OPTIMIZING ORGANIC MATERIALS REDUCTION FROM HAZARDOUS INDUSTRIAL BIO-EFFLUENT BY THE AID OF C/N ENRICHED INOCULUM: AN APPROACH TO USE TRADITIONAL ANAEROBIC REACTOR TO ACHIEVE ENVIRONMENTAL SUSTAINABILITY

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ABSTRACT: *The aim of this paper is to present research conducted to increase organic materials reduction from waste bio-mass enriched palm oil mill effluent (POME). This POME is also known to be the hazardous bio-effluent responsible for the air, water and soil pollution. This research conducted to address the problem of poor performance experienced by the industries while using the anaerobic reactor for reducing effluent quality. The novelty of this research is of using C/N enriched inoculum (11<C/N< 40) in a two-stage continuous stirred tank reactor (CSTR) based anaerobic process at different pH for increasing COD reduction performance to a sustainable level. The research findings demonstrated that COD reduction has mostly occurred at the C/N of 20 to 32. The optimum level of COD reduction was 80% at C/N 32.5 with pH 7.0. The COD digestion performance as COD reduction was found significant at 95% level (p-value <0.05) with 53.2% input utilization factor (R^2=53.2). The study concludes that POME digestion process for achieving higher COD reduction, CSTR based anaerobic*

Keywords: Chemical Oxygen Demand; Palm Oil Mill Effluent; Carbon-to-Nitrogen Ratio; Continuous Stirred Tank Reactor; Anaerobic Digestion

1.0 INTRODUCTION AND RESEARCH BACKGROUND

This paper aims to present research conducted on improving COD reduction performance from POME by using a two-stage standard CSTR based anaerobic reactor by the aid of inoculum with higher C/N (11<C/N<40). Indeed, over 90 percent of palm oil mills have been using traditional waste stabilization pond (WSP) instead of anaerobic digester. Various published papers have suggested that the performance of the currently available CSRT based anaerobic reactors is significantly poor and not technically and financially feasible to use [1, 2]. It is also claimed that due to the poor performance of CSTR base anaerobic reactor, the palm oil mills are reluctant to install this machinery [1, 2]. And the consequences of this, industries are continuing with WSP as their means for POME treatment. Indeed, WSP process is a potential source of CH_4 and CO_2 emission. Both CH_4 and CO_2 are known to be the greenhouse gases (GHG) and the sources of global warming potentials [3]. This research was designed to address this vital issue.

The novelty of this research is of using a two-stage traditional engineered CSTR based anaerobic reactor wian an inoculum of C/N between 11 to 40 to measure the effects on COD reduction performance of POME.

2.0 LITERATURE REVIEW

. POME is generated during the extraction of crude palm oil (CPO) from the fresh fruit bunch (FFB). In one tonne of CPO production requires about 1.0 to 2.5 m³ of water whiturns as as a POME [4, 5]. POME contains water, biomass and a larnumberity of organic materials of FFB. These organic materials include carbohydrates, proteins, lipid, and other micronutrients to be known as chemical oxygen demand (COD). To decompose all these materials require oxygen which is known to be Biochemical Oxygen Demand (BOD) [6]. The properties of POME are listed in Table 1.

Table 1: Elements of POME Effects on Biodegradation [7]

Parameter	Properties of POME	
	Units	Range
Organic Material	mg/L	15,000–100,000
pH	-	3.4–5.2
Total Solids (TS)	mg/L	11,500–79,000
Volatile Suspended Solids (VSS)	mg/L	9,000–72,000
Oil and Grease	mg/L	130–18,000
Ammoniacal Nitrogen	mg/L	4–80
Total Nitrogen	mg/L	180–1,400
C/N	-	7-10

POME tends to utilize available oxygen from the water bodies to decompose biodegradable organic materi, andand make water pollute.

Durithe ng the biodegrading process, methane (CH_4) and carbon dioxide (CO_2) produce and emits to air [8] These both gases known to be the greenhouse gas(GHG). In order to reduce water pollution and to minimize GHG emission from POME, various types of anaerobic reactor have been used to digest organic materials of POME [9]. The outputs of these anaerobic reactors are methane ($CH_4 \approx$ 65%), carbon dioxide ($CO_2 \approx$ 33%), and hydrogen sulphide ($H_2S \approx$ 2.5%) and some other gases [10]. These gases are captured and being used as biogas.

It has been reported that the major independent manipulating variables of anaerobic digestion process are C/N, pH, HRT, SRT, temperature, OLR, and velocity of POME inside reactor [2, 11, 12]. It was also reported that among these variables, pH, HRT, C/N, and OLR have a significant (p-vale <0.05) contribution in breaking down the COD elements and accelerate to reduce COD in POME.

Several authors statth at an an optimal C/N between 20 to 35 [13, 14] exhibited a moderate Nitrogen concentration for an anaerobic digestion process. A study conducted by Sidik *et al.* on POME digestion process with a C/N range of 25 to 30. Their research finding demonstratthat thethe highest COD removal efficiency was 67% [15].

Nurul Adela et al. (2014) reported that the C/N of the POME was in the range of 10.08–11.44 [16]; which exhibited a poor COD digestion efficiency.

Several studies concluded that COD reduction efficiency is a result of balanced nutrition in the POME digestion process. And in this regards, C/N is a potential source to provide with carbon as food and nitrogen as an enzyme for bacterial growth [17–19]. However, pH in the digestion process is also a potential factor that controls digestion efficiency [9].

Esposito *et al.* stated that organic materials digestion (biodegradability) of effluent depends on a few potential factors including C/N, pH, OLR and HRT, but pH plays a vital role in increasing microbial population growth in digestion process [20]. The pH is associated with microbial activities in the digestion process; specially the Methanogens bacteria. It has been reportthat at at pH range of 6.5 to 7.8; the growth of methanogens bacteria is significantly higher [21]. Zhang *et al*. found that at pH levels below 6.6, the environment inside anaerobic reactor becomes acidic, and the methanogenic activities tend to decrease[22]. A few reports on COD reduction efficiency have stated that the POME digestion process performance is highly dependent on pH [7, 18, 23].

This literature review concludes that C/N and pH are the two potential process parameters of POME digestion need to optimize in achieving COD reduction at desired level.

2.1 Problem Statement

POME treatment is essential to reduce COD, BOD and other pollutants in effluent prior to discharge. Currently, two methods have been used in POME treatment such as the waste stabilization pond method (WSP) and the anaerobic reactor. However, various studies on POME treatment demonstrated that the COD and BOD reduction performance of both methods have appeared insignificant [9, 16]. It was also stated that the reason for the overall poor performance of POME treatment is of using the C/N, HRT, SRT and pH inadequately in the digestion process [7, 24–26].

Nurliyana *et al.* stated that the C/N ratio is a potential element for increasing biodegradability of organic materials of POME. In these regards, the authors suggested to increase C/N at optimum level in the digestion process [19]. Ohimain and Izah stated that pH plays a vital role in growing bacteria in the POME digestion process; and inadequate pH adjustment is one of the identified reasons for poor performance [24] of the anaerobic process.

Indeed, the current scenarios of using anaerobic digestion process demonstrate that in the major POME treatment the C/N and pH are not used adequately [19, 24]. This phenomenon of anaerobic digestion has appeared as a major problem in the POME treatment. With this background, the current research is designed to answer the question “What is the required level of C/N and pH that need to maintain in anaerobic digestion to optimize COD reduction from POME?”

2.2 Research Objective

The broad objective of this paper is to present the effect of C/N and pH on COD reduction from POME; and the specific objectives are:

(a) To determine the effects of C/N on COD reduction from POME

(b) To determine the effects of pH on COD reduction from POME.

3.0 RESEARCH METHODOLOGY

This section describes the methodology used to conduct experiment to achieve the research objective. The research methodology has divided into a few parts including POME sample collection, experiment setup, data collection, data analysis, and report writing. A series of experiments were conducted by passing substrate through the rector operated 35℃. The Design Expert (version 2018) software was used as a perfect tool to estimate the required experimental runs to achieve accurate results [7]. This software also known as Design of Experiment (DOE). This software was also used as a tool for data analysis to get the optimum value of inputs relating to outputs [7].

3.1 POME Sample collection

Fresh POME was collected from Salcra Palm Oil Mill operating at Bau Sarawak and the samples transported to the Operations Research laboratory in Universiti Malaysia Sarawak (UNIMAS). Based on the Design of Experiments (DOE) outputs, a total of 49 samples were collected to conduct the required experiments.

3.2 Experimental Setup

To improve the efficiency of anaerobic reactor and shorten the digestion cycle, two CSTR type anaerobic reactors have used to conduct the experiments. The CSTR is used in this research due to its simplicity in design, operation, and also for its advantages in experimentation. The CSTR provides greater uniformity of system parameters, such as temperature, chemical concentration, pH, and substrate concentration [24].

The first reactor was setup for hydrolysis and acidogenesis and it was operated at pH of 5 in order to breakdown long chain organic materials into short chain. Acidogenesis is a biological process, in which the further breakdown of the remaining complex organic compounds in POME occurs [25]. The greatest degree of hydrolysis and acidogenesis occurred when the pH was controlled between pH 4.5 to 6 [26].

In the second stage, the acetogenesis and the methanogenesis processes were performed at pH from 6.5–7.5. For all the experiments reported here were conducted with an inoculum prepared from waste banana peel (C/N 83) and was added into the digestion process.

The number of experiments conducted and reported were estimated by using DOE software (2018). To meet the requirements of the research, a total of 49 experiments are conducted at mesophilic temperature of 35 ℃ [27]. The C/N in the substrate was adjusted by varying the inoculum dossing rate which ranges from 11.8 to 40.3. The pH in the digestion process adjusted by adding sodium hydroxide (NaOH) in the range of 5.2 to 8. The experiment setup is shown in Fig. 2.

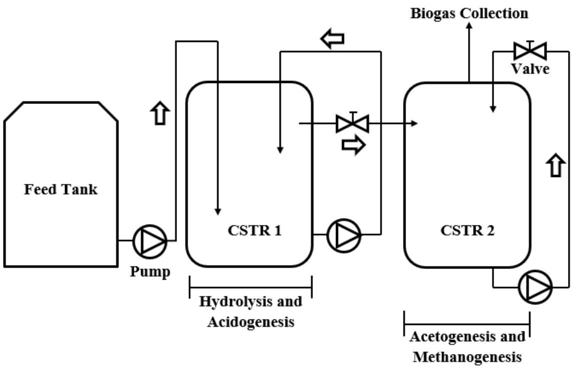

Fig. 1 Experimental Setup

The substrate was prepared with POME and inoculum to achieve research objectives. The feedstock properties used in this experiment listed in Table 3.1.

Table 3.1: Characterization of Feedstock

Variables	Quantity of Feedstock		
	POME	Inoculum	Substrate*
COD g/L	96	0.0	75
pH	4.5	5.5	7.5**
C/N	7	83	30

*The properties of substrate listed due to mixing of POME and inoculum.
**pH of substrate was adjusted to 7.5 by using of sodium hydroxide (NaOH).

3.3 Research Design for Achieving Research Objective One

This section describes the methodology used to achieve research objective one stated in section 2.2 (a). The experiment setup relating to objective one is presented in Fig. 2. The input values of C/N were obtained from DOE [7], which are listed in Table 3.2.

Table 3.2: Independent Variables estimated by CCD

Variables	-α (2.3784)	Low (-1)	Central (0)	High (1)	+α (2.3784)
	Range and Levels				
X_1(pH)	5.31	6	6.5	7.0	7.69
X_2(C/N)	11.729	20	26	32	40.27

The required experimental runs to achieve research objective were estimated by using the DOE [7]. The estimated experimental runs were 13 and it is carried out in triplicate of total 49; which are listed in Table 3.3.

Table 3.3: Experimental Runs for Research Objectives

Std	ID	Run	Factor 1 A: pH	Factor 2 B: C/N
1	1	1	6	20
8	8	2	6.5	40.27
4	4	3	7	32
12	9	4	6.5	26
6	6	5	7.69	26
9	9	6	6.5	26
2	2	7	7	20
13	9	8	6.5	26
3	3	9	6	32
10	9	10	6.5	26
11	9	11	6.5	26
7	7	12	6.5	11.29
5	5	13	5.31	26

The experimental data were analysed by using Design Expert software. The findings were presented by a 2D graph.

3.4 Research Design for Achieving Research Objective Two

This section describes the methodology used to achieve research objective two stated in section 2.2 (b). The experiment setup relating to objective two is presented in Fig. 2. The input values of pH were obtained from DOE [7], which are listed in Table 3.1. The required experimental runs to achieve objective were also estimated by using the DOE [7]. The estimated experimental runs were 13 and it is carried out in triplicate of total 49; which are listed in Table 3.2. The experimental data were analysed by using Design Expert software. The findings were presented by a 2D graph.

4.0 RESULTS AND DISCUSSION

This section developed to present the research findings and to answer the research question. This section has dived into two parts. The first part is developed to state the findings of the investigation made relating to research objective one. The second part is developed to describe the findings of the investigation made relating to objective two.

4.1 Determination of the Effects of Carbon-to-Nitrogen Ratio on Chemical Oxygen Demand Reduction

Experimental data were analyzed to establish the relationship between C/N and COD in order to evaluate the effect of C/N on COD reduction; the findings are plotted in Fig.
3.

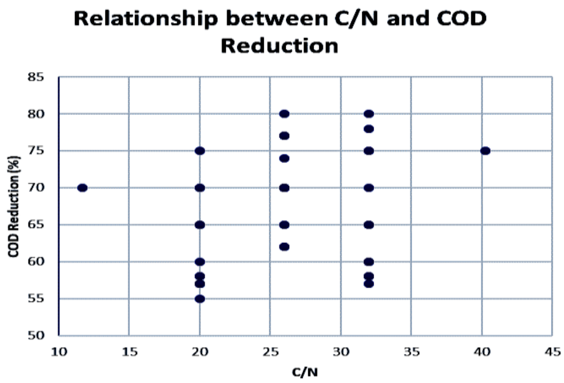

Fig. 3 Relationship between C/N and COD Reduction

Fig. 3 demonstrates the COD reduction behavior with respect to C/N; the 2D graph indicates that mostly COD reduction occurred within C/N of 20 to 32. The highest COD reduction was obtained between C/N 26 to 32, which contributed to reduce 80% of COD from POME. The digestion performance as COD reduction was found significant at 95% level of confidence (p-value = 0.037; which $p\text{-value} < 0.05$) with substrate utilization rate 52.2% (R^2 = 53.2%).
A high C/N in the substrate means, the carbon content is higher with lower content of nitrogen. In aspect of this research, it could be stated that higher carbon has contributed to an increase in the production of carbon dioxide resulting in decreasing of pH. The lower level of nitrogen contents in the substrate has also contributed to deterring the neutralization of volatile fatty acid produced

by fermentative bacteria. On the other hand, the lower level of nitrogen has contributed to reducing the growth of anaerobic bacteria, and resulting in the death of microorganisms. Also, lower growth or death of bacteria is the main cause of the poor performance of COD reduction from POME.

A lower level of C/N in the substrate indicates a higher value of nitrogen with respect to carbon. In this situation, the digestion process would contribute to produce excessive ammonia; and resulting in increasing the pH in the digestion process [26]. Low carbon content means less food for microorganisms and resulting in the starvation of anaerobic microorganisms, and eventually the bacteria would definitely die. As the microbial population in the anaerobic process decreased, the digestion process performance would tend to reduce and the COD performance would also reduce [16, 19]. A few studies conducted on the effects of C/N on anaerobic digestion performance have demonstrated that carbon and nitrogen density in the digestion process has a vital role in creating the environment to grow anaerobic bacteria. Indeed, the C/N ratio in the POME process between 26–32 would have a significant role [19, 27] for higher microbial activities.

Thus, the research findings demonstrated that a C/N between 26–32 is required to provide with sufficient carbon and nitrogen for the growth of anaerobic bacteria [27]. Indeed, this finding concludes that a healthy digestion environment with required C/N, the microbial activities in the substrate with POME would contributed to accelerate digestion performance, and at the same time enhance to reduce COD from POME to the desired level.

4.2 Determination of the Effects of pH on Chemical Oxygen Demand Reduction

Experimental data were analyzed to establish the relationship between pH and COD in order to evaluate the effect of pH on COD reduction. The relationship between pH and COD reduction is plotted in Fig. 4.

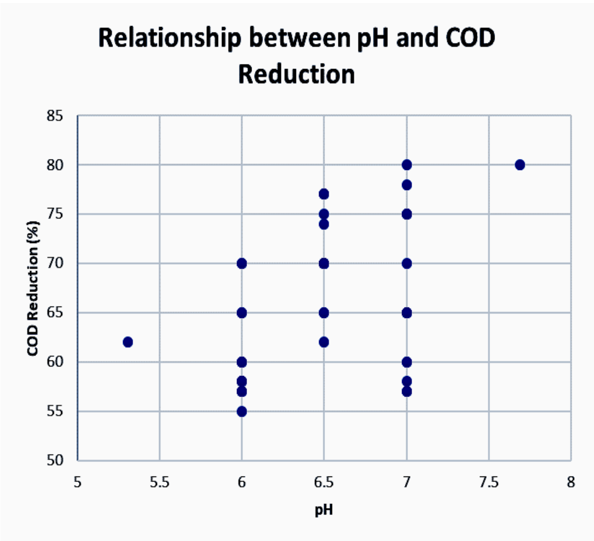

Fig. 4 Relationship between pH and COD Reduction

Fig. 4 demonstrates the COD reduction behavior with respect to pH; which indicates that mostly COD reduction occurred within pH of 6 to 7. The highest COD reduction was obtained at pH 7, which contributed to reduce 80% of COD from POME. The digestion performance as COD reduction was found significant at 95% level of confidence (p-value = 0.039; which p-value < 0.05) with substate utilization rate 52.2% (R^2 = 53.2%).

Methanogens activities require a neutral pH conditions to thrive during the digestion process because they are sensitive to the changes in pH. At pH level below 6.5, the methanogenic activities decrease due to the slowed growth rate of methanogens bacteria in the digestion process [28]. Shahidul *et al*. revealed that the environment for POME digestion becomes toxic at pH less than 5.5 and pH more than 8, resulting in the death of methanogenic microorganism and ultimately affect COD reduction [7]. A few similar studies have stated that pH has a vital effect on anaerobic digestion performance. It was also demonstrated that pH level in the digestion process has a dynamic role in creating environment to grow anaerobic bacteria. Indeed, pH in POME process between 4.5 to 5.5 in hydrolysis and acidogenesis; and pH 6.6 to 7.2 in acetogenesis and methanogenesis would have a significant role on bacteria growth performance [18, 23]; which contribute to increase COD reduction performance.

Thus, the research findings revealed that a pH between 6–7 is required to provide with sufficient sustainable environment in digestion process for the growth of anaerobic bacteria [27]. Indeed, this finding concludes that a healthy digestion environment with required pH (7), the microbial activities in the substrate with POME would contributed to accelerate digestion performance, and at the same time increase to reduce COD from POME to the desired level.

5.0 CONCLUSIONS AND RECOMMENDATION

To achieve the research goal, a two-stage CSTR based anaerobic reactor was used to digest biomass and organic material of POME. The research findings demonstrated that COD reduction mostly occurred at the C/N of 20 to 32 and the highest COD reduction (80%) was obtained at the C/N 32.

It was also found that the pH has shown significant effect on COD reduction from POME. It was revealed that COD reduction mostly occurred at the pH of 6 to 7 and the highest COD reduction (80%) was obtained at the pH 7.

This study concludes that the performance of COD reduction in the CSTR based anaerobic reactor could be achieved to 80%, which is a satisfactory performance for POME treatment process [29], [30]. Thus, this study answers the research question and achieve the research objectives.

The study concludes that the C/N and pH must be optimized in the digestion process in order to maximize the COD reduction to have a desired effluent quality of POME. This finding would be a useful reference for engineers and researchers working with palm oil mills with aiming to provide quality service in improving effluent quality. The findings would also be a reference for policymakers dealing with the environment. However, the application of these findings could be implemented in the palm oil industry to produce effluent which is environmentally friendly.

6.0 ACKNOWLEDGEMENT

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