSM) is powerful tool to determine the influences of individual factors and also their interactive manipulates [16]. RSM is a statistical technique for designing experiments, building models, evaluating the effects of various factors and searching optimum conditions for desirable responses. With RSM, the interactions of possible influencing parameters on treatment efficiency can be evaluated with a minimum number of planned experiments without the need for studying all possible combinations of the parameters.

Table 1
Characteristic of typical anaerobically digested POME

Parameters[a]	[5]	[6]	[7]	[8]
pH	7.4	7.1	7.24	7.8
BOD	1,355	655	1938	–
COD	13,650	5,430	20,314	1,372
TS	19,370	8,300	20,889	–
TSS	12,750	3,100	14,686	512
TN	320	–	–	134

[a] All parameters in mg/L except pH.

In this study central composite design (CCD) and RSM were used to design the experiments, build models and determine the optimum conditions to treat anaerobically digested POME using coagulation-flocculation process. The statistical design was based on three factors (pH, coagulant dosage, and slow mixing) and COD removal efficiency as response.

2. Materials and methods

2.1. Anaerobically treated POME preparation and characterization

Effluent from the anaerobic pond system treating, a local POME was used for this study. After collection, the samples were transported to the laboratory and placed in a cool storage at 4℃ to stop any microbiological activity and to avoid any composition changes. The pH was not adjusted and no chemicals were added to the wastewater. The required volume was thawed to room temperature (28 ± 2℃) before performing coagulation–flocculation experiment. The pH of the wastewater sample was determined using HACH pH meter (Sension 4, USA). COD was measured using HACH spectrophotometer (DR 2800, USA). BOD_3 was analyzed on samples incubated for three days at 27℃ [17]. The initial and final dissolved oxygen (DO) were measured using a DO meter (YSI 5000, USA). TSS were determined by filtering 50 mL of the wastewater sample through a 47 mm filter disk and the residue retained on the filter was dried in a drying oven at 105℃ for one h. TKN (Total Kjeldahl Nitrogen) was found through colorimetric method using HACH spectrophotometer (DR 2000, USA). TOC of the wastewater was analyzed using a total organic carbon analyser (1020A, USA) in accordance with the Standard Methods for the Examination of Water and Wastewater [18]. Turbidity of the wastewater sample was determined in NTU (nephelometric

Table 2
Characteristics of anaerobically treated POME

Parameter	Range[a]
Temperature (℃)	29 ± 4
pH	8.63 ± 0.008
COD (mg/L)	682 ± 14
BOD_3 (mg/L)	367 ± 15
TKN (mg N/L)	186 ± 44
TSS (mg/L)	29 ± 7
TOC (mg/L)	282 ± 13
Turbidity (NTU)	106 ± 3

[a] The values are average of three measurements.

turbidity unit) using a HACH portable turbidimeter (2100P, USA). Table 2 shows characteristics of anaerobically treated POME.

2.2. Coagulation–flocculation

The coagulation–flocculation experiment was carried out in a Phipps and Bird jar-test apparatus (USA) equipped with six beakers of 1 L volume, each. The time and speed for rapid and slow mixing were set with an automatic controller. In this study, alum as metal salt coagulant was used. Alum was in powdered form with the formula $Al_2(SO_4)_3{\cdot}18H_2O$ ($M = 666.42$ g/mol, 51–59% $Al_2(SO_4)_3{\cdot}18H_2O$, pH 2.5–4). Table 3 shows a summary of test conditions for POME treatment obtained from other researchers' studies. Therefore, in this research the operating parameters were varied as pH 6–8, coagulant dosage 1,800–2,400 mg/L, and slow mixing time 10–30 min.

Table 3
Range of critical parameters obtained from literatures

Critical parameters	Range	References
pH	4–8	[15,19,20]
Coagulant dose (mg/L)	600–3,000	[20]
Duration of rapid mixing (min)	5–30	[15]
Duration of slow mixing (min)	10–60	[19]

Table 4
Experimental factors and their levels

Variables	Range and levels		
	−1	0	1
X_1, pH	5	6	7
X_2, coagulant dosage (mg/L)	1,200	1,800	2,400
X_3, slow mixing time (mins)	10	20	30

2.3. Experimental design and data analysis

A full factorial composite experimental design and RSM was employed in order to obtain the relationship between the variables and the response. The CCD, which is the standard RSM, was selected for optimization of parameters. Knowing the constraint of the variables owing to their difference in units and/or difference in limits of variation, the variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\delta X} \tag{1}$$

where x_i is the coded value of the i^{th} independent variable, X_i is the natural value of the i^{th} independent variable, X_o is the natural value of the i^{th} independent variable at the centre point, and δX is the value of step change. pH (X_1), coagulant dosage (X_2), and slow mixing time (X_3) were choosen as three independent variables in the coagulation–flocculation process. Their range and levels are displayed in Table 4.

Table 5
CCD and response results for the study of three experimental variables in coded units

Run	Factors			Response
	pH (code)	Coagulant dosage (code)	Slow mixing time (code)	COD removal efficiency (%)
1	6 (0)	1,800 (0)	20 (0)	58.3
2	7 (1)	1,200 (−1)	30 (1)	33.0
3	5 (−1)	2,400 (1)	10 (−1)	31.8
4	7 (1)	2,400 (1)	10 (−1)	52.0
5	6 (0)	1,800 (0)	20 (0)	57.3
6	5 (−1)	2,400 (1)	30 (1)	34.3
7	7 (1)	2,400 (1)	30 (1)	53.2
8	7 (1)	1,200 (−1)	10 (−1)	31.3
9	5 (−1)	1,200 (−1)	30 (1)	37.1
10	5 (−1)	1,200 (−1)	10 (−1)	26.1
11	6 (0)	1,800 (0)	20 (0)	54.9
12	6 (0)	1,800 (0)	20 (0)	53.5
13	6 (0)	1,800 (0)	20 (0)	55.8
14	6 (0)	1,800 (0)	20 (0)	56.6

COD of the treated POME was chosen as the dependant output variables. The response variable was fitted by a second-order model in the form of quadratic polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i \times X_i + \sum_{i=1}^{k} \beta_{ii} \times X_i^2 + \sum_{i_{i \leq j}}^{k} \sum_{j}^{k} \beta_{ij} \times X_i \times X_j + \cdots + e \tag{2}$$

where Y is the predicted response, β_0 is the offset term, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, and β_{ij} is the interaction coefficient. Table 5 presents the coded experiments conducted as per experimental design along with the response values.

The Design Expert Software (version 6.0.7, Stat-Ease, Inc., Minneapolis, MN) was used for regression and graphical analysis. The interactive effects of the independent variables on the dependent one were illustrated by three-dimensional response surfaces. From these three-dimensional plots, the simultaneous interaction of two factors on the response was studied. Additional experiment was conducted to verify the validity of the statistical experimental strategies.

3. Results and discussion

3.1. Statistical analysis

The RSM was employed for the optimal experimental design of the coagulation–flocculation process. The following quadratic regression model for COD removal efficiency in terms of coded factors was obtained:

$$Y_{COD} = 56.22 + 5.33X_1 + 4.96X_2 + 1.57X_3 - 9.65X_1^2 - 6.29X_2^2 - 1.03X_3^2 + 4.75X_1X_2 - 1.32X_1X_3 - 1.13X_2X_3$$

where X_1, X_2, and X_3 are the coded values of the process variables pH, alum dosage, and slow mixing time, respectively. The response surface analysis allowed the development of an empirical relationship in which the response variable (Y_{COD}) was assessed as a function of pH (X_1), alum dosage (X_2) and slow mixing time (X_3), three first-order effects (linear term in X_1, X_2, and X_3), three second-order effects (quadratic terms in X_1^2, X_2^2, and X_3^2) and; three interaction effects (interactive terms in X_1X_2, X_1X_3, and X_2X_3). The result of the Analysis of Variance (ANOVA) for COD is shown in Table 6.

ANOVA provides the statistical results and diagnostic checking tests which enables the adequacy of the models to be evaluated [21]. It was found that the quadratic model was significance to give less than 0.05 of probability of error (P). The value of the correlation coefficient ($R^2 = 0.962$) indicates that only 3.8% of the total variation could not be explained by the empirical model. Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than four indicate adequate model discrimination [22]. The AP value which is greater than four (15.726 in this study) is adequate and can be used to navigate the design space defined by the CCD. According to ANOVA, the AP value suggests that most of the differences in the response can be explained using the regression equation. The associated P-value is used to estimate, whether AP value is large enough to show statistical significance. If the P-value is lower than 0.05, it then demonstrates that the model is statistically significant. The low standard deviation certainly is also evident that the quadratic model is seemingly the best. The coefficient of variance (CV) as the ratio of the standard error of estimated to the mean value of the observed response defines reproducibility of the model. A model normally can be considered reproducible if its CV is not greater than 10% [23]. The results in Table 6 show that the regression, linear, interaction, and quadratic terms are significant and the model is considered to be adequate in terms of reproducibility with CV = 7.31. The plot of predicted versus experimental COD removal efficiency of treated POME is close to $y = x$, indicating the prediction of experimental data is rather satisfying (Fig. 1).

According to regression equation, the optimal conditions for COD were obtained as follow: pH = 6.42, alum dosage = 2124 mg/L and slow mixing time = 20 min. With COD as the response, the response surfaces of the quadratic model are shown in Figs. 2–4. The surface graphs indicate that the optimal conditions were exactly located inside the design boundary. The curves with noticeable bend imply that there are significant interactions between the COD removal efficiency and the process variables.

Table 6
ANOVA for response surface quadratic model

Response	P	R^2	Adequate precision	Standard deviation	Coefficient of variance
COD	<0.0001	0.962	15.726	3.26	7.31

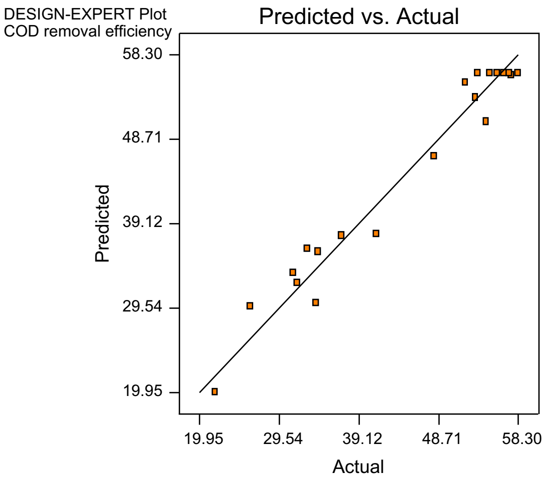

Fig. 1. Predicted vs. actual data for POME COD removal efficiency.

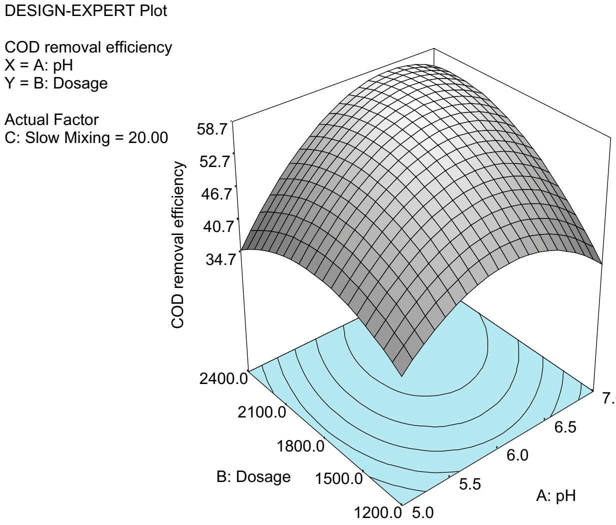

Fig. 2. Design-expert plot; response surface plot for COD removal at different pH and alum dosage.

Fig. 2 shows the changes in COD removal efficiency with varying pH and dosage. It is clear that the optimal conditions for the COD removal efficiency were located in the region where pH ranged from 6.0 to 7.0 and alum dosage from 1,800 to 2,400 mg/L. Alum is most effective between pH ranges of 5.0 and 7.5 [24]. Hence, pH 6.0 to 7.0 was reasonably an optimal and effective range for maximum COD removal of 58.7%. Figs. 3 and 4 portray fairly the same trend of surface graphs. It can be seen that at higher slow mixing time of 20–30 min, the COD removal efficiency increased slightly with increasing alum dosage at 1,800–2,400 mg/L and pH at 6.0–6.5, respectively.

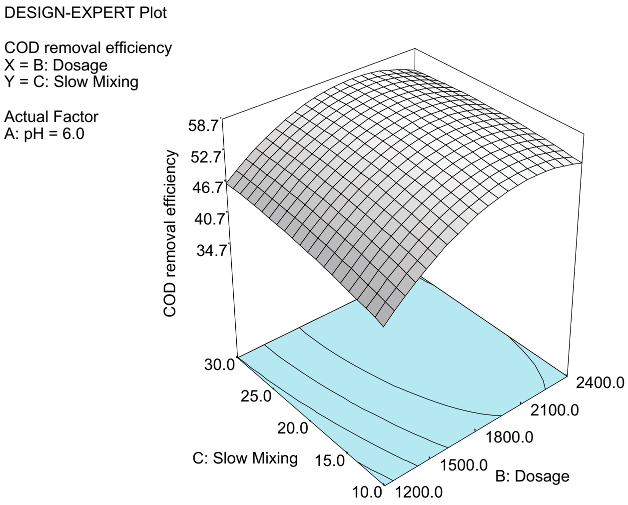

Fig. 3. Design-expert plot; response surface plot for COD removal at different alum dosage and slow mixing duration.

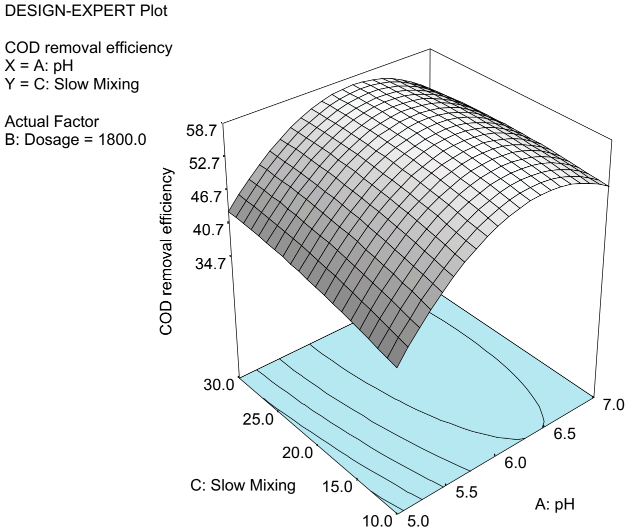

Fig. 4. Design-expert plot; response surface plot for COD removal at different pH and slow mixing duration.

3.2. Experimental condition optimization

To confirm the validity of the statistical experimental strategies, additional verification experiments were conducted at optimum conditions determined from RSM in previous step. The samples were stirred at a constant speed of 150 rpm for 5 min. This was followed by slow mixing at 30 rpm to keep all the solids in suspension and to promote collisions between destabilized particles. The contents of each beaker were then allowed to sediment with the settling time of 60 min. The COD removal efficiency was predicted by the model to be 58.7% under the optimum conditions. This model prediction from the regression equation agreed reasonably well with the data from the verification experiments. Based on optimized experimental condition COD removal efficiency of 59.0% was achieved under optimized condition. This testifies that the RSM approach was appropriate for optimizing operational conditions of the coagulation–flocculation process in COD removal efficiency of POME. Therefore, the optimum values of the process variables were: pH 6.42, alum dosage 2,124 mg/L, and slow mixing time 20 min. According to the Environmental Quality Act 1974 which is implemented by Department of Environment (DOE), Malaysia, the COD of effluent discharge for crude palm oil mills should not be above 400 mg/l [25]. As a result, the effluent after current process is met the discharge requirements.

4. Conclusions

The study reveals that COD removal efficiency of up to 59% can be achieved during coagulation process by optimization of the experiment procedures at pH 6.4, alum dosage 2,124 mg/L, and rapid and slow mixing 5 and 20 min by application of RSM. Obtained results in this study are useful in purposing coagulation process using alum to palm oil mill industries to be applied as polishing for anaerobically treated POME, since it is energy and cost efficient, controllable, and has short and predictable duration and is able to reduce the COD to the level which meets the discharge limits enforced by Malaysian DOE.

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List of symbols

x_i — coded value of the *i*th independent variable
X_i — natural value of the *i*th independent variable
X_o — natural value of the *i*th independent variable at the centre point
δX — value of step change
Y — predicted response
β_o — the offset term
β_i — the linear coefficient
β_{ii} — the quadratic coefficient
β_{ij} — the interaction coefficient
ANOVA — analysis of Variance
AP — adequate precision
BOD — biochemical Oxygen Demand
CCD — central composite design
COD — chemical oxygen demand
CV — coefficient of variance
DOE — Department of Environment
NTU — nephelometric turbidity unit
POME — palm oil mill effluent
RSM — response surface methodology
TKN — total Kjeldahl nitrogen
TN — total nitrogen
TOC — total organic carbon
TS — total solids
TSS — total suspended solids

References

[1] Y.J. Zhang, L. Yan, X.L. Qiao, L. Chi, X.J. Niu, Z.J. Mei, Integration of biological method and membrane technology in treating palm oil mill effluent, J. Environ. Sci. 20 (2008) 558–564.
[2] S. Yacob, Y. Shirai, M.A. Hassan, M. Wakisaka, S. Subash, Start-up operation of semi-commercial closed anaerobic digester for palm oil mill effluent treatment, Process Biochem. 41 (2006) 962–964.
[3] M.D. LaGrega, P.L. Bukingham, J.C. Evans, Hazardous Waste Management and Environmental resource management, second ed., McGraw-Hill series in Water Resources and Environmental Engineering, International Edition, Biological Sciences Series, 2001. ISBN 0-07-039365-6.
[4] Laws of Malaysia, Act 127, Environmental quality act 1974, The commissioner of law revision, Malaysia under the authority of the revision of laws act 1968 in collaboration with Percetakan Nasional Malaysia Bhd, (2006).
[5] Y.J. Chan, M.F. Chong, C.L. Law, Biological treatment of anaerobically digested palm oil mill effluent (POME) using Lab-Scale Sequencing Batch Reactor (SBR), J. Environ. Manage. 91 (2010) 1738–1746.
[6] C.C. Ho, Y.K. Tan, Comparison of chemical flocculation and dissolved air flotation of anaerobically treated palm oil mill effluent, Water Res. 23 (1989) 395–400.
[7] S.M. Phang, K.C. Ong, Algal biomass production in digested palm oil mill effluent, Biol. Waste 25 (1988) 177–191.
[8] K. Vijayaraghavan, D. Ahmad, M. Ezani Bin Abdul Aziz, Algal biomass production in digested palm oil mill effluent, J. Environ. Manage. 82(1) (2007) 24–31.
[9] M. Ahmadi, H. Amiri, S.S. Martinez, Treatment of phenol-formaldehyde resin manufacturing wastewater by the electrocoagulation process, Desalin. Water Treat. 39 (2012) 176–181.
[10] E. Ellouze, D. Ellouze, A. Jrad, R. Ben Amar, Treatment of synthetic textile wastewater by combined chemical coagulation/membrane processes, Desalin. Water Treat. 33 (2011) 118–124.
[11] A. Felder, R. Epsztein, N. Villensky, V. Gitis, Optimization of coagulation step in membrane treatment of municipal secondary effluents, Desalin. Water Treat. 35 (2011) 62–67.

[12] W.K. Lafi, M. Al-Anber, Z.A. Al-Anber, M. Al-shannag, A. Khalil, Coagulation and 7118 advanced oxidation processes in the treatment of Olive Mill Wastewater, Desalin. Water Treat. 24 (2010) 251–256.

[13] A.K. Yadav, L. Singh, A. Mohanty, S. Satya, T.R. Sreekrishnan, Removal of various pollutants from wastewater by electrocoagulation using iron and aluminium electrode, Desalin. Water Treat. 46 (2012) 352–358.

[14] A. Mahtab, M. Tariq, T. Shafiq, A. Nasir, Coagulation/adsorption combined treatment of slaughterhouse wastewater, Desalin. Water Treat. 12 (2009) 270–275.

[15] A.L. Ahmad, S. Sumathi, B.H. Hameed, Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC, Chem. Eng. J. 118 (2006) 99–105.

[16] A.R. Khataee, B. Habibi, Photochemical oxidative decolorization of CI basic red 46 by UV/H_2O_2 process: Optimization using response surface methodology and kinetic modelling, Desalin. Water Treat. 16 (2010) 243–253.

[17] N. Chaudhuri, P.C. Tyagi, N. Niyogi, V.P. Thergaonkar, P. Khanna, BOD test for tropical countries, J. Environ. Eng. 118 (1992) 298–303.

[18] APHA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, 1992.

[19] S. Bhatia, Z. Othman, A.L. Ahmad, Coagulation-flocculation process for POME treatment using *Moringa oleifera* seeds extract: Optimization studies, Chem. Eng. J. 133 (2007) 205–212.

[20] A.L. Ahmad, S. Ismail, S. Bhatia, Optimization of coagulation–flocculation process for palm oil mill effluent using response surface methodology, Environ. Sci. Technol. 39 (2005) 2828–2834.

[21] A. Talebi, T.T. Tjoon, A.F.M. Alkarkhi, I. Norli, W.L. Ling, Optimization of nickel removal using liquid–liquid extraction and response surface methodology, Desalin. Water Treat. 47 (2012) 334–340.

[22] P.D. Saha, A. Dey, P. Marik, Batch removal of chromium (VI) from aqueous solutions using wheat shell as adsorbent: process optimization using Response Surface Methodology, Desalin. Water Treat. 39 (2012) 95–102.

[23] S. Chowdhury, P. Das, Scale-up of a dye adsorption process using chemically modified rice husk: Optimization using response surface methodology, Desalin. Water Treat. 37 (2012) 331–336.

[24] H.S. Peavy, D.R. Rowe, G. Tchobanoglous, Environmental Engineering, McGraw-Hill, New York, NY, 1985.

[25] Laws of Malaysia Reprint Act 127 Environmental Quality Act 1974, The Commissioner of law revision, Malaysia under the authority of the revision of laws act 1968 in collaboration with percetakan nasional Malaysia, (2006).