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Optimization of NaOH Thermo-Chemical Pretreatment to Enhance Solubilisation of Organic Food Waste by Response Surface Methodology

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Abstract**—**This study investigates the influence of low temperature thermo-chemical pretreatment of organic food waste on performance of COD solubilisation. Both temperature and alkaline agent were reported to have effect on solubilizing any possible biomass including organic food waste. The three independent variables considered in this pretreatment were temperature (50-90^{o}C), pretreatment time (30-120 minutes) and alkaline concentration, sodium hydroxide, NaOH (0.7-15 g/L). The maximal condition obtained were 90^{o}C, 15 g/L NaOH for 2 hours. Solubilisation has potential in enhancing methane production by providing high amount of soluble components at early stage during anaerobic digestion.

Keywords**—**Food waste, pretreatments, respond surface methodology, ANOVA, anaerobic digestion.

I. Introduction

CURRENTLY, active research have been pursued on every possible sustainable waste resource including organic food waste as a substrate for anaerobic digestion (AD). The large amount of organic waste availability in landfills has led to this effort in order to reduce environmental problems created due to lack of planning in waste handling. Food waste is part of municipal solid waste (MSW) that is dumped straight into landfill. It includes the non-readily biodegradable part that requires external assistant as pretreatment to break down bonds of lignin and hemicellulose to obtain soluble component which is a crucial supplies in producing biogas mainly methane via anaerobic digestion.

Anaerobic digestion constitutes of a basic process which includes hydrolysis, acidogenesis, acetogenesis, and methanogenesis [1]-[3]. However the most critical and rate limiting step in anaerobic digestion are hydrolysis and acidogenesis processes where complex molecule of organic waste need to be broken down into monomers that requires longer time with slow rate of solubilisation [4], [5]. This hydrolysis process requires assistance in reducing the time taken during digestion process with pretreatment.

Pretreatment is needed to improve accessibility of soluble organic material as represented by the value of soluble chemical oxygen demand (SCOD) for microbial population during digestion process. At early stage of anaerobic digestion, high content of SCOD indicates the readiness of a substance to be converted into methane without having to go through longer hydrolysis process. Source of energy availability in the process maintain the activity and condition of microbes throughout the entire process. Therefore, by providing the pretreated substrate which contain readily available monomers will eventually uplift methane production in less possible retention time. According to Jayashree et al. [6] SCOD is one of the parameters that can considered in assessing particulate material ultimately leading to be optimal solubilisation analysis and to identify the quantity of soluble organic content in the subjected substrate. The SCOD value expresses solubilisation, S as described in (1) [7], [8].

$$\text{Solubilisation, S (\%)} = [(SCOD_f - SCOD_i) / TCOD] * 100 \quad (1)$$

where $SCOD_f$ and $SCOD_i$ refer to final and initial value of SCOD respective. And TCOD represent total chemical oxygen demand.

Pretreatment processes have been extensively further studied and explored to enhance solubilisation process. In chemical pretreatment process, alkaline pretreatment is preferable to treat substrate compared to acid treatment due to browning effect of glucose and fructose content [9]. Furthermore, NaOH was preferable as an alkaline agent to treat variety of substrate in most of the established studies to enhance both solubilisation [6], [10]-[12] and methane production [13]-[18]. Yi et al. [19] found that combination between alkaline and low temperature had effects on chemical characteristics of waste activated sludge such as removing suspended solids, SS and increase in SCOD.

Effect of thermo-chemical pretreatment in treating kitchen waste was studied by [9] by using NaOH concentration up to 1.5% and 50^{o}C as starting temperature for the treatment. The study stated that at low temperature of 75^{o}C, it resulted in reduction of soluble sugars, which may be attributed to browning reactions. The lowest concentration of NaOH used in this study within the range of 0.8-7 g/L was referred to [20] in treating organic fraction of the municipal solid wastes (OFMSW).

Based on findings from other similar studies on effect of thermal pretreatment on biogas production temperature of 90^{o}C was considered as maximum temperature approached in

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thermal pretreatment in this study [16], [21]-[23]. According to [9], temperature above 100°C can lead to decrease in soluble sugar due to Mailard browning reactions. Meanwhile the optimal time taken in pretreating the substrate is less than 120 min. Thus, by considering the extra cost of energy consumption, temperature up to 90°C and 120 minutes pretreatment time were chosen. In this study, concentration, temperature and time ranges of 0.7-15 g/L, 50-90°C for 30 to 120 minutes are studied. The three parameters were tested to find optimal COD solubilisation using the software, Response Surface Methodology (RSM).

A collection of mathematical and statistical techniques is referred to RSM that involved both dependent, (Y) and independent, (X_1, X_2,…X_k) variables in determining either maximum or maximum output depends on the objectives required. Independent variables refer to the factors that independent of each other and can be changed without affecting other variables involved. Some of the factors been investigated in pretreating possible biomass such as chemical concentration [24], particle size [25], temperature and time [16]. The desired output that is affected by any changes of independent variable is referred to response or dependent variable.

RSM is applied in optimization process to reduce the number of runs that can cut extra cost and time needed as compared to conducting one-variable-at-a-time. One-variable-at-a-time method required a change of one parameter while keeping the other parameters constant where interactions between parameters involved cannot be estimated. In addition, first order models are used to represent the experimented data in linear function. If with the presence of a curvature, the quadratic design should be used such as centre composite design (CCD) which allows estimation of curvatures [26]. In the case of abundant number of variables to be determined, screening design can be chosen to select the only variables that largely affecting the whole process.

II. Methodology

A. Preparation of Substrates and Inoculum

Food Waste (FW) prepared manually representing the main components of Malaysian food waste was made up of steamed rice, vegetable (cooked cabbage and carrot), bread, fried chicken, fried fish and fried noodle. The indigestible material such as bones was removed manually before food waste was shredded. The component mixture was further homogenized using a blender and sieved to produce a homogeneous substrate with <2mm particle size.

B. Thermo-Chemical Pretreatment

Thermo-chemical pretreatment was carried out using a stainless steel container equipped with stirrer and heater. The substrate was tested for range 0.7-15 g/L of NaOH, 50-90°C for 30-120 minutes.

C. Analytical and Computational Method

Determination of total solids (TS), total suspended solids (TSS), total volatile solids (VS) and chemical oxygen demand (COD) were tested accordingly to the Standard Methods for the Examination of Water and Wastewater (APHA). Soluble COD was obtained from filtered sample through 0.45 µm filter paper. Titration was used to determine volatile fatty acids in term of acetic acids.

TABLE I
SAMPLE CHARACTERISTICS

Characteristics	Unit	**Food waste**
pH	mg/L	4.33
Total solids	mg/L	88,933
Total volatile solids	mg/L	85,267
Total suspended solids	mg/L	46,233
TCOD	mg/L	153,611
SCOD	mg/L	30,611
VFA	mg/L	241.34
Alkalinity	mg/L	530.15

D. Experimental Design and Procedure

Central composite design (CCD) was employed for the selected factors to obtain the desired output from the experimental design produced by the software. The level and code of variables considered in this study are shown in Table II.

TABLE II
LEVEL CODE FOR CENTRAL COMPOSITE DESIGN

Factor	Variable	Coded levels		
		-1	0	1
Temperature, °C	A	50	70	90
Treatment time, min	B	30	75	120
NaOH concentration, g/L	C	0.7	7.85	15

For three variables (n=3), and three levels (low, medium and high, coded as -1, 0 and +1), the total number of 20 runs were determined by the expression 2^n (2^3=8 factorial points), 2n (2*3=6 axial points), 6 centre points (point of replications) as given in Table III. The average of triplicated values of each run was taken as response in term of COD solubilisation.

A quadratic polynomial equation was developed to predict the response as a function of independent variables and their interactions. In general, the response for the quadratic polynomials is described in (2):

$$Y = \beta_0 + \sum\beta_i x_i + \sum\beta_{ii} x_i^2 + \sum\sum\beta_{ij} x_{ij} x_j \quad (2)$$

where Y is the response (COD solubilisation), β_0 is the intercept coefficient, β_i is the linear terms, β_{ii} is the squared terms and β_{ij} is the interaction terms.

III. Result and Discussion

A Central Composite Design (CCD) under RSM was used to optimize COD solubilisation based on the interactive effect of thermo-chemical pretreatment that consist of three parameters which are NaOH concentration, temperature and treatment time.

TABLE III
CCD WITH EXPERIMENTAL AND PREDICTED VALUES OF COD SOLUBILISATION (%)

Temperature (°C)	Treatment time (min)	Conc. (g/L)	COD solubilisation (%)	
			Experimental	Predicted
50	30	0.7	9.7	9.7
50	120	0.7	11.0	10.9
70	75	0.7	11.9	12.8
90	30	0.7	12.9	12.2
90	120	0.7	16.8	16.7
50	75	7.85	11.9	11.6
70	30	7.85	13.0	13.8
70	75	7.85	13.9	14.9
70	75	7.85	15.2	14.9
70	75	7.85	15.2	14.9
70	75	7.85	15.1	14.9
70	75	7.85	16.0	14.9
70	75	7.85	15.3	14.9
70	120	7.85	15.4	15.3
90	75	7.85	16.8	17.9
50	30	15	23.0	22.9
50	120	15	20.9	21.4
70	75	15	27.0	26.9
90	30	15	29.9	29.8
90	120	15	31.9	31.7

A. Thermo-Chemical Pretreatment

Based on the matrix design of coded variables tabulated in Table III, both experimental and predicted value were shown as representing the value of response (COD solubilisation). All the values were obtained from quadratic model using the software Design Expert. Thermo-chemical pretreatment was tested for different concentration, temperature and treatment time to enhance solubilisation prior to biogas production. The quadratic model given by the Software for thermo-chemical pretreatment is represented in (3):

$$Y = 14.86 + 3.18A + 0.74B + 7.04C - 0.13A^2 - 0.28B^2 + 4.97C^2 + 0.84AB + 1.11AC - 0.66BC \quad (3)$$

where Y (yield) is COD solubilisation (%); A is the temperature (°C); B is the time (min) and C is the NaOH concentration (g/L).

The statistical model was checked by F-test and analysis of variance (ANOVA) for the response surface quadratic model is tabulated in Table IV. The Model F-value of 127.12 implies the model is significant. There is only a 0.01% chance that Model F-value this large could occur due to noise. Value of "Prob > F" less than 0.0500 indicate model terms are significant. The Lack-of-Fit "F-value" of 1.78 implies the Lack of fit is insignificant. There is a 27.18% chance that Lack-of-Fit "F-value" this large could occur due to noise. Non-significance of Lack of fit is good as we need the model to be fit. Therefore, model coefficients, namely A, B, C, C^2, AB, AC and BC are significant (Table IV) to affect COD solubilisation. In addition to that, determination of coefficient (R^2) and adjusted R^2 can also be used to check the model effectiveness. R^2 value represent the amount of variance accounted for in the relationship between two or more variables. The closeness of R^2 value to 1 illustrates that the model exactly explains the variability in dependent variable, Fig. 1. Hence, the value larger than 0.5 can be considered a significant relationship [27]. The value of adjusted R^2 (0.9835) for (1) indicates that 98.35% of variance can be predicted from the independent variables and only 1.65% of the total variation cannot be explained by the model. The predicted R^2 (0.9535) is in reasonable agreement with adjusted R^2. "Adeq precision" measures the signal to noise ratio and a ratio greater than 4 is desirable. The ratio of 38.760 of the Model (Table IV) indicates an adequate signal. This model can be used to navigate the design space.

TABLE IV
ANOVA FOR THE RESPONSE SURFACE QUADRATIC POLYNOMIAL MODEL

Source	Sum of square	df	Mean square	F-value	Probability (p)>F
Model	733.18	9	81.46	127.12	<0.0001
A	101.12	1	101.12	157.80	<0.0001
B	5.62	1	5.62	8.78	0.0142
C	495.62	1	495.62	773.39	<0.0001
A^2	0.048	1	0.048	0.075	0.7904
B^2	0.22	1	0.22	0.34	0.5723
C^2	67.88	1	67.88	105.92	<0.0001
AB	5.61	1	5.61	8.76	0.0143
AC	9.90	1	9.90	15.45	0.0028
BC	3.51	1	3.51	5.48	0.0413
Residual	6.41	10	0.64		
Lack of fit	4.10	5	0.82	1.78	0.2718
Pure error	2.31	5	0.46		
Cor total	739.59	19			

R^2= 0.9913; adjusted R^2= 0.9835; predicted R^2= 0.9535 and adeq precision= 38.760

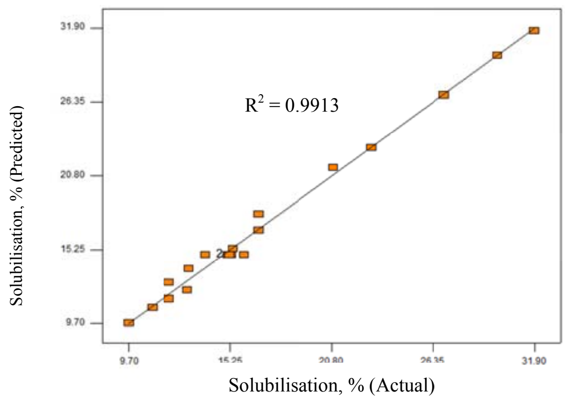


Fig. 1 Parity plot for relation between observed and predicted COD solubilisation value

Most of the studies reported that thermal pretreatment do affect in hydrolyse of substrate at low temperature (<100°C) with longer time [6], [16], [22], [23] and higher concentration of alkaline [18]. By taking into consideration on high energy consumption, low temperature and shorter time were selected in performing thermo-chemical pretreatment. In this study, COD solubilisation was evaluated for relatively low temperature of 50-90°C, 0.7-15 g/L NaOH concentration for 30-120 minutes.

The generated surface plot described the interaction between parameters to yield optimum output (COD solubilisation). Two parameters were considered at any time in plotting both three-dimensional and contour plot. At any one time the third parameter is kept at its centre point [28]. Fig. 2 shows the effect of temperature and time on COD solubilisation while keeping NaOH concentration at 7.85 g/L. Result from Fig. 2 shows that at 30 minutes pretreatment time, there is 21.2% more solubilisation at 90^{o}C as compared to 50^{o}C. Stirring time does not seem to affect solubilisation between 30 minutes to 120 minutes for all the temperatures. As observed in the study from [16], temperature was found to not affecting in releasing protein and carbohydrate during thermo-chemical pretreatment.

Figs. 3 and 4 showed the same pattern on solubilisation. Increase of NaOH concentration did affect solubilisation (Fig. 3) as can be seen by an additional 11.4% when 15 g/L and 90^{o}C of NaOH was applied. In addition, alkaline enhance solubilisation regardless of temperature, a 10.6% increase was observed for 15 g/L of NaOH at 50^{o}C. It was stated that temperature had significant influence on high NaOH dosage [11], as observed in this study as well for 15 g/L, 90^{o}C at 120 minutes went up to 31.7% by 2.8 fold. This phenomena was also observed by [18] where increase in both temperature and NaOH loading lead to increase of SCOD of grass silage due to break off linkages between lignin monomer or lignin carboxylic and phenolic groups that leads to solubility of single fragments. Similar observation can be seen in Fig. 4 at higher concentration of NaOH regardless of time stirring taken, the solubilisation was about the same. Therefore, NaOH concentration can be elucidated as important factor that affect COD solubilisation in treating organic food waste.

For optimization purpose, the function of desirability was applied to obtain predicted solubilisation for the model and its lower and upper limit of each variables (temperature, time and NaOH concentration) were selected based on contour and surface plot obtained previously. The ultimate goal of this optimization was to obtain the maximum response that simultaneously satisfies all the variables properties. Table V displays the possible solutions generated by the software which fulfilled all required conditions that give desirability value close to 1. In this study, solution number 1 (90^{o}C, 120 minutes and 15 g/L NaOH) was selected to be tested for biomethane potential test. For validation purposes, the predicted solubilisation was close to the experimental value that was performed with only 0.94% error.

Review from other studies showed that thermo-chemical pretreatment has potential in improving COD solubilisation for different types of biomass. Pretreatment of dairy waste activated sludge at 60^{o}C and pH 12 enhanced COD solubilisation by 23% [16] which can also be observed in this study with an increase of 155% at a temperature of 90^{o}C. Similar effect has been monitored from the study by Li et al. [17] that there was 39% increase in SCOD for mixture of pretreated waste activated sludge and kitchen waste at a lower temperature of 55^{o}C and pH 8. Meanwhile, low total soluble sugars were detected in the study of thermo-chemical pretreatment of kitchen waste due to browning-promoting effect of glucose and fructose at high pH level [9]. Comparison to another alkaline used in treating press mud, $Ca(OH)_2$ resulted up 38% of solubilisation (10 g $Ca(OH)_2$/100 g TS, 3 hours) [29], while in this study 16.87 g NaOH / 100 g TS was used for 2 hours did enhance solubilisation to 51%.

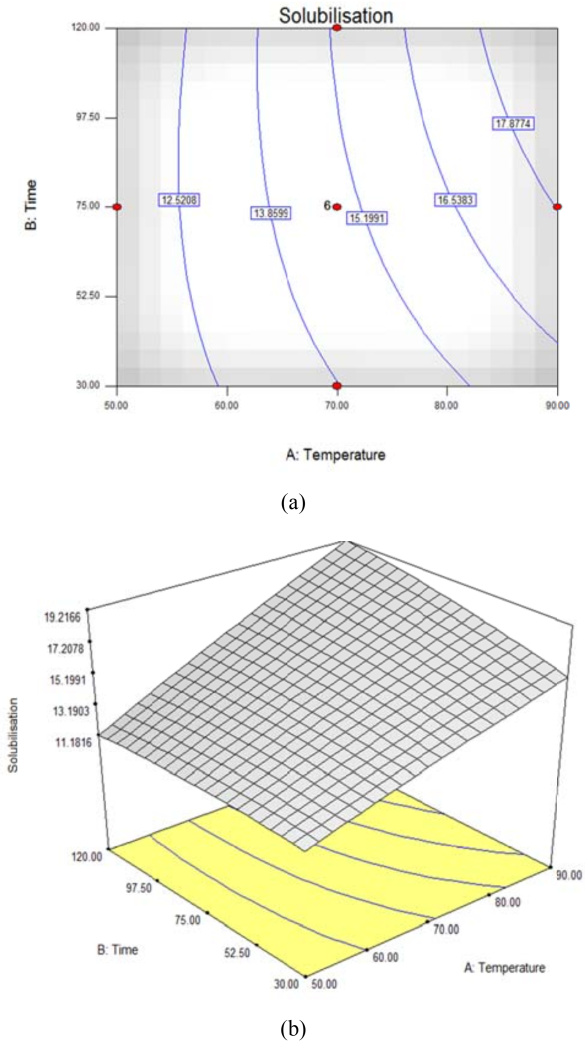
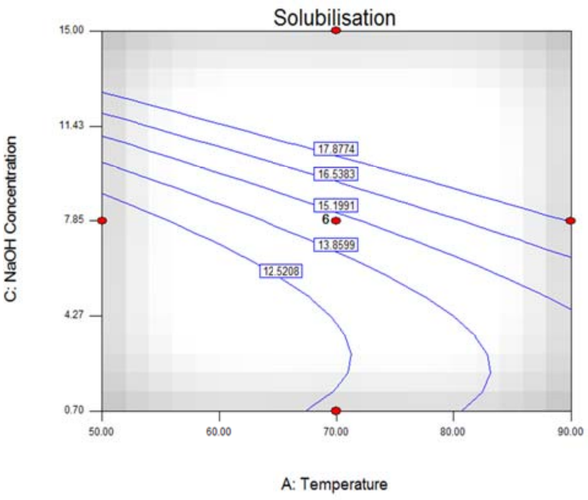
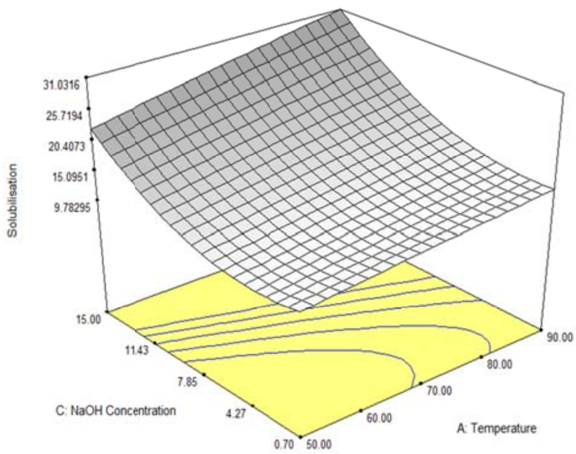


Fig. 2 Effect of temperature and time on COD solubilisation (a) contour; (b) 3-dimensional AB

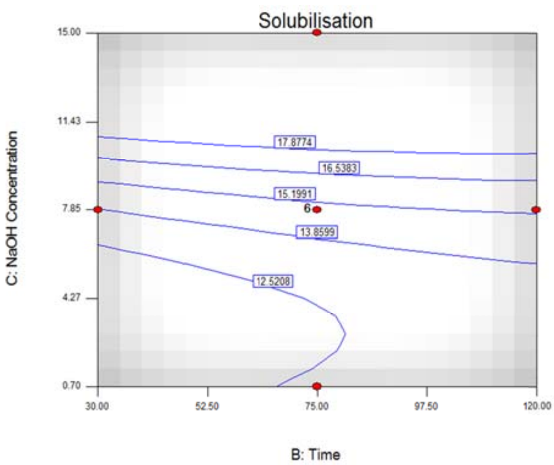


(a)

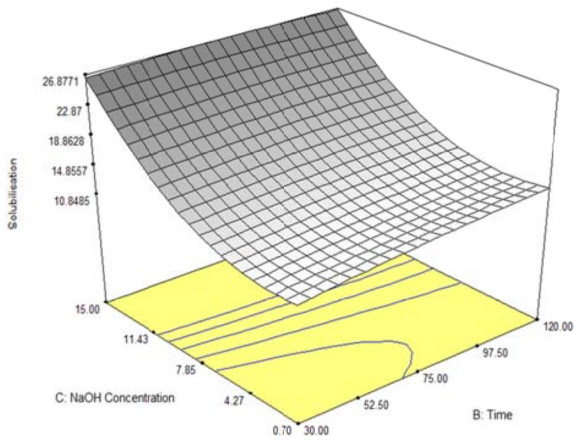


(b)

Fig. 3 Effect of temperature and concentration of NaOH on COD solubilisation (a) contour; (b) 3-dimensional AC



(a)



(b)

Fig. 4 Effect of time and concentration of NaOH on COD solubilisation (a) contour; (b) 3-dimensional BC

TABLE V
OPTIMUM CONDITIONS FOR MAXIMUM COD SOLUBILISATION

No.	Temperature	Time	NaOH Conc.	Solubilisation	Desirability
1	90.00	120.00	15.00	31.6747	0.990
2	90.00	114.24	15.00	31.6238	0.988
3	90.00	107.50	15.00	31.5526	0.984
4	90.00	92.35	14.94	31.2086	0.969
5	89.70	69.23	15.00	30.8498	0.953
6	90.00	66.91	15.00	30.8440	0.952
7	90.00	63.00	15.00	30.7647	0.949
8	81.99	30.00	15.00	28.5262	0.848
9	89.78	120.00	0.71	16.6627	0.314
10	90.00	120.00	1.01	16.5967	0.311

Since the solubilisation kept increasing after pretreatment at 90^{o}C, 15 g/L and 120 minutes, another continuation can be considered to determine the optimal condition for NaOH thermo-chemical pretreatment beyond this point. Meanwhile in this study, the pretreated food waste will be further used in anaerobic digestion to test biomethane potential. Temperature below 100^{o}C was considered to avoid Mailard reaction [30] and high NaOH concentration could lead to anaerobic inhibition according to previous studies. The inhibition of methane production was observed from the study by [31] which found that NaOH enhance solubilisation of chicken feathers but inhibit methane production due to high tested value of ammonium. Ammonium was produced through degradation of protein-rich-substrate that can cause toxicity for methanogenic bacteria instead of serving as buffering to the digestion system [32]. Furthermore, high-dose NaOH addition that causes toxicity to anaerobic digestion microorganisms may be due to the residual alkali in the treated substrate that created saline environment [21], [22]. High solubilisation with lower methane production was monitored by [22] due to increase in NaOH concentration and also addition of HCl while neutralizing during digestion could cause inhibition to anaerobic digestion. In addition, [9] observed that addition of NaOH at higher temperature (100 and 120^{o}C) contributes to an increase in pH and reduced soluble sugars due to Mailard browning reactions. The formation dry and dark brown colour material was detected during high temperature pretreatment as well as NaOH loading indicates that the substrate became hard and hardly degradable eventually lead to methane reduction [33]. The coloured compounds known as melanoidins were formed from condensation reactions of nitrogenous compounds (amine/amino acids) with reducing saccharides (mailard reaction) [34]. The higher the pH of pretreatment, the higher browning reaction tend to occur even more with heated solution that eventually lead to high glucose and fructose degradation [9].

IV. Conclusion

COD solubilisation of organic food waste is well extracted by thermo-chemical pretreatment. Pretreatment is introduced to enhance solubilisation in order to provide soluble compound at the early stage of anaerobic digestion during hydrolysis process by the means of reducing retention time. The mathematical model developed could predict percentage of solubilisation at any point in the experimental domain as well as determination of optimal solubilization conditions with sufficient degree of accuracy. The model suggested for this study was quadratic model in a way to optimize the solubilisation. The interaction between the three parameters showed high potential for COD solubilisation at 90^{o}C, 15 g/L and 120 min. In addition, further research will be continued to investigate the effect of thermo-chemical pretreatment on COD solubilisation in increasing methane potential through biomethane potential test, BMP.

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