Optimization of ultrasound irradiation for palm oil mill effluent

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Abstract. The objective of this work was to investigate the effect of ultrasound irradiation on palm oil mill effluent (POME) treatment. The experiment was statistically designed by response surface methodology (RSM) based on central composite design (CCD) to evaluate individual and interactive effects of operational independent variables including ultrasonication amplitude, ultrasonication time and total solids concentration. The treatment performance was assessed by three dependent variables, viz., particle size reduction, total suspended solid reduction and organic solubilisation improvement. Experimental results showed that ultrasonication irradiation has positive effect on POME treatment. The optimum operation condition suggested by RSM were ultrasonication amplitude of 50%, ultrasonication duration of 18.94 mins and total solids concentration of 6.47% with expected organic disintegration results as 47.7% particle size reduction, 18.9% of solid reduction and 31.5% of solubilisation improvement.

1. Introduction

The production of crude palm oil in wet processing mill generates large amount of palm oil mill effluent (POME) in the ratio of 1: 3 [1]. Based on the ratio, it is estimated that 43.3 million tonnes of POME was produced in year 2016 in Malaysia. POME with high pollution material i.e. chemical oxygen demand (COD) and high organic suspended solids (SS) [2] impose adverse impact on the natural water course if discharged without treatment. Various pretreatment methods such as phase separation treatment [3], chemical treatment [4], ozone treatment [5] and ultrasound treatment [6] have been used prior to biological treatment.

Ultrasound is an oscillating sound wave generated through compression and rarefraction pressure with a frequency greater than 20 kHz. Low frequency ultrasound (20-100 kHz) has been used as irradiation treatment in advanced wastewater treatment technology [7]. Generally, the mechanism of ultrasonication treatment is based on the generation of cavitation phenomenon by high energy sound waves in the liquid solution. The mechanism can change depending on the characteristics of the ultrasonication system including types of samples, presence of air and solids; and the ultrasonication conditions including ultrasonication power and duration [8]. The effects of the mechanisms viz., hot spots theory, hydrodynamic shear forces, sonochemical reaction, etc. create a change in spatial
structure of the sonicated materials. Application of ultrasound treatment facilitates the reaction rate along with time saving [7]. For example, low frequency ultrasound has high efficiency in sludge disintegration by creating large cavitation bubbles and generating powerful hydrodynamic shear forces [9]. The physical and sonochemical effects increase the mass transfer rate of sonicated materials across bubbles. Ultrasonication pretreatment has been used to expedite the anaerobic digestion in the biological treatment system [6,7]. Organic compounds are disintegrating to aqueous phase making them easily available to microorganisms and resulting in increased biodegradability. Therefore, anaerobic digestion rate can be enhanced by ultrasonication pretreatment.

Study related to ultrasound pretreatment for optimum organic solubilisation of POME is limited. Based on the properties of POME, we hypothesized that ultrasound irradiation may disintegrate the cellulose particles in POME and enhance the solubility of particles in POME. Response surface methodology (RSM) based on central composite design (CCD) was employed for model variation trend of three significant responses, i.e., particle size reduction, total suspended solid (TSS) and solubilisation improvement.

2. Materials and methods

2.1. Preparation of sample and analytical test
Ultrasonication process was performed in batch mode with 100 mL POME samples using a Cole-Parmer 500-W ultrasound processor. The operating frequency of the ultrasonicator processor was 20 kHz with adjustable ultrasonication time and amplitude.

The ultrasonicated and un-ultrasonicated POME was subjected to analytical testing in accordance with the Standard Methods for Examination Water and Wastewater (APHA) [10]. TS and TSS were determined according to APHA2540B and 2540D respectively. BOD was measured as BOD₅ accordance with APHA 5210B. The determination of COD and SCOD were accomplished according to APHA 5520D with Hach spectrophotometer. Particle size analysis was conducted using a Malvern Mastersizer Hydro2000 MU laser diffractometer.

2.2. Experimental procedure design by RSM
CCD is a statistical tool to assess the effects of independent (process) to dependent variables (response) and the relations between the variables [10]. CCD uses a five level fractional design for the construction of second order response surface and provides more reliable data by including repetition of centre points to calculate the experimental error [11].

The three independent variables chosen were: (A) ultrasonication amplitude, 20-50%; (B) ultrasonication duration, 1-30 mins; and (C) TS concentration, 3-7% [6]. The range of the independent variables chose was based on the preliminary study [2]. Twenty experiments including six replications based on the suggested three independent variables at the design centre. The corresponding dependent variables assessed were: (a) particle size reduction; (b) TSS reduction; and (c) solubilisation improvement. Process performance was validated by analysis of variance (ANOVA).

3. Results and discussion

3.1. Organic profile and particle size of POME
As shown in table 1, COD of POME collected was 95.4 g/L due to the presence of high concentration of organic matters. This brownish acidic suspension with pH of 4.44 to 5.07, and total solids of 49 to 58 g/L is considered as high strength wastewater with moderate biodegradability; BOD₅:COD ratio of 0.3. Therefore, physicochemical pretreatment is required before biological treatment.
Table 1. Organic profile and particle size of POME

| Parameter                        | Unit  | Mean value     |
|----------------------------------|-------|----------------|
| Biochemical oxygen demand (BOD₅) | mg/L  | 28,800 ± 423   |
| Chemical oxygen demand (COD)     | mg/L  | 95,400 ± 1050  |
| Soluble COD (SCOD)               | mg/L  | 39,500 ± 2330  |
| Total solid (TS)                 | mg/L  | 53,810 ± 4000  |
| Total suspended solid (TSS)      | mg/L  | 25,000 ± 2200  |
| Particle size                    | µm    | 100.481 ± 20   |

3.2. Experimental design and optimization study

RSM is a statistical method used to assist modeling analysis for response that are affected by several variables. The objective of using RSM is to optimize the response [12]. Table 2 shows the CCD of three experimental variables with results. The quadratic polynomial model (Eq. 1) is used to assess the results (Y) as a function of ultrasonication amplitude (A), ultrasonication duration (B) and Total solids (TS) concentration (C). The results were calculated as a sum of a constant, first order effect (A, B, C), interaction effect (AB, AC, BC) and second order effect (A², B² and C²) (equation (1)).

Table 2. CCD of three experimental variables and responses.

| Run no. | Experimental design | Results |
|---------|---------------------|---------|
|         | A: ultrasonication amplitude (code) | B: ultrasonication duration (mins) | C: TS concentration (code) | Particle size reduction (%) | TSS reduction (%) | Solubilisation improvement (%) |
| 1       | 20.0 (-1)           | 30.00 (+1) | 3 (-1) | 51.7 | 1.5 | 12.1 |
| 2       | 50.0 (+1)           | 30.00 (+1) | 3 (-1) | 49.8 | 4.0 | 19.1 |
| 3       | 50.0 (+1)           | 1.00 (-1)  | 7 (+1) | 31.0 | 13.4 | 24.1 |
| 4       | 35.0 (0)            | 15.50 (0)  | 5 (0)  | 58.8 | 5.7 | 11.1 |
| 5       | 42.5 (+0.5)         | 15.50 (0)  | 5 (0)  | 58.9 | 8.0 | 23.2 |
| 6       | 35.0 (0)            | 15.50 (0)  | 5 (0)  | 59.2 | 6.2 | 19.1 |
| 7       | 50.0 (+1)           | 1.00 (-1)  | 3 (-1) | 41.2 | 12.3 | 12.1 |
| 8       | 27.5 (-0.5)         | 15.50 (0)  | 5 (0)  | 58.8 | 2.4 | 13.8 |
| 9       | 35.0 (0)            | 8.25 (-0.5) | 5 (0)  | 55.0 | 0.8 | 13.2 |
| 10      | 20.0 (-1)           | 1.00 (-1)  | 7 (+1) | 26.0 | 7.0 | 10.6 |
| 11      | 35.0 (0)            | 22.75 (+0.5) | 5 (0)  | 60.0 | 2.0 | 11.1 |
| 12      | 20.0 (-1)           | 1.00 (-1)  | 3 (-1) | 24.4 | 9.3 | 3.9  |
| 13      | 35.0 (0)            | 15.50 (0)  | 5 (0)  | 58.2 | 1.4 | 13.5 |
| 14      | 35.0 (0)            | 15.50 (0)  | 5 (0)  | 58.7 | 2.4 | 11.1 |
| 15      | 35.0 (0)            | 15.50 (0)  | 4 (-0.5) | 54.9 | 1.0 | 4.5 |
| 16      | 50.0 (+1)           | 30.00 (+1) | 7 (+1) | 37.3 | 26.8 | 45.5 |
| 17      | 35.0 (0)            | 15.50 (0)  | 5 (0)  | 57.7 | 0.8 | 13.4 |
| 18      | 20.0 (-1)           | 30.00 (+1) | 7 (+1) | 47.6 | 11.6 | 18.6 |
| 19      | 35.0 (0)            | 15.50 (0)  | 6 (+0.5) | 51.0 | 13.6 | 9.4 |
| 20      | 35.0 (0)            | 15.50 (0)  | 5 (0)  | 57.2 | 0.3 | 11.4 |

\[ Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_j X_j^2 + \sum_{i<j=2}^{k} \beta_{ij} X_i X_j + e_i \]  

where \( Y \) is the response, \( X_i \) and \( X_j \) are the operational variables, \( \beta_0 \) is the constant coefficient, \( \beta_j \) is linear, \( \beta_{ij} \) is quadratic and \( \beta_{ij} \) is second order terms coefficients [13]. Generally, the second order polynomial model is used to predict the optimal conditions. The experimental data were then validated using ANOVA to assess the goodness of fit".

Table 3. ANOVA analysis summary.

| Statistical parameters | Abbreviation | Particle size reduction | TSS reduction | Solubilisation improvement |
|------------------------|--------------|-------------------------|--------------|---------------------------|
| Probability of error   | PLOF > F     | <0.0001                 | 0.0002       | <0.0001                   |
| Probability of lack of fit | PLOF   | 0.18                    | 0.40         | 0.44                      |
| Standard deviation     | St. Dev.     | 0.97                    | 2.75         | 2.49                      |
| Coefficient of determination | R²    | 0.99                    | 0.87         | 0.86                      |
| Adjusted R²            | Adj. R²     | 0.99                    | 0.79         | 0.79                      |
| Adequate precision     | AP          | 53.09                   | 12.44        | 14.62                     |
| Predicted residual error sum of square | PRESS | 97.78                   | 256.86       | 164.33                    |

Table 3 shows the fit summary and ANOVA analysis obtained from the experimental data. ANOVA was used to test the validity of the linear and interaction terms between the responses and the process. Model terms were estimated based on the probability with a 95% confidence level. The ANOVA of the three responses indicates that the design model was significant with small PLOF>F (<0.05). Meanwhile, the PLOF-values were greater than 0.05 for all three responses implied the insignificant lack of fit. The insignificant lack of fit indicating that the model was valid. To sum up, particle size reduction, TSS reduction and solubilisation improvement models were well fitted to the experimental data due to a significant regression and a non-significant lack of fit [14].

The coefficient of determination of this model were in the range of 0.86-0.99 indicating a close linearity between predicted values and the experimental data points. Adequate precision (AP) compares the signal to noise ratio. The test results show AP values higher than 4 (12.4-53.1) indicates adequate model discrimination and the reliability of the experimental data [15,16].

3.3. Three-dimensional (3D) plots

Figures 1 to 3 demonstrated 3D plots as graphical analysis based on experimental data from Table 2. 3D plots were used as graphical analysis to assess the relationship between the variables. In Figure 1, particle size reduction increased when TS concentration increased from 3-5% at different ultrasonication amplitude and achieved maximum reduction of 70% at 5% TS concentration, 20% ultrasonication amplitude and 30 mins ultrasonication duration. Figure 1(b) shows that particle size reduction increased with an increase in ultrasonication time while ultrasonication amplitude had a minor effect on particle size reduction.

Particle size reduction is one of the important ultrasonication effects on samples with sludge and particles. The reduction of particle size indicated that the particles were degraded, free substances were released and solubility was increased. This condition offer a better circumstances for subsequent biological digestion process [17].

Microbubbles cavitation phenomenon produces a high turbulence and hydro-mechanical disruption that reduce the particle size of the sonicated materials in the liquid phase [18]. When the liquid suspension containing particles are subjected to ultrasonication, the physical characteristics of the particles are exposed to surface erosion, shape distortion and size reduction [19]. Theoretically, the particle size reduction rate is inversely proportional to the hydrolysis rate. In addition, intense shockwaves are produced during cavitation collapse which propagate through the liquid [20,21]. Hydroxyl radicals were generated through sonochemical effects induced by these shock waves which further enhance the disintegration process [22].

Figure 2 illustrates the interaction of operational variables on TSS reduction efficiency. The higher the value of TSS reduction after ultrasonication irradiation, the more POME particles which were disintegrated from solid to liquid phase. Maximum TSS reduction achieved was 31% with total solids concentration of 7%, ultrasonication amplitude at 50% and ultrasonication duration of 15.5 mins. Erden and his group [23] have verified that ultrasonic irradiation enhanced the anaerobic biodegradability of meat processing effluent in terms of solid's solubilisation and 24% increase in methane yield. High ultrasonication amplitude, ultrasonication duration and TS concentration are...
considered as the best conditions for this study.

Figure 1. 3D surface plots: (a) the effect of TS concentration and ultrasonication amplitude on particle size reduction (ultrasonication time 30 min); and (b) the effect of ultrasonication time and ultrasonication amplitude on particle size reduction (TS: 5%).

Figure 2. 3D surface plots: (a) the effect of TS concentration and ultrasonication amplitude on TSS reduction (ultrasonication duration 15.5 mins); and (b) the effect of ultrasonication time and ultrasonication amplitude on TSS reduction (TS: 7%).

Figure 3 illustrates the effect of operation parameters on solubilisation improvement. Solubilisation was improved with the increase of ultrasonication time. With the total solids concentration of 5.6%, the ultrasonication amplitude of 50% and ultrasonication duration of 30 mins, the maximum solubilisation improvement was 54%. Similar to the trends observed by Wong et al [6] where by SCOD increased in the range of 8.5-15% after ultrasonication irradiation for 15 mins. Similar study by Saifuddin and Fazlili [24] revealed that the SCOD/COD ratio increased almost 29% after 30 mins sonication.
Figure 3. 3D surface plots: (a) the effect of TS concentration and ultrasonication amplitude on solubilisation improvement (ultrasonication duration 30 mins); and (b) the effect of ultrasonication time and ultrasonication amplitude on solubilisation improvement (TS: 5%).

4. Conclusion
RSM was employed to assess the effect of ultrasonication amplitude, ultrasonication duration and TS concentration on POME treatment in addition to obtaining the corresponding optimum conditions. The statistical analysis demonstrated that these three factors had an individual significant effect on the organics disintegration of POME. Ultrasound irradiation could alter the physical properties of POME by decreasing particle size and total suspended solids and enhance the solubilisation of COD. The optimum operations conditions were obtained as 50% ultrasonication amplitude, 18.94 mins ultrasonication duration and 6.47% TS concentration. Further investigation would be performed to validate the model suggested using RSM to optimise ultrasonication pretreatment condition for feasibility study of POME disintegration prior to subsequent anaerobic digestion.

References
[1] Yussoff S 2006 Renewable energy from palm oil - Innovation on effective utilization of waste J. Clean Prod. 14 87-93
[2] Wong L-P, Isa M H and Bashir M J K 2018 Low frequency ultrasound treatment of palm oil mill effluent for solubilization of organic matter Desalin Water Treat 108 164-70
[3] Show K Y and Wong L P 2012 Application of ultrasound pretreatment for sludge digestion Biogas Production: Pretreatment Methods in Anaerobic Digestion ed A. Mudhoo (United State of America: Scrivener Publishing LLC) pp 91-136
[4] Mohmod S S, Jahim J M and Abdul P M 2017 Pretreatment conditions of palm oil mill effluent (POME) for thermophilic biohydrogen production by mixed culture Int. J Hydrogen Energy 42 27512-22
[5] Chaiprapat S and Laklam T 2011 Enhancing digestion efficiency of POME in anaerobic sequencing batch reactor with ozonation pretreatment and cycle time reduction Bioresour Technol. 102 4061-8
[6] Wong L-P, Isa M H and Bashir M J K 2018 Disintegration of palm oil mill effluent organic solids by ultrasonication: Optimization by response surface methodology Process Saf Environ 114 123-32
[7] Adulkar T V and Rathod V K 2014 Ultrasound assisted enzymatic pre-treatment of high fat content dairy wastewater Ultrason Sonochem. 21 1083-9
[8] Barati A H, Mokhtari-Dizaji M, Mozdarani H, Bathaie Z and Hassan Z M 2007 Effect of exposure parameters on cavitation induced by low-level dual-frequency ultrasound Ultrason Sonochem. 14 783-9
[9] Tiehm A, Nickel K, Zellhorn M and Neis U 2001 Ultrasonic waste activated sludge
disintegration for improving anaerobic stabilization \textit{Water Res.} \textbf{35} 2003-9

[10] Asadi A, Zinatizadeh A A L and Isa M H 2012 Performance of intermittently aerated up-flow sludge bed reactor and sequencing batch reactor treating industrial estate wastewater: A comparative study \textit{Bioresour Technol.} \textbf{123} 495-506

[11] Mark J A and Whitcomb P J 2016 \textit{RSM Simplified: Optimizing Processes Using Response Surface Methods for Design of Experiments} 2nd Ed, Productivity, Inc., USA: New York

[12] Zinatizadeh A A L, Mohamed A R, Abdullah A Z, Mashitah M D, Isa M H and Najafpour G D 2006 Process modeling and analysis of palm oil mill effluent treatment in an up-flow anaerobic sludge fixed film bioreactor using response surface methodology (RSM) \textit{Water Res.} \textbf{40} 3193-208

[13] Bashir M J K, Lim J H, Amr S S A, Wong L P and Sim Y L 2019 Post treatment of palm oil mill effluent using electro-coagulation-peroxidation (ECP) technique \textit{J. Clean. Prod.} \textbf{208} 716-27

[14] Shehzad A, Bashir M J K, Sethupathi S and Lim J-W 2016 Simultaneous removal of organic and inorganic pollutants from landfill leachate using sea mango derived activated carbon via microwave induced activation \textit{Int J Chem React Eng} \textbf{14} 991-1001

[15] Azmi N B, Bashir M J K, Sethupathi S, Wei L J and Ng C A 2015 Stabilized landfill leachate treatment by sugarcane bagasse derived activated carbon for removal of color, COD and NH3-N – Optimization of preparation conditions by RSM \textit{J. Environ. Chem. Eng.} \textbf{3} 1287-94

[16] Mason R L and Young J C 2010 The statistical engineer \textit{Quality Progress} \textbf{43} 50-2

[17] Show K Y, Mao T H, Tay J-H and Lee D-J 2006 Effects of ultrasound pretreatment of sludge on anaerobic digestion \textit{J Residuals Sci Tech} \textbf{3} 51-9

[18] Matias V R F, Cammarota M C and Sant’Anna Jr G L 2003 Extraction of activated sludge bacteria exopolymers by ultrasonication \textit{Biotechnol Lett} \textbf{25} 1351-6

[19] Jeganathan J, Nakhla G and Bassi A 2007 Hydrolytic pretreatment of oily wastewater by immobilized lipase \textit{J Hazard Mater} \textbf{145} 127-35

[20] Suslick K S, Eddingsaas N C, Flannigan D J, Hopkins S D and Xu H 2011 Extreme conditions during multibubble cavitation: Sonoluminescence as a spectroscopic probe \textit{Ultrason Sonochem.} \textbf{18} 842-6

[21] Gallego-Juárez J A, Riera-Francisco D S E, Rodríguez-Corral G, Hoffmann R L, Gálvez-Moraleda J C, Rodríguez-Maroto J J \textit{et al} 1999 Application of acoustic agglomeration to reduce fine particle emissions from coal combustion plants \textit{Environ Sci Technol} \textbf{33} 3843-9

[22] Suslick K S 1990 Interparticle collisions driven by ultrasound \textit{Science} \textbf{247} 1439-45

[23] Erden G, Buyukkamaci N and Filibeli A 2010 Effect of low frequency ultrasound on anaerobic biodegradability of meat processing effluent \textit{Desalination} \textbf{259} 223-7

[24] Safiuddin N and Fazlili S A 2009 Effect of microwave and ultrasonic pretreatments on biogas production from anaerobic digestion of palm oil mill effluent \textit{Am. J. Eng. Appl. Sci.} \textbf{2} 139-46