Effect on Ca(OH)\textsubscript{2} pretreatment to enhance biogas production of organic food waste

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Abstract. This study investigated the effect of calcium hydroxide, Ca(OH)\textsubscript{2} pretreatment in optimizing COD solubilisation and methane production through anaerobic digestion process. Two different parameters, chemical concentration (40-190 mEq/L) and pretreatment time (1-6 hours) were used to pretreat food waste. A central composite design and response surface methodology (RSM) was applied in obtaining the optimized condition for COD solubilisation. Result showed COD solubilisation was optimized at 166.98 mEq/L (equivalent to 6.1 g Ca(OH)\textsubscript{2}/L) for 1 hour. These conditions were applied through biomethane potential test with methane production of 864.19 mL/g VS\textsubscript{d}
 and an increase of 20.0% as compared to untreated food waste.

1. Introduction
Currently, active studies have been pursued on every possible sustainable waste resources including organic food waste as substrate for anaerobic digestion (AD). Anaerobic digestion constitutes of a basic process which includes hydrolysis, acidogenesis, acetogenesis and methanogenesis. However the most critical and rate limiting step in anaerobic digestion is the hydrolysis process where complex molecule of organic waste need to be broken down into monomers that requires longer time with slow rate of solubilisation. This hydrolysis process requires assistance in reducing the time taken during digestion process called pretreatment. Pretreatment is required to improve accessibility of soluble organic material as represented by value of the soluble chemical oxygen demand (SCOD) to be an essential source for microbial population during digestion process. SCOD represent the source of energy available to maintain the activity of microbes and its condition throughout the entire process. Therefore, by providing the pretreated substrate with readily available monomers will eventually uplift methane production in shorter retention time. According to Jayashree et al. [1], SCOD is one of the parameters used in assessing particulate material for optimal solubilisation and to identify the quantity of soluble organic content in the subjected substrate. The SCOD value expresses solubilisation, S as described in (1) [2,3].

Solubilisation, S (%) = \[ \frac{SCOD_f - SCOD_i}{TCOD} \] \times 100 \tag{1}
where SCOD$_f$ and SCOD$_i$ refer to final and initial value of SCOD respectively. And TCOD represent total chemical oxygen demand.

In optimizing solubilisation in term of soluble COD, higher SCOD indicates the readiness of a substance to produce methane through anaerobic digestion. Torres and Espinosa Lloréns [2] had reported in his study, a chemical pretreatment with 62.0 mEq/L for 6 hours was optimized with 11.5% increase in COD solubilisation and 150 mL CH$_4$/g VS (172% higher) as compared to untreated substrate. This paper aims to investigate the effect of Ca(OH)$_2$ in enhancing solubilisation of organic food waste as a promising way to provide soluble component to enhance digestion rate and reduce hydraulic retention time. Response surface method is an approach used to determine the maximum response for an optimum condition within the selected range of factors.

2. Methodologies

2.1. Preparation of substrates and inoculum

Food waste (FW) prepared manually represented the main component in Malaysian food waste composition comprising steamed rice, vegetable (cooked cabbage and carrot), bread, fried chicken, fried fish and fried noodle. The indigestible material such as bones were removed manually. The component mixture was further homogenized using a crusher and sieved to produce a homogeneous substrate with <2mm particle size. Sewage sludge was used as a source of inoculum.

2.2. Chemical pretreatment

Chemical pretreatment was carried out using a stainless steel container equipped with stirrer. The substrate was tested for range 40–190 mEq/L for 1–6 hours. Chemical oxygen demand (COD) were tested according 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.

2.3. Experimental design and procedure

Central composite design (CCD) was employed for the selected factors to obtain the desired output from the experimental design with Design Expert 6.0.8 software. The level and code of variables considered in this study are shown in Table 1.

| Factor                        | Variable | Coded levels |
|-------------------------------|----------|--------------|
| Chemical Concentration, mEq/L | A        | -1  0  1     |
| Pretreatment Time, hour       | B        | 1  3.5  6    |

For two variables (n=2), and three levels (low, medium and high, coded as -1, 0 and +1), the total number of 11 runs were determined by the expression $2^n (2^2=4$ factorial points), $2n (2*2=4$ axial points), 3 centre points (point of replications) as given in Table 3. 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):

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

where Y is the response (COD solubilisation), $\beta_0$ is the intercept coefficient, $\beta_i$ is the linear terms, $\beta_{ii}$ is the squared terms and $\beta_{ij}$ is the interaction terms.

2.4. Biomethane potential (BMP) tests

The BMP tests were used to analyse the potential methane production for chemically treated food waste as compared to untreated one. Batch assays were performed in 2L glass AD vessel (Schott Duran, Germany) filled with 1.8L of substrate which contain 90% inoculum and 10% of food waste under
mesophilic condition (room temperature). All the AD vessel were connected to a 1L Schott bottle containing an alkaline solution 2M (scrubber) before releasing into gas collection set up. The scrubber was used to absorb CO₂ and H₂S in biogas. The headspace of digester was flushed with nitrogen gas for about 2 minutes for anaerobic environment. Control bottles were prepared using the food waste without pretreatment. All samples were adjusted to pH 7.0 with either 1 M HCl or 1 M NaOH solution and were stirred for one hour per three hours interval. Daily methane production was monitored by measuring the volume of water displaced from eudiometer. The biogas composition was analysed by using gas analyser (BINDER, Germany) to detect methane content.

3. Result and discussion

A Central Composite Design (CCD) under RSM was used to optimize COD solubilisation based on the interactive effect of chemical concentration and treatment time. The baseline range followed Torres and Espinosa Llorens [2] that treated organic fraction of municipal solid waste (OFMSW). The preliminary result (data was not shown) indicated solubilisation continued increasing after 100 mEq/L Ca(OH)₂ at 6 hours. Therefore, the concentration was increased up to 190 mEq/L for the optimization of Ca(OH)₂ pretreatment.

3.1. Chemical pretreatment

Based on the matrix design of coded variables tabulated in Table 2, 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. Ca(OH)₂ pretreatment was tested for different concentration 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):

\[
Y = 3.17 + 1.25A - 0.41B - 1.881A^2 + 1.69B^2 - 1.29AB
\]

where Y (yield) is COD solubilisation (%); A is the temperature (°C); B is the treatment time (hour). The statistical model was checked by F-test and analysis of variance (ANOVA) for the response surface quadratic model as tabulated in Table 3. The Model F-value of 169.44 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 13.22 implies the Lack of fit is insignificant. There is a 7.11% chance that Lack-of-Fit “F-value” 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, A², B² and AB are significant (Table 3) to affect COD solubilisation. In addition to that, determination of coefficient (R²) and adjusted R² can also be used to check the model effectiveness. R² value represents the amount of variance accounted for in the relationship between two or more variables. The closeness of R² 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 [4]. The value of adjusted R² (0.9883) indicates that 98.83% of variance can be predicted from the independent variables and only 1.17% of the total variation cannot be explained by the model. The predicted R² (0.9404) is in reasonable agreement with adjusted R². “Adeq precision” measures the signal to noise ratio and a ratio greater than 4 is desirable. The ratio of 42.487 of the Model (Table 3) indicates an adequate signal. This model can be used to navigate the design space.

For optimization purpose, the function of desirability was applied to obtain predicted solubilisation for the model at its lower and upper limit of each variables (Ca(OH)₂ concentration and treatment time) based on contour and surface plot obtained in Fig 1. The possible solutions generated by the software which fulfilled all required conditions will give desirability value close to 1. In this study, 166.98 mEq/L and 1 hour was selected for biomethane potential test. For validation purposes, the predicted solubilisation (6.13%) was close to the experimental value (5.95%) that was performed with only 2.94% error.
### Table 2: CCD with experimental and predicted values of COD solubilisation (%)

| Chemical Concentration (mEq/L) | Pretreatment Time (hour) | COD solubilisation (%) | Experimental | Predicted |
|-------------------------------|--------------------------|-------------------------|--------------|-----------|
| 40.00                         | 1.00                     | 0.69                    | 0.85         |
| 40.00                         | 3.50                     | 0.27                    | 0.04         |
| 40.00                         | 6.00                     | 2.54                    | 2.61         |
| 115.00                        | 1.00                     | 5.38                    | 5.27         |
| 115.00                        | 3.50                     | 3.17                    | 3.17         |
| 115.00                        | 3.50                     | 3.23                    | 3.17         |
| 115.00                        | 3.50                     | 3.10                    | 3.17         |
| 115.00                        | 6.00                     | 4.37                    | 4.45         |
| 190.00                        | 1.00                     | 5.99                    | 5.93         |
| 190.00                        | 3.50                     | 2.34                    | 2.54         |
| 190.00                        | 6.00                     | 2.68                    | 2.53         |

### Table 3. ANOVA for the response surface quadratic polynomial model

| Source       | Sum of square | df  | Mean square | F-value | Probability (p)>F |
|--------------|---------------|-----|-------------|---------|-------------------|
| Model        | 29.88         | 5   | 5.98        | 169.44  | <0.0001           |
| A            | 9.40          | 1   | 9.40        | 266.50  | <0.0001           |
| B            | 1.02          | 1   | 1.02        | 28.83   | 0.0030            |
| A²           | 8.97          | 1   | 8.97        | 254.35  | <0.0001           |
| B²           | 7.22          | 1   | 7.22        | 204.68  | <0.0001           |
| AB           | 6.66          | 1   | 6.66        | 188.71  | <0.0001           |
| Residual     | 0.18          | 5   | 0.035       |         |                   |
| Lack of fit  | 0.17          | 3   | 0.056       | 13.22   | 0.0711            |
| Pure error   | 8.467E-003    | 2   | 4.233E-003  |         |                   |
| Cor. total   | 30.06         | 10  | 3.06        |         |                   |

$R^2=0.9941$; adjusted $R^2=0.9883$; predicted $R^2=0.9404$ and adeq precision=42.487

### Fig. 1 Three dimensional surface plot (a) for NaOH pretreatment (b) and Ca(OH)$_2$ pretreatment

3.2. **BMP tests**

The batch anaerobic digestions were tested to investigate the effect of chemical pretreatment, Ca(OH)$_2$ on the production of methane from food waste based on the optimal condition from the pretreatment process. Anaerobic digestion is expressed by volume of methane produce per mass of volatile solid (VS) of a substrate that is destructed throughout the digestion process (mL CH$_4$/g VS$_{destructured}$) [5]. Cumulative and specific methane production were represented in Fig. 2. The pretreated food waste showed similar pattern to untreated sample in daily basis methane production. In Fig. 2(a), methane production started to increase after day 6 for both treated and untreated food waste as supported by [6] that biogas production can be optimally produced as early as 8 days as insignificant COD changes in further degradation. Furthermore, there is an increase of 5.4% in cumulative methane production for Ca(OH)$_2$ pretreated food waste which illustrates enhancement of anaerobic digestion process by providing soluble components in pretreatment process. Compared to study by [2], higher Ca(OH)$_2$ concentration was used
in this study which resulted in increment of specific methane potential by 20.0% when compared with control digester. Higher production of methane in this study occurred due to higher volatile solids content (84,860 mg/L) as compared to the study by [2] with organic fraction municipal solid waste (OFMSW) as a substrate. Other studies had shown positive effect of Ca(OH)$_2$ pretreatment with increased biogas production for extruded rice straw [7] and feather waste [8].

Fig. 2 Methane production (a) cumulative production; (b) specific production throughout 35 days of digestion

4. Conclusion
The aim of this study is to investigate the effect of chemical pretreatment on solubilization in enhancing methane production. Calcium hydroxide showed potential as an alkaline chemical to be used in pretreatment of food waste that can enhance up to 20.0% of specific methane production compared to untreated food waste.

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